A Fully Coupled Thermal- Hydrological- Mechanical- Chemical Model for CO₂ Geological Sequestration

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Abstract

The importance of thermal-hydrological-mechanical-chemical (THMC) interactions is well recognized in the procedure of CO₂ geo-sequestration. Geomechanics and geo-chemistry may have significant effects on the aqueous phase composition, porosity and permeability of the formation, which in turn affect flow and transport processes. Using a mean stress formulation, geomechanical effects are considered such as stresses, displacements, and rock deformation in CO₂ sequestration. Chemical equilibrium and kinetics are taken into account in the mass balance equation, which is able to quantitatively simulate fluid flow, solute transport and geo-chemical reaction in the operation of CO₂ geo-sequestration. Since rock strength decreases with increasing amounts of reactive minerals, substantial dissolution/precipitation of rock composition may lead to significant changes in the mechanical behavior, a generic computational scheme has been developed to take the mechanical and chemical coupling effects into account. Based on these theories, a novel mathematical model of the THMC processes is developed in this paper. A fully 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

[☆]Fully documented templates are available in the elsarticle package on CTAN.

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THMC processes. The coupled THMC simulators focus on: (1) fluid and heat flow, solute transport in a three-phase mixture, (2) stress and displacement related to mean stress, (3) non-isothermal effects on fluid properties and reaction processes, and (4) the equilibrium and kinetics of water-rock and gas-rock chemical interactions. A practical reactive transport examples with cold supercritical CO₂ injection into saline aquifer has been proposed to analyze the THMC processes quantitatively. It is indicated that the geochemical reactions do not have significant impact on pore pressure, mean stress and temperature. The thermal energy transport with low temperature significantly affects the mean stress and geochemical reactions in the saline aquifer. Low temperature accelerates equilibrium dissolution of gas and mineral, but slows down kinetic dissolution/precipitation of minerals, such as anorthite and kaolinite.

Keywords: THMC Processes, Fully Coupled Method, CO₂ Geo-sequestration, Numerical Simulation, Non-isothermal Reactive Transport, Mean Stress, MC coupling, TH coupling, HM coupling

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1. Introduction

Based on the technical report of Intergovernmental Panel on Climate Change (IPPC), the concentration of CO₂ 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 CO₂ reacting with the molecules of water in the atmosphere, soil and ocean system, carbonic acid and hydrogen ions are formed, leading to an acidized environment. 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 have significant effects on the environment. Therefore, CO₂ geo-sequestration into saline aquifers is the most effective solution to reduce CO₂ emissions. Saline aquifers have the largest

volumetric capacity among the many options for long term geological storage
15 of CO₂ (IPCC, 2005). The sketch of CO₂ geo-sequestration is shown in Fig. 1.
After a large amount of CO₂ is injected into the aquifers, there are several primary mechanisms controlling the percolation and ultimate fate of CO₂(IPCC, 2005). The effectiveness of geological storage depends on a combination of the trapping mechanisms (IPCC, 2005):

20 *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 sequesterate gaseous CO₂ in geological reservoirs(Yao et al., 2012; Zhang et al., 2014). Fig. 1 (a) shows that CO₂ injected in the saline aquifer can be sealed between the cap rock and the bed
25 rock. 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. In addition, CO₂ can be trapped in the pore space by capillary forces
30 and relative permeability, which is shown in Fig. 1 (b).

Solubility trapping. It occurs in the saline aquifers where fluids transport very slowly over long distances. After CO₂ is injected into the aquifer, it displaces aqueous water and migrates upwards. Under the formation pressure, gaseous CO₂ becomes equilibrated with formation water, leading to aqueous CO₂ in the
35 formation water. Dispersion and fingering of aqueous CO₂ may be formed due to permeability heterogeneity, gravity override and mobility contrast between CO₂ and formation fluid, which is shown in Fig. 1 (d). These mechanisms also operate over relatively short timescales (injection period).

Mineral trapping. After CO₂ is dissolved into formation water, carbonic acid
40 is released to dissolve certain amount of rock minerals, leading to a decrease of the pH value. Dissolved ions and minerals may further react to form stable carbonate and silicate minerals. The interaction between CO₂ and water is

shown in Fig. 1 (c). Reaction of dissolved CO_2 with minerals can be very rapid (days) for some carbonate minerals, but very slow (hundreds to thousands
 45 of years) for others (silicate minerals). This mechanism operates over long
 timescales (thousand years) and relatively small site scale (formation scale).

The trapping contributions for the CO_2 mass that can be trapped by the different mechanisms are show in Fig. 1 (e) schematically. The extent of the contribution is in the order of structural and residual trapping, solubility and
 50 mineral trapping.

Figure 1: The Sketch for trapping mechanism during CO_2 geo-sequestration: (a) Structural Trapping; (b) Residual Trapping (Szulczewski et al., 2012); (c) Mineral Trapping; (d) Solubility Trapping (Szulczewski et al., 2012); (e) Trapping Contribution (IPCC, 2005).

1.1. Description for THMC Processes

The physical mechanisms of CO₂ geo-sequestration discussed above is a thermal-hydrological-mechanical-chemical processes. The trapping mechanism is in the macroscopic perspective, however it is resulted from the change in the pore structure subjected to supercritical CO₂ injection. The THMC processes due to supercritical CO₂ injection in the perspective of pore structure are described as follows: (a) The original pore structure in the saline aquifer is under hydrostatic equilibrium with water and a small amount of non-aqueous liquid phase (NAPL) saturated in the small pores. The chemistry between water, NAPL and mineral is in equilibrium condition. There is a small amount of mineral dissolved into the aquifer water, resulting in salinity at the original state of the aquifer. The phase between water and NAPL is also in equilibrium, a small amount of NAPL is dissolved in the water phase and the same with water in the NAPL phase. Fig. 2 (a) illustrates the original pore structure in the target saline aquifer for CO₂ geo-sequestration; (b) The pore structure is shrunk due to pressure buildup at the beginning of the CO₂ injection, especially the volume of the rock matrix tends to decrease. Fig. 2 (b) illustrates the shrunk rock matrix and the enlarged pore space due after CO₂ injection; (c) The pore structure is changed due to large amount of supercritical CO₂ injection in a short period, in the perspective of pore compressibility and thermal expansivity. When the CO₂ gas (in blue color as in Fig. 2 (c)) is squeezed into the pore space, the pressure and stress in the target aquifer increase greatly. The rock matrix tends to shrink under great pore pressure and stress, which result in the increase of space in the pore structure. The porosity and permeability of the formation increase due to the pore space increase. Fig. 2 (c) illustrates that the pore space increases by a large amount of CO₂ injection; (d) The phase is equilibrated between saline water and gas simultaneously after CO₂ injection into the saline aquifer. In the perspective of phase equilibrium, the saline water is evaporated into the gaseous CO₂ phase ($\text{H}_2\text{O}(\text{aq}) = \text{H}_2\text{O}(\text{gas})$), and the gaseous CO₂ is dissolved into aquifer water ($\text{CO}_2(\text{gas}) = \text{CO}_2(\text{aq})$). Both processes are under high pressure and high temperature. As you may see in Fig. 2

(d), the molecules of $\text{CO}_2(\text{aq})$ (compounds with blue color in aquifer water) are distributed into the aquifer water gradually, and small molecules of H_2O (compounds with white color in gaseous CO_2 phase) is trapped in the gaseous CO_2 phase; (e) The pH value is evolved due to dissolution of gaseous CO_2 in aquifer water. In the perspective of chemical reaction, the gaseous CO_2 is dissolved into aquifer water ($\text{CO}_2(\text{gas}) = \text{CO}_2(\text{aq})$). The large amount of chemical species $\text{CO}_2(\text{aq})$ releases into aquifer water, when the phases achieve equilibrium state. Then, $\text{CO}_2(\text{aq})$ reacts with H_2O molecules ($\text{CO}_2(\text{aq}) + \text{H}_2\text{O} = \text{H}^+ + \text{HCO}_3^-$) forming H^+ and HCO_3^- . Because of more independent H^+ releasing into the saline aquifer, the environment become acidized with a low pH value. As you may see in Fig. 2 (e), the pH value become lower as the color of water near the phase contact surface become darker; (f) The salinity in the aquifer increases due to the change of pH value in a relatively long period. The pH value become lower with $\text{CO}_2(\text{gas})$ dissolves into aquifer water. The independent H^+ is more than sufficient in the aquifer water, which leads to the dissolution of rock minerals. The carbonate minerals tend to be dissolved rapidly in an acidized environment. A large amount of ions (Fe^{2+} , Fe^{3+} , Mg^{2+} , Al^{3+} , Si^{4+} and Ca^{2+} , etc.) release into aquifer water, then the salinity of aquifer increase to a certain level. As you may in Fig. 2 (f), a large amount of chemical species dissolve into the aqueous phase from the rock matrix; (g) The rock mineral continues to be dissolved due to the acidized environment in a long period. There are different types of rock minerals in different saline aquifers. Most target saline aquifers in North America are in sandstone formations, and the common rock minerals are feldspar, clay, smectite, oligoclase, dolomite, calcite, illite, etc. The colors of rocks are changed to represent the different kinds of rock minerals in Fig. 2 (g). Within a long period after CO_2 injection, the mass and volume of rock minerals become decreased and shrunk due to the dissolution of the minerals. A certain amount of H^+ has been consumed due to the dissolution of rock minerals. This is a process of pH buffering, and the pH value tends to increase to be above 7. The porosity and permeability in the pore structure tend to increase, see Figs. 2 (g) and 2 (h). The minerals are precipitated due to interacting of

different chemical species in a very long period. After the dissolution of rock minerals and CO₂ gas, different chemical species precipitate new rock minerals, especially carbonate mineral and silicate minerals (siderite, dolomite, calcite, quartz, illite, ankerite, dawsonite, etc.). The newly precipitated rock minerals is coated on the surface of the shrunk original rock minerals, which resulting in a decrease of porosity and permeability of the saline aquifer. As you may see in Fig. 2 (h), the pore space is reduced due to the precipitation of newly generated rock minerals, and pH value continues to increase due to the consumption of H⁺ (the color of the aquifer water become lighter); (i) The pore structure evolution due to mineral evolution in thousands of years. Fig. 2 (i) shows that the rock minerals newly precipitated on the surface of the aquifer rocks, which extend into the pore spaces, causing a decrease of porosity and permeability. The saturation of supercritical CO₂ decreased due to mineralization of CO₂ in solid phase. The pore structure has been changed significantly as shown in the figure. As mechanical behavior is closely related to the petrophysical properties of the rock material, supercritical CO₂induced chemical changes may lead to significant mechanical weakening in porous and permeable saline aquifer. Rock strength increases with increasing content of strong/hard minerals (e.g. quartz, feldspar), and decreases with increasing amounts of weak/soft minerals (e.g. clay, mica) and porosity. Few studies has concluded that in the case of substantial dissolution/precipitation of framework grains or framework-supporting cements, significant changes in the mechanical behavior are to be expected, and the elastic parameters are proportional to the rock compositions (Marbler et al., 2013; Busch et al., 2014; Hangx et al., 2015). The lack of a simple correlation and a clear computational scheme between rock elastic parameters and rock strength suggests that more experimental studies needs to be conducted. However, We proposed a generic computational scheme to take the mechanical and chemical coupling effects in the numerical model.

Figure 2: Sketch for THMC processes during CO_2 injection into the saline aquifer in the perspective of pore structure: (a) original pore structure under hydrostatic equilibrium; (b) shrunk pore structure under fluid injection; (c) pore structure after CO_2 injection of short period; (d) phase re-equilibrium between water and gas after CO_2 injection; (e) pH value evolution due to solubility of gaseous CO_2 ; (f) aquifer salinity evolution due to pH change in a relatively long period; (g) mineral dissolution due to acidized environment in a long period; (h) mineral precipitation due to interacting of different species in a very long period; (i) pore structure evolution due to mineral evolution in thousands of years.

1.2. Chemical Reaction Pathway

The chemical reaction pathway depends upon rock compositions. According to the mineral compositions of the CO₂ geo-sequestration 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. Oligoclase 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 given by Xu et al. 2006, 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/m²·s), 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 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. 3. 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,
175 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
180 dissociate into different chemical species in Fig. 3. 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
185 the new minerals are relatively fast in the magnitude of 10^{-8} mol/m²·s after the mineral 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
190 reaction pathway of supercritical CO₂ with rock minerals is complicated due to the key factors (rock type, rock composition, reaction rate, etc.)

Figure 3: The sketch for the chemical reaction pathway in the THMC processes during CO₂ geo-sequestration

1.3. 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 CO₂, water and the rock minerals are much more complex. 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 non-linearities 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 geo-sequestration, 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 THC process is much more complex than THM. 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 THC processes, i.e. sequentially coupled approach and fully coupled approach. The first 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; Šimnek and Suarez, 1994; Walter et al., 1994; Zysset et al., 1994; Xu, 1996; Wei, 2012; Zhang et al., 2015). 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, TOUGHREACT are developed to solve the multi-dimensional and multi-phase fluid flow, solute transport, and chemical reactions in groundwater and petroleum systems, respectively. There are few studies of the fully coupled approach (Guimarães et al., 2007; Zheng and Samper, 2008; Zhang et al., 2012a,b; Xiong et al., 2013; Zhang, 2013; Wu et al., 2014; Zheng et al., 2015), it substitutes the geochemical reaction into the fluid flow equations directly, forming a fully coupled reactive solute transport model. This approach solves the fluid flow, solute transport, and geochemical reactions simultaneously with a high accuracy. Therefore, we use the fully coupled approach to solve the THC processes together, in order to get accurate solutions.

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; Zhao et al., 2015a,b). 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
 255 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 par-
 260 tial differential equations, which represents all the related physical mechanisms
 (Minkoff et al., 2003). Thus, the equations of heat flow, fluid flow and geome-
 chanics 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.

265 In this paper, a fully coupled computational framework is proposed and
 used to simulate reactive transport of water, CO₂ gas and species in subsurface
 formation with geomechanics. A novel mathematical model of the THMC pro-
 cesses is developed based on the TOUGHREACT simulator (Xu et al., 2004) and
 TOUGH2_CSM simulator (Winterfeld and Wu, 2012). A set of partial differen-
 270 tial equations is presented to model the THMC processes of the fluid and heat
 flow, solute transport in aqueous and gaseous phase, mean stress, and geochem-
 ical reactions under both equilibrium and kinetic conditions. Practical reactive
 transport examples with complex chemical compositions are presented to ana-
 lyze the THMC processes quantitatively on the coupled effects of geochemical
 275 reaction and geomechanics during CO₂ geo-sequestration process. Heat transfer
 affects mean stress and geochemical reactions, mean stress impacts the solute
 transport and successive chemical reactions. The proposed modeling approach
 can also be used to simulate CO₂ EOR and other secondary and EOR processes
 in petroleum reservoirs.

280 2. Mathematical Model

The THMC processes are described mathematically, including mass balance equation to describe the fluid flow and mass transport, momentum balance equation to describe the mean stress field, energy balance equation to describe the heat flow and energy transport, and geochemical reaction equation to describe
285 the geochemistry occurring during CO₂ geo-sequestration. Geo-chemical equilibrium and kinetics equations are based on TOUGHREACT simulator (Xu et al. 2006), and mean stress equation is based on TOUGH- CSM simulator (Winterfeld and Wu 2012). The assumptions and the mathematical formulations of the THMC model are shown as below.

290 2.1. Assumptions

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
295 the calculation of physical, geomechanical and geochemical properties. Multi-phase 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.
300 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 pre-defined in the model can occur either under local equilibrium or kinetic conditions.
305 The porosity is subject to the mutual change of stress and chemical reactions under the coupling effects of HM and HC. The geomechanical modulus is subject to the change of chemical compositions of the porous medium under the coupling effect of MC. The contingent TH effects such as thermal osmosis are not taken into account in the model.

310 2.2. 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
 315 Darcy's law can be written in the following form:

$$\frac{dM^\kappa}{dt} = \nabla \cdot F^\kappa + q^\kappa + R^\kappa \quad (1)$$

The quantity M is the accumulation term, representing mass of a primary components or species, with $\kappa = 1, \dots, N_k$ κ 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
 320 H₂O and CO₂ due to chemical reactions, which are the feedbacks from the third part of geochemical reaction module.

The general form of the mass accumulation term is

$$M^\kappa = \phi \sum_{\beta} S_{\beta} \rho_{\beta} X_{\beta}^{\kappa} \quad (2)$$

The total mass of primary component or species κ is obtained by summing over the fluid phases β (= water and gas). ϕ is porosity, S_{β} is the saturation of
 325 phase β , ρ_{β} is the density of phase β , X_{β}^{κ} is the total mass fraction of primary component or chemical species κ in phase β , and X_{β}^{κ} is the function of the concentration of related primary chemical species $c_{p,j}$, i.e., $X_{\beta}^{\kappa} = f(c_{p,j})$.

Total mass fraction of primary chemical species

In order To represent the whole geochemical system, a set of N_C aqueous
 330 species is chosen as primary species or components. All the other species are treated as secondary species, including aqueous complexes, precipitated minerals and gaseous species. The secondary species can be represented as a linear combination of the associated primary species. Therefore, all the mass of the secondary species can be transferred to the mass of primary chemical species.

335 The total concentration of primary species can be expressed as:

$$C_j = c_j + \sum_{k=1}^{N_x} v_{kj} c_k \quad j = 1, \dots, N_C \quad (3)$$

where C and c are the total concentrations and individual concentrations; subscripts j and k are the indices of primary species and aqueous complexes; N_C and N_x are the number of the primary and secondary species; v_{kj} is the stoichiometric coefficient of the basis species in the aqueous complexes.

340 The total mass fraction of the primary chemical species can be defined as:

$$X^\kappa = \frac{C^\kappa M^\kappa}{\rho_l} \quad \kappa = 1, \dots, N_C \quad (4)$$

where M^κ is the molecular weight of the primary chemical species, and ρ_l is the density of the aqueous phase.

Aqueous complexation

The aqueous chemical reactions are always under local equilibrium. By
345 means of the mass action equation of the dissociation of the i -th aqueous complex, the concentrations of aqueous complexes can be represented as functions of the concentrations of primary species:

$$c_k = K_k^{-1} \gamma_k^{-1} \prod_{j=1}^{N_c} c_j^{v_{kj}} \gamma_j^{v_{kj}} \quad (5)$$

where c_k is the molal concentration of k -th secondary aqueous complexation, and c_j is molal concentration of the j th basis species, γ_k and γ_j are thermodynamic
350 activity coefficients of secondary and primary species, and K_k is the equilibrium constant of the k -th secondary complexation reaction.

Kinetic mineral dissolution/precipitation

The expression of kinetic rate is given by Lasaga et al. (1994):

$$r_n = f(c_1, c_2, \dots, c_{N_C}) = \pm K_n A_n |1 - \Omega_n^\theta|^\eta \quad n = 1, \dots, N_q \quad (6)$$

where A_n is the specific reactive surface area, Ω_n is the saturation ratio of
355 kinetic mineral, the definition of saturation ratio is explained later. The param-

eters 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 H_2O (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):

$$k_n = k_{25}^n \exp \left[\frac{-E_a^n}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] + k_{25}^{\text{H}^+} \exp \left[\frac{-E_a^{\text{H}^+}}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] a_{\text{H}^+}^{n_{\text{H}^+}} + k_{25}^{\text{OH}^-} \exp \left[\frac{-E_a^{\text{OH}^-}}{R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right] a_{\text{OH}^-}^{n_{\text{OH}^-}} \quad (7)$$

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

2.3. 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.

$$\frac{dU}{dt} = \nabla \cdot F + q_h \quad (8)$$

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.

2.4. Geomechanical Equation of Mean Stress

The mean stress equation in this THMC model is based on the equation by Winterfeld et al. (2012), which is to solve the normal mean stress. The mean stress equation is given below.

$$\frac{3(1-v)}{1+v}\nabla^2\tau_m - \frac{2(1-2v)}{1+v}(\alpha\nabla^2p + 3\beta K\nabla^2T) + \nabla \cdot \bar{F} = 0 \quad (9)$$

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 Lamé's constant, G is the shear modulus, T is the temperature, and subscript m is the label of mean stress.

The geomechanical properties are expected to be correlated with the chemical compositions in the formation in a certain way, we proposed a generic computational scheme to incorporate the MC coupling effect into the numerical model. The geomechanical moduli is proportional to the rock compositions as follows:

$$K = K(c_1, c_2, \dots, c_j) j = 1, \dots, N_C + N_p + N_g \quad (10)$$

$$G = G(c_1, c_2, \dots, c_j) j = 1, \dots, N_C + N_p + N_g \quad (11)$$

Where c_j is primary variable in the numerical model, then we can use the correlation between bulk modulus and shear modulus to calculate the other geomechanical properties in the model.

2.5. Geochemical Reaction Equations 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:

$$F_g = \log \Omega_g = \log \Gamma_g^{-1} p_g^{-1} K_g^{-1} \prod_{j=1}^{N_c} c_j^{v_{gj}} \gamma_j^{v_{gj}} = 0 \quad (12)$$

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

2.6. Geochemical Reaction Equations 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:

$$F_m = \log \Omega_m = \log X_m^{-1} \lambda_m^{-1} K_m^{-1} \prod_{j=1}^{N_c} c_j^{v_{mj}} \gamma_j^{v_{mj}} = 0 \quad (13)$$

where m is the equilibrium mineral index, X_m is the mole fraction of the m^{th} 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 j^{th} basis species in the m^{th} mineral equilibrium reaction, and γ_j is the activity coefficient of primary chemical species.

2.7. Porosity and Permeability Computational Scheme for THMC Coupling Effects

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:

$$\phi_M = \phi(\tau'_m) \quad (14)$$

where subscript M indicates mechanical effects on porosity, τ'_m is the current effective mean stress as $\tau'_m = \tau_m - \alpha p$, and α is Biot coefficient,.

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

$$\phi_c = 1 - \sum_{m=1}^{N_m} f_m - f_u \quad (15)$$

420 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 $\Delta\phi_c = \phi_c^{k+1} - \phi_c^k$:

$$\phi^{t^{k+1}} = \phi^{t^k} + \Delta\phi_M + \Delta\phi_c \quad (16)$$

425 The permeability change is related to the porosity as follows:

$$k^{t^{k+1}} = k(\phi^{t^{k+1}}) \quad (17)$$

2.7.1. Porosity Correlation

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.

- 430 1. Porosity Equation for sedimentary rock by Rutqvist and Tsang (2002)
- Rutqvist and Tsang (2002) presented the following function for porosity, obtained from the laboratory experiment by Davies and Davies (2001) on sedimentary rock :

$$\phi = \phi_r + (\phi_0 - \phi_r)e^{-a\tau'} \quad (18)$$

435 where ϕ_0 is zero effective stress porosity, ϕ_r is high effective stress porosity, the exponent a is a constant parameter, and τ' is effective mean stress.

2. Porosity Equation by McKee et al. (1988)

McKee et al. (1988) presented a relationship between porosity and effective stress from hydrostatic poroelasticity theory by assuming incompressible rock grains:

$$\phi = \phi_0 + \frac{e^{-c_p(\tau' - \tau'_0)}}{1 - \phi_0 (1 - e^{-c_p(\tau' - \tau'_0)})} \quad (19)$$

440 where c_p is the average pore compressibility, ϕ_0 is the original porosity, τ'_0 is the original effective mean stress, and τ' is the effective mean stress.

2.7.2. Permeability Correlation

1. Permeability Equation by Bear (1972)

445 The changes of rock permeability are calculated from changes in porosity using ratios of permeabilities calculated from the Carman-Kozeny relation (Bear 1972), and ignoring changes in grain size, tortuosity and specific surface area as follows:

$$k = k_o \left(\frac{1 - \phi_o}{1 - \phi} \right)^2 \left(\frac{\phi}{\phi_o} \right) \quad (20)$$

where k_o and ϕ_o are the initial permeability and porosity, respectively.

2. Permeability Equation for sedimentary rock by Rutqvist and Tsang (2002)

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

$$k = k_0 e^{c \left(\frac{\phi}{\phi_0} - 1 \right)} \quad (21)$$

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

3. Permeability Equation by Verma and Pruess (1988)

455 Verma and Pruess (1988) presented a power law expression relating permeability to porosity as follows:

$$\frac{k - k_c}{k_0 - k_c} = \left(\frac{\phi - \phi_c}{\phi_0 - \phi_c} \right)^n \quad (22)$$

where k_c and ϕ_c are asymptotic values of permeability and porosity, respectively, and exponent n is a parameter.

4. Permeability Equation by Davies and Davies (2001)

One example from the study by Davies and Davies (2001) is given as follows:

$$k(\tau'_m) = k_i \frac{(1 - \phi_i^2)^2}{(1 - \phi_i)^2} \left(\frac{\phi}{\phi_i} \right)^3 \quad (23)$$

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.

2.8. Discretization and Solution Method

465 The discretizations for mass conservation, energy conservation, mean stress
and geochemistry equations have already been presented by Eqs. 1 - 13. For
the fully coupled approach, the mathematical equations for fluid and heat flow,
geomechanics, and geochemical reaction are solved simultaneously. Based on
single cell, all the governing equations are lumped together in residual forms,
470 and all the primary variable are defined as c_j . The discretized equation system
can be expressed in residual forms as follows:

$$R_n^{\kappa,k+1} = M_n^{\kappa,k+1} - M_n^{\kappa,k} - \frac{\Delta t}{V_n} \left[\sum_m A_{nm} F_{nm}^{\kappa,k+1} + V_n q_n^{\kappa,k+1} + V_n R_{\text{req},n}^{\kappa,k+1} + V_n R_{r,n}^{\kappa,k+1} \right]$$

$\kappa = 1, \dots, N_C$
(24)

$$F_m^{k+1} = F_m(c_{j,k+1}) \quad j = 1, \dots, N_C + N_p + Ng \quad (25)$$

$$F_g^{k+1} = F_g(c_{j,k+1}) \quad j = 1, \dots, N_C + N_p + Ng \quad (26)$$

$$M^{k+1} = M(c_{j,k+1}) \quad j = 1, \dots, N_C + N_p + Ng \quad (27)$$

For each volume element V_n , there are N_{EQ} equations to describe the THMC
processes. The total number of the non-linear equations representing the THMC
system with N_{el} grid blocks is $N_{el} \times N_{eq}$. The unknown primary variables has
475 the same number as the equations c_j ; $j = 1, \dots, N_{EL} \times N_{EQ}$, which define the
state of the THMC system at a specific time step t^{k+l} . The method of Newton-
Raphson iteration is employed to solve the equation system. A Newton-Raphson
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

480 in terms of primary variables are as follows:

$$R_n^{\kappa,k+1}(c_{j,p+1}) = R_n^{\kappa,k+1}(c_{j,p}) + \sum_{j=1}^{N_C+N_p+N_g} \frac{\partial R_n^{\kappa,k+1}}{\partial c_j} \Big|_p (c_{j,p+1} - c_{j,p}) \quad \kappa = 1, \dots, N_C \quad (28)$$

$$F_m^{k+1}(c_{j,p+1}) = F_m^{k+1}(c_{j,p}) + \sum_{j=1}^{N_C+N_p+N_g} \frac{\partial F_m^{k+1}}{\partial c_{j,p}} \Big|_p (c_{j,p+1} - c_{j,p}) \quad (29)$$

$$F_g^{k+1}(c_{j,p+1}) = F_g^{k+1}(c_{j,p}) + \sum_{j=1}^{N_C+N_p+N_g} \frac{\partial F_g^{k+1}}{\partial c_{j,p}} \Big|_p (c_{j,p+1} - c_{j,p}) \quad (30)$$

$$M^{k+1}(c_{j,p+1}) = M^{k+1}(c_{j,p}) + \sum_{j=1}^{N_C+N_p+N_g} \frac{\partial M^{k+1}}{\partial c_{j,p}} \Big|_p (c_{j,p+1} - c_{j,p}) \quad (31)$$

Retaining only terms up to first order, a set of $NEL \times NEQ$ linear equations for the increments $(c_{j,p+1} - c_{j,p})$ can be obtained as follows:

$$\sum_{j=1}^{N_C+N_p+N_g} \frac{\partial R_n^{\kappa,k+1}}{\partial c_j} \Big|_p (c_{j,p+1} - c_{j,p}) = -R_n^{\kappa,k+1}(c_{j,p}) \quad \kappa = 1, \dots, N_C + N_p + N_g \quad (32)$$

$$\sum_{j=1}^{N_C+N_p+N_g} \frac{\partial F_m^{k+1}}{\partial c_{j,p}} \Big|_p (c_{j,p+1} - c_{j,p}) = -F_m^{k+1}(c_{j,p}) \quad (33)$$

$$\sum_{j=1}^{N_C+N_p+N_g} \frac{\partial F_g^{k+1}}{\partial c_{j,p}} \Big|_p (c_{j,p+1} - c_{j,p}) = -F_g^{k+1}(c_{j,p}) \quad (34)$$

$$\sum_{j=1}^{N_C+N_p+N_g} \frac{\partial M^{k+1}}{\partial c_{j,p}} \Big|_p (c_{j,p+1} - c_{j,p}) = -M^{k+1}(c_{j,p}) \quad (35)$$

For the fully coupled approach, the fluid flow and reactive solute transport equations are solved simultaneously until the prescribed convergence criteria are
485 satisfied.

2.9. Convergence Criteria

Referred to the Toughreact simulator (Xu et al. 2004), the convergence is achieved when the absolute value of the ratio between the relative increment of concentration and the concentration of primary components or species is less than a given convergence tolerance. The convergence criteria can be expressed as:

$$\frac{|\Delta c_{j,p+1}^{k+1}|}{c_{j,p}^{k+1}} \leq \tau \quad j = 1, 2, \dots, N_c + N_p + N_g \quad (36)$$

where, τ is the convergence criterion.

2.10. Code Structure of Fully Coupled THMC Model

Fig. 4 shows the flow chart to solve the fully coupled THMC model. It solves the fluid and heat flow, geomechanics and geochemical reactions simultaneously in one time step. The governing equations for the geochemical reaction system interested are highly non-linear algebraic equations. They are solved by Newton-Raphson iteration method, and the matrix coefficients are calculated by the numerical derivatives related to the primary unknown variables.

Figure 4: The flow chart of the proposed fully coupled THMC simulator.

500 **3. Numerical Modeling for THMC Processes during CO₂ Geological Sequestration**

The fully coupled THMC model is verified against different analytical solutions for the mechanisms involved in the THMC processes, including equilibrium chemical reaction, kinetic chemical reaction, heat conduction and geomechanical consolidation, and the numerical results have a good match with analytical solutions (Wu et al., 2014). In the THMC processes of CO₂ geo-sequestration, one mechanism may effect the others. The thermal effect influences the temperature, pressure, stress, and chemical reaction. High temperature can reduce the amount of gaseous CO₂ dissolved into aqueous phase, but may accelerate the chemical reaction, especially for mineral dissolution and precipitation of rock minerals, and may increase the stress when subjected to CO₂ gas injection. In addition, the pressure increases subjected to CO₂ gas injection, which influence the phase equilibrium between CO₂ gas and aquifer water. This model is designed to show the mutual THMC effects during CO₂ geo-sequestration

515 *3.1. Hydrological and Geomechanical Description*

A 1D numerical model is subjected to large amount of CO₂ injection with low temperature. The model is assumed to be sealed by upper caprock and lower bedrock. A CO₂ injection well is located at the center of the radial system. The temperature of gaseous CO₂ is 32 °C, which corresponds to the enthalpy of 5.632×10⁵ J/kg and keep the gaseous CO₂ under supercritical condition (31.1°C and 7.4×10⁶Pa). The model is then discretized into 500 grid blocks in logarithmic distribution in the radial direction. The sandstone aquifer is assumed to be initially homogenous and isotropic in terms of hydrological and geological properties. The parameters of the model are given in Tab. 1. The initial condition of the temperature is set equal to 75 °C in the model. For the boundary conditions, no-flow boundaries are assumed due to the impermeable seal layers along the top and bottom of this model. No-flow boundary conditions are assumed due to the radial symmetry of the CO₂ injection point at the left boundary.

The constant boundary conditions of pressure and mean stress are assigned to
 530 the infinite radius of the simulation model at the right boundary. It is assumed
 that only small amounts of the primary chemical species in the original aquifer
 water. In terms of geochemical reaction, 3 runs have been designed to evaluate
 the effects of pure CO₂ dissolution, mineral dissolution under equilibrium con-
 dition and mineral dissolution/precipitation under kinetic condition, each run
 535 of the model has different mineral compositions. Each run of the model has two
 scenarios: isothermal and non-isothermal, in order to exam the thermal effect
 on the THMC processes. The pressure and stress changes dramatically dur-
 ing CO₂ injection period, therefore we analyze the thermal, hydrological, and
 geomechanical effects in this section.

540 3.1.1. *The hydrological and thermal effects of low temperature supercritical CO₂ injection*

For the numerical solution, two scenarios for this THMC model is conducted:
 the first one under non-isothermal condition, and the second one is isothermal
 condition. Figs. 5 shows the spatial distribution of pressure profile for non-
 545 isothermal case. Figs. 6 shows the spatial distribution of CO₂ gas saturation
 profile for non-isothermal cases. The profiles for pressure and gas saturation
 after 1 year, 3 years, 5 years and 10 years are much similar for both cases.
 The thermal effect do not have a significant impact on the pressure and fluid
 transport subject to CO₂ injection.

550 In Figs. 5, the pressure continues to build up in the two phase mixtures
 areas, and then moves laterally with CO₂ injecting into saline aquifer. The
 pressure near the injection point continues to increase after 1 year, then tends
 to decrease with the pressure transporting to far area of the aquifer, and CO₂
 gas moving along the radial coordinates after 3 years, 5 years and 10 years. The
 555 pressure profiles in the two phase area have a sharp tendency compared with
 the single phase gas and water areas. Figs. 6 indicates the CO₂ gas front during
 10 years' CO₂ injection. The CO₂ gas transports to the location of 550 m after
 1 year, 850 m after 3 years, 1,150 m after 5 years, and 1,450 m after 10 years.

The two phase of gas and liquid coexists within these distances for the different
560 periods, and the pressure buildup is significant in the two phase area in Figs. 5.

Fig. 7 show the spatial distribution of temperature for the non-isothermal
case. The gaseous CO₂ with a temperature of 32 °C is injected into the for-
mation. The temperature transports with the CO₂ gas moving laterally. The
thermal effect has a significant impact on the temperature of the model. The
565 temperature of formation become 32 °C within 38 m of the wellbore after 1
year, 70 m after 3 years, 95 m after 5 years and 130 m after 10 years.

3.1.2. *The thermal effect on mean stress*

Figs. 8 and 9 show the spatial distribution of mean stress profile for both
non-isothermal and isothermal cases. For the change in geo-mechanical field,
570 the mean stress is proportional to the pore pressure in saline aquifer. Fig. 8 indi-
cates that the thermal effect has a significant impact on the mean stress profile.
When subjected to low temperature supercritical CO₂, the mean stress tends to
decrease. Mean stress decreases significantly with a maximum value of 2×10^6 Pa
in the low temperature area in Fig. 7. After that, the temperature within the
575 area near wellbore is the same with the supercritical CO₂, the mean stress tends
to increase in these areas because of the continued CO₂ injection. However, the
mean stress tends to decrease when cold CO₂ transports into the far areas, then
to increase after the temperatures in these areas are the same with supercritical
CO₂. Fig. 9 shows that the mean stress profile has the same tendency with
580 pressure profile during 10 years' CO₂ injection in isothermal case. The mean
stress continues to build up within the area of two-phase mixtures. The mean
stress increases rapidly when the front of two phase area moves laterally with
CO₂ injection. Figs. 10 and 11 show the spatial distribution of volumetric strain
profile for both non-isothermal and isothermal cases. The volumetric strain is
585 related to the surface uplift of the formation in terms of the volume change of
aquifer due to CO₂ injection. The tendencies of the volumetric strain profile for
both cases are the same with the mean stress for both cases.

3.2. Run 1 with pure CO_2 dissolution under equilibrium

The objective of this run is to exam the effects of pure CO_2 dissolution on the THMC processes of CO_2 sequestration. The chemical reaction system is defined as pure CO_2 dissolution. The chemical reaction is only between gaseous CO_2 and H_2O . The chemical formulations in this system are listed in Tab. 2. There are three primary chemical species (H_2O , H^+ , and HCO_3^-) that can represent the total mass or mole in the chemical reaction system of gaseous CO_2 dissolution, in which there are three aqueous equilibrium reactions and one gas dissolution into aqueous phase. The three aqueous chemical complexations are controlled by equilibrium constant, and the CO_2 gas dissolution is controlled by partial pressure and fugacity coefficient.

Three primary aqueous species (H_2O , H^+ , and HCO_3^-) and one primary gaseous species ($\text{CO}_2(\text{g})$) have been selected to dominate this chemical reaction system ($\text{CO}_2(\text{g})$ dissolution), there are five governing equations, of which four mass balance equations for all the primary chemical species, and one saturation index equation to solve dissolution concentration of CO_2 gas. In addition, one energy balance equation is to solve temperature, and one momentum balance equation to solve mean stress. Therefore, the equation system includes seven main equations which can represent the THMC system (CO_2 dissolution) numerically. Seven unknown variables are selected as the primary variable for the fully coupled reactive solute transport model.

3.2.1. The thermal effect on CO_2 dissolution under chemical equilibrium

Figs. 12 and 13 show the spatial distribution of dissolved concentration of $\text{CO}_2(\text{g})$ for both non-isothermal and isothermal cases. The CO_2 dissolution only occurs within the two phase area of CO_2 and H_2O coexisting. The maximum dissolved concentrations of $\text{CO}_2(\text{g})$ occur near the wellbore area with values of 2.32 mol/l for nonisothermal case (Fig. 12) and 1.75 mol/l for nonisothermal case (Fig. 13). It is obvious that the the dissolved concentration of CO_2 gas in the lower temperature area for non-isothermal case are bigger than that for isothermal case. Therefore, thermal effect has a significant impact on the

chemical reaction process. Low temperature can help more supercritical CO₂ dissolving into the aqueous phase, which can assist the solubility trapping of
620 supercritical CO₂.

3.2.2. *The geochemical effects of CO₂ dissolution under chemical equilibrium*

Figs. 14 - 19 show the spatial distribution of the concentration of related chemical species for both non-isothermal and isothermal cases. In terms of the tendency of the profile, the independent concentration of CO₂(aq) (Fig. 14),
625 HCO₃⁻ (Fig. 16) and H⁺ (Fig. 18) has the maximum values within the low temperature area for nonisothermal case. All these chemical species are byproducts of CO₂ dissolution. In terms of the amount of the concentration, the chemical species CO₂(aq) has the biggest concentration among these three chemical species.

630 3.2.3. *The thermal effect on pH values of CO₂ dissolution*

Figs. 20 - 21 show the spatial distribution of the pH value for both both cases. The formation is acidized in two phase area. The pH value decreases to 3.0 within the low temperature area for nonisothermal case. However, the The pH value decreases to about 3.1 within the two phase area for isothermal case
635 (Fig. 20). The dissolved concentrations of CO₂ gas in the nonisothermal case are bigger than those in isothermal case, which are shown in Figs. 12 and 13. The CO₂ dissolution releases H⁺, which determines pH value. Therefore, the nonisothermal case is much more acidized.

3.3. *Run 2 with mineral dissolution under equilibrium*

640 The objective of this run is to exam the effects of CO₂ gas dissolution and mineral dissolution under equilibrium condition on the THMC processes of CO₂ sequestration. This chemical reaction system includes not only CO₂ gas dissolution but also mineral dissolution between mineral and aquifer water. The chemical reaction system is defined as CO₂ dissolution plus CaCO₃(s) dissolution.
645 Therefore, the chemical reactions involved in this chemical reaction system are between gaseous CO₂ and H₂O, and between CaCO₃(s) and H₂O.

The chemical formulations in this system are listed in Tab. 2. There are six aqueous equilibrium reactions, one gas dissolution into aqueous phase and one mineral dissolution into aqueous phase.

650 For the geochemical parameters, the volume fraction of $\text{CaCO}_3(\text{s})$ in the rock is 5 percent and the $\text{CaCO}_3(\text{s})$ dissolution is set to be in equilibrium. The other 95 percent is treated as unreactive minerals. This numerical model is to evaluate the effects of supercritical CO_2 injection on hydrological, mechanical properties, and the effect of gas and mineral dissolution on hydrological, mechanical and 655 chemical properties, the effect of temperature on the hydrological, mechanical and chemical properties.

The geochemical system in this run is an equilibrium system ($\text{H}_2\text{O}(\text{l})$ - $\text{CO}_2(\text{g})$ - $\text{CaCO}_3(\text{s})$), including the equilibrium geochemical reactions among three phases. The four primary aqueous species (H_2O , H^+ , HCO_3^- , and Ca^{2+}), one primary 660 gaseous species ($\text{CO}_2(\text{g})$) and one primary mineral species ($\text{CaCO}_3(\text{s})$) are selected to represent this chemical reaction system, there are seven governing equations, of which five mass balance equation for all the primary chemical species, one gas saturation index equation to solve dissolution concentration of CO_2 gas, and one mineral saturation index equation to solve dissolution con- 665 centration of $\text{CaCO}_3(\text{s})$. In addition, one energy balance equation is to solve temperature, and one momentum balance equation to solve mean stress. Therefore, the equation system includes nine main equations which can represent the THMC system (CO_2 dissolution + $\text{CaCO}_3(\text{s})$ dissolution) numerically.

3.3.1. The thermal effect on the equilibrium constant of CaCO_3 dissolution

670 Fig. 22 shows the spatial distribution of equilibrium constant for CaCO_3 dissolution for non-isothermal case. The equilibrium constant is a function of temperature. In the low temperature area, the value of $\log K_{\text{eq}}$ increases to maximum value of 1.75. However, the value of $\log K_{\text{eq}}$ maintains 1.12 at the area with original temperature. The change of equilibrium constant for CaCO_3 675 results in different chemistry in the aqueous phase compared with the isothermal case, especially for the dissolved concentration of $\text{CaCO}_3(\text{s})$.

3.3.2. The thermal effect on CaCO_3 dissolution under chemical equilibrium

Figs. 23 and 24 show the spatial distribution of dissolved concentration of $\text{CaCO}_3(\text{s})$ for both non-isothermal and isothermal cases. The $\text{CaCO}_3(\text{s})$ dissolution only occurs within the two phase area of CO_2 and H_2O coexisting. The maximum dissolved concentrations of $\text{CaCO}_3(\text{s})$ occur near the wellbore area with values of 0.056 mol/l for nonisothermal case (Fig. 23) and 0.026 mol/l for nonisothermal case (Fig. 24). The maximum dissolved concentration for the nonisothermal case is more than two times of isothermal case. It is indicated that there are areas with high dissolution concentrations of $\text{CaCO}_3(\text{s})$ in Fig. 23. These areas are under low temperature condition. Therefore, the low temperature is favorable for both supercritical CO_2 dissolution and $\text{CaCO}_3(\text{s})$ dissolution into the aqueous phase.

3.3.3. The thermal effect on pH values of CaCO_3 dissolution

Figs. 25 - 26 show the spatial distribution of the pH value for both non-isothermal and isothermal cases. The formation is acidized within the two phase area. The pH value decreases to about 4.81 within the low temperature area for nonisothermal case (Fig. 25), and the pH value decreases to about 4.65 within the two phase area for isothermal case (Fig. 26). The isothermal case is more acidized than nonisothermal case. Furthermore, the pH value in both cases is much higher than those in Section 3.2.3. The cases in Section 3.2.3 are more acidized. In this case, the $\text{CaCO}_3(\text{s})$ dissolution is taken into account to evaluate the mutual effect of $\text{CO}_2(\text{g})$ and $\text{CaCO}_3(\text{s})$ dissolutions on the chemistry. The CO_2 dissolution releases large amount of H^+ , which is consumed by the dissolution of $\text{CaCO}_3(\text{s})$. Therefore, the case in this section is less acidized. Moreover, the pH values within the areas close to wellbore in nonisothermal case are higher than those in isothermal case in Fig. 25, especially within 38 m of the wellbore after 1 year, 70 m after 3years, 95 m after 5 years and 130 m after 10 years. Low temperature areas have larger dissolved concentrations of $\text{CaCO}_3(\text{s})$. More chemical species H^+ is consumed in these areas for nonisothermal case. Therefore, pH value is higher in these areas in the nonisothermal case.

3.3.4. The geochemical effects of CO_2 dissolution and CaCO_3 dissolution

Figs. 27 - 30 show the spatial distribution of the concentration of associate chemical species for both $\text{CO}_2(\text{g})$ and $\text{CaCO}_3(\text{s})$ dissolutions in non-isothermal and isothermal cases. $\text{CO}_2(\text{aq})$ and HCO_3^- are the byproducts of $\text{CO}_2(\text{g})$ dissolution. Figs. 27 and 28 show the spatial distribution of concentration of $\text{CO}_2(\text{aq})$ for both cases. The maximum concentrations of $\text{CO}_2(\text{aq})$ are 2.15 mol/l for non-isothermal case and 1.69 mol/l for isothermal case. The magnitudes of these values are similar with those in Figs. 14 and 15 of Section 3.2.3. It is indicated that the $\text{CaCO}_3(\text{s})$ dissolution does not have a significant impact on the concentration of $\text{CO}_2(\text{aq})$ for $\text{CO}_2(\text{g})$ dissolution. Furthermore, Figs. 29 and 30 show the spatial distribution of concentration of HCO_3^- for both cases. The maximum concentrations of HCO_3^- are 0.095 mol/l for nonisothermal case and 0.050 mol/l for isothermal case. In the low temperature area, the concentrations of HCO_3^- are higher than those in isothermal case. However, the magnitudes of these values are much bigger than those in Figs. 16 and 17 of run 1. The maximum concentrations of HCO_3^- are 0.0015 mol/l for nonisothermal case (Fig. 16) and 0.0010 mol/l for isothermal case (Fig. 17). The values in these cases are about six times of those in Section 3.2.3. The concentration of HCO_3^- comes from both $\text{CO}_2(\text{g})$ and $\text{CaCO}_3(\text{s})$ dissolutions. It is obvious that majority of the HCO_3^- is released by $\text{CaCO}_3(\text{s})$ dissolutions.

3.4. Run 3 with mineral dissolution and precipitation under kinetics

The objective of this run is to evaluate the effects of CO_2 gas dissolution and kinetic reactions on the THMC processes of CO_2 geo-sequestration. In this case, the chemical reaction system includes the dissolution and precipitation of multiple minerals (calcite, kaolinite and anorthite). This chemical reactions are not only equilibrium dissolutions of gas and mineral but also kinetic dissolutions and precipitations of minerals. All the chemical reaction are between gaseous CO_2 and water, and between solid mineral and water. The example problems of CMG GEM-GHG module also has selected calcite, kaolinite and anorthite minerals in the geochemical system. Anorthite is a typical plagioclase feldspar

mineral, kaolite is a typical clay mineral, and calcite is typical carbonate mineral. These three minerals are the typical composition for the target saline aquifer.

The initial concentrations of the primary chemical species in this model is given in Tab. 1. For the geochemical parameters, the initial volume fraction of $\text{CaCO}_3(\text{s})$ in the rock is 5.88 percent and the $\text{CaCO}_3(\text{s})$ dissolution/precipitation is set to be in equilibrium. The initial volume fractions of kaolinite and anorthite in the rock are 5.76 percent and 5.88 percent. The dissolution/precipitation of kaolinite and anorthite are set to be in kinetic condition. The other 82.48 percent is treated as unreactive minerals. The supercritical CO_2 is injected for 10 years and sequestered for 800 years. This THMC model is to evaluate the thermal effects on the long term CO_2 sequestration, the effects of kinetic reaction on the dissolution of supercritical CO_2 .

The chemical formulations in this geochemical system are listed in Tab. 2. There are six primary chemical species (H_2O , H^+ , HCO_3^- , Ca^{2+} , SiO_2 and AlO_2^-) that can represent the total mass or mole in the chemical reaction system of gaseous CO_2 dissolution and mineral dissolution/precipitation, in which there are twelve aqueous equilibrium reactions, one gas dissolution into aqueous phase under equilibrium condition, one mineral dissolution into aqueous phase under equilibrium condition, and two mineral dissolution or precipitation into aqueous phase under kinetic condition. All of the potential chemical reactions occurring in aqueous phase are set to be equilibrium. The kaolinite and anorthite dissolution/precipitation and dissolution/precipitation are controlled by kinetic reaction rate.

The six primary aqueous species (H_2O , H^+ , HCO_3^- , Ca^{2+} , SiO_2 and AlO_2^-), one primary gaseous species ($\text{CO}_2(\text{g})$) and three primary mineral species ($\text{CaCO}_3(\text{s})$, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(\text{s})$, and $\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)(\text{s})$) are selected to represent this chemical reaction system, there are nine governing equations, of which seven mass balance equations for all the primary chemical species, one gas saturation index equation to solve dissolution concentration of CO_2 gas, and one mineral saturation index equation to solve dissolution concentration of $\text{CaCO}_3(\text{s})$. In addition, one energy balance equation is to solve temperature, and one mo-

momentum balance equation to solve mean stress. The equation system includes eleven main equations which can represent the THMC system (CO_2 dissolution + calcite dissolution + kaolinite dissolution/precipitation + anorthite dissolution/precipitation) numerically. This THMC model in run 3 has the most complex geochemical reaction system. Therefore, the detailed derivation of this THMC model can provide a good example to show the numerical equation system in Appendix A.

3.4.1. *The thermal effect on kinetic reaction rate of anorthite dissolution*

Figs. 37 and 38 show the kinetic reaction rate profile of anorthite dissolution during 800 years' storage period for both cases. Positive value of kinetic reaction rate represents dissolution and negative value represents precipitation. It is indicated that the kinetic reaction rate for anorthite dissolution reaches the maximum value of about 3.0×10^{-10} mol/kg $\text{H}_2\text{O}/\text{s}$ in the areas with high temperature, and it is around 0.2×10^{-10} mol/kg $\text{H}_2\text{O}/\text{s}$ within about 500 m close to the wellbore areas with low temperature (Fig. 37). The kinetic reaction rate under high temperature condition of 70°C is fifteen times higher than that under low temperature condition of 30°C . Fig. 38 shows the kinetic reaction rate of anorthite dissolution for isothermal case, and its value is decreasing along the horizontal distance.

3.4.2. *The thermal effect on kinetic reaction rate of kaolinite precipitation*

Figs. 39 and 40 show the kinetic reaction rate profile of kaolinite precipitation during 800 years' storage period for both cases. It is shown in Fig. 39 that the kinetic reaction rate for kaolinite precipitation reaches the maximum value of about 3.0×10^{-10} mol/kg $\text{H}_2\text{O}/\text{s}$ in the areas with high temperature, and it is less than 0.3×10^{-10} mol/kg $\text{H}_2\text{O}/\text{s}$ within about 400 m close to the wellbore areas. Fig. 40 shows the kinetic reaction rate of kaolinite precipitation for isothermal case, and its value of kinetic reaction rate is decreasing along the horizontal distance.

3.4.3. The thermal and geochemical effect on anorthite dissolution volume

Figs. 31 - 36 show the volume fraction change profile for rock minerals during 800 years' storage period for both non-isothermal and isothermal cases. It is obvious that anorthite tends to dissolved to the maximum amount after 800 years, and koalinite and calcite tend to precipitate to the maximum amounts at 800 years. Figs. 31 and 32 show the volume fraction change profile of anorthite during 800 years' storage period for both cases. It is obvious that the volume fractions of anorthite dissolved into the mineral phase achieve the maximum values (about 4 percent) in the area with high temperature. However, the volume fractions of anorthite dissolved into aqueous phase is only a small amount in the areas with low temperature. The volume fraction of anorthite only decreases by 0.6 percent at the injection point (Fig. 31) after 800 years for nonisothermal case, but the volume fraction of anorthite decreases by 3.75 percent at the injection point (Fig. 32) after 800 years for the isothermal case. Fig. 32 shows that the volume fractions of anorthite precipitated into mineral phase are larger in the areas near wellbore for isothermal case.

3.4.4. The thermal and geochemical effect on calcite precipitation volume

Figs. 33 and 34 show the the volume fraction change profile of calcite during 800 years' storage period for both cases. At the injection period, the calcite tends to dissolved into the aqueous phase, as shown in Figs. 23 and 24. It is an equilibrium chemical reaction controlled by equilibrium constant. The chemical species of Ca^{2+} and HCO_3^- is not supersaturated at the injection period due to the short time period. With time increasing, kinetic chemical reaction dominates the chemical system. These two chemical species become supersaturated after the dissolution of anorthite. It is obvious that the calcite precipitates into mineral phase in Figs. 33 and 34. It is obvious that the volume fractions of calcite precipitated into the mineral phase achieve the maximum values (about 4 percent) in the area with high temperature. However, the volume fractions of calcite precipitated into mineral phase is only a small amount (less than 2 percent) in the areas with low temperature.

3.4.5. The thermal and geochemical effect on kaolinite precipitation volume

Figs. 35 and 36 show the the volume fraction change profile of kaolinite during 800 years' storage period for both cases. The volume fractions of kaolinite precipitated into the mineral phase achieve the maximum values (about 4 percent) in the area with high temperature. However, the volume fractions of kaolinite precipitated into mineral phase is only a small amount (less than 7 percent) in the areas with low temperature. The tendencies of Figs. 35 and 36 are similar with Figs. 33 and 34. Therefore, the thermal effect has a significant effect on the evolution of rock compositions.

Figs. 32, 34 and 36 show the volume fraction change profiles of anorthite, calcite and kaolinite during 800 years' storage period for isothermal case. Figs. 38 and 40 show the kinetic reaction rate profiles of anorthite and kaolinite during 800 years' storage period for isothermal case. It is indicated that the absolute value of volume fraction change for these minerals are smaller within 400 m of wellbore than the far areas. However, the kinetic reaction rates for anorthite and kaolinite tend to be larger in the wellbore area. The supercritical CO₂ is highly saturated in the wellbore areas due to large amount of supercritical CO₂ injection. The amount of water near wellbore area is less than the far areas. Therefore, there is not much rock minerals dissolved/precipitated near wellbore, even though the kinetic reaction rate is larger in the area near wellbore.

3.4.6. The thermal and geochemical effect on CO₂ dissolution concentration

Figs. 41 and 42 show the spatial distribution of dissolved concentration of CO₂(g) for both non-isothermal and isothermal cases. The CO₂ dissolution only occurs within the two phase area of CO₂ and H₂O coexisting. Fig. 41 shows that the amount of CO₂ dissolved into aqueous phase in the area with low temperature is larger than the other areas at 50 years' storage period, after that, it becomes smaller than the other areas with time increasing. The kinetic reaction starts to dominate the chemical reaction system during long term storage period, and the kinetic reaction rate tend to be larger under high temperature condition. Therefore, the supercritical CO₂ dissolved faster to supply HCO₃⁻ for

calcite precipitation. Fig. 42 shows that the dissolved concentration of $\text{CO}_2(\text{g})$ is decreasing along horizontal distance.

Table 1: Initial parameters for the THMC Model.

Hydrological parameter	
Permeability	10^{-13} m^2
Formation thickness	100 m
Formation length	10000 m
Porosity	0.30
Temperature	75 °C
Initial pressure	$2 \times 10^7 \text{ Pa}$
CO ₂ injection rate	90 kg/s
CO ₂ enthalpy	$5.632 \times 10^5 \text{ J/kg}$
Relative permeability	
Liquid	van Genuchten Function (1980)
Gas	Corey Function (1954)
Capillary pressure	van Genuchten function (1980)
Stress	
Biot coefficient	1.0
Poisson's ratio	0.25
Young's modulus	$5.0 \times 10^9 \text{ Pa}$
Initial mean stress	$4.71 \times 10^7 \text{ Pa}$
Linear thermal expansion	$1 \times 10^{-5} \text{ 1/}^\circ\text{C}$
Chemical Species Concentration	
H ⁺	$0.4320 \times 10^{-8} \text{ mol/l}$
HCO ₃ ⁻	$0.1960 \times 10^{-7} \text{ mol/l}$
Ca ²⁺	$0.4737 \times 10^{-5} \text{ mol/l}$
SiO ₂ (aq)	$0.8603 \times 10^{-10} \text{ mol/l}$
AlO ₂ ⁻	$0.1078 \times 10^{-11} \text{ mol/l}$
Kinetic Reaction Rate Constant	
Anorthite	$2.5119 \times 10^{-12} \text{ mol/m}^2/\text{s}$

Kaolinite	$6.9183 \times 10^{-14} \text{ mol/m}^2/\text{s}$
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Table 2: Chemical Reaction Formulation (Wolery, 1992)

1	2		<p>Aqueous complexation under equilibrium state</p> $\text{OH}^- \rightleftharpoons \text{H}_2\text{O} - \text{H}^+$ $\text{CO}_3^{2-} \rightleftharpoons \text{HCO}_3^- - \text{H}^+$ $\text{CO}_2(\text{aq}) \rightleftharpoons \text{HCO}_3^- + \text{H}^+ - \text{H}_2\text{O}$ <p>Gas dissolution under equilibrium state</p> $\text{CO}_2(\text{g}) \rightleftharpoons \text{HCO}_3^- + \text{H}^+ - \text{H}_2\text{O}$
		3	<p>Aqueous complexation under equilibrium state</p> $\text{CaCO}_3(\text{aq}) \rightleftharpoons \text{Ca}^{2+} - \text{H}^+ + \text{HCO}_3^-$ $\text{CaHCO}_3^+ \rightleftharpoons \text{Ca}^{2+} + \text{HCO}_3^-$ $\text{CaOH}^+ \rightleftharpoons \text{Ca}^{2+} + \text{H}_2\text{O} - \text{H}^+$ <p>Calcite dissolution or precipitation under equilibrium state</p> $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+} - \text{H}^+ + \text{HCO}_3^-$
			<p>Aqueous complexation under equilibrium state</p> $\text{Al}^{3+} \rightleftharpoons 4\text{H}^+ + \text{AlO}_2^- - 2\text{H}_2\text{O}$ $\text{HAlO}_2(\text{aq}) \rightleftharpoons \text{H}^+ + \text{AlO}_2^-$ $\text{AlOH}^{2+} \rightleftharpoons 3\text{H}^+ - \text{H}_2\text{O} + \text{AlO}_2^-$ $\text{Al}(\text{OH})_2^+ \rightleftharpoons 2\text{H}^+ + \text{AlO}_2^-$ $\text{Al}(\text{OH})_3(\text{aq}) \rightleftharpoons \text{H}^+ - \text{H}_2\text{O} + \text{AlO}_2^-$ $\text{H}_3\text{SiO}_4^- \rightleftharpoons \text{SiO}_2(\text{aq}) - \text{H}^+ + 2\text{H}_2\text{O}$ <p>Kaolinite dissolution or precipitation under kinetic state</p> $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \longleftrightarrow 2\text{H}^+ + 2\text{SiO}_2(\text{aq}) + \text{H}_2\text{O} + 2\text{AlO}_2^-$ <p>Anorthite dissolution or precipitation under kinetic state</p> $\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8) \longleftrightarrow \text{Ca}^{2+} + 2\text{SiO}_2(\text{aq}) + 2\text{AlO}_2^-$

Figure 5: Pressure evolution subjected to low temperature supercritical CO₂ injection

Figure 6: CO₂ gas saturation evolution subjected to low temperature supercritical CO₂ injection

Figure 7: Temperature evolution subjected to low temperature supercritical CO₂ injection

Figure 8: Mean stress evolution subjected to low temperature supercritical CO₂ injection

Figure 9: Mean stress evolution subjected to supercritical CO₂ injection

Figure 10: Volumetric strain evolution subjected to low temperature supercritical CO₂ injection

Figure 11: Volumetric strain evolution subjected to supercritical CO₂ injection

Figure 12: Dissolved concentration of CO₂(g) in aqueous phase for nonisothermal case

Figure 13: Dissolved concentration of CO₂(g) in aqueous phase for isothermal case

Figure 14: Concentration of aqueous CO₂(aq) subjected to low temperature supercritical CO₂ injection

Figure 15: Concentration of aqueous $\text{CO}_2(\text{aq})$ subjected to supercritical CO_2 injection

Figure 16: Concentration of bicarbonate ion (HCO_3^-) subjected to low temperature supercritical CO_2 injection

Figure 17: Concentration of bicarbonate ion (HCO_3^-) subjected to supercritical CO_2 injection

Figure 18: Concentration of H^+ subjected to low temperature supercritical CO_2 injection

Figure 19: Concentration of H^+ subjected to supercritical CO_2 injection

Figure 20: pH value evolution subjected to low temperature supercritical CO_2 injection

Figure 21: pH value evolution subjected to supercritical CO₂ injection

Figure 22: Equilibrium constant of calcite (CaCO_3) subjected to low temperature supercritical CO_2 injection

Figure 23: Concentration of dissolved CaCO_3 subjected to low temperature supercritical CO_2 injection

Figure 24: Concentration of dissolved $\text{CaCO}_3(\text{s})$ subjected to supercritical CO_2 injection

Figure 25: pH value evolution subjected to low temperature supercritical CO_2 injection

Figure 26: pH value evolution subjected to supercritical CO₂ injection

Figure 27: Concentration of aqueous CO₂(aq) subjected to low temperature supercritical CO₂ injection

Figure 28: Concentration of aqueous CO₂(aq) subjected to supercritical CO₂ injection

Figure 29: Concentration of bicarbonate ion (HCO_3^-) subjected to low temperature supercritical CO_2 injection

Figure 30: Concentration of bicarbonate ion (HCO_3^-) subjected to supercritical CO_2 injection

Figure 31: Volume fraction change of anorthite subjected to low temperature supercritical CO₂ injection

Figure 32: Volume fraction change of anorthite subjected to supercritical CO₂ injection

Figure 33: Volume fraction change of calcite subjected to low temperature supercritical CO₂ injection

Figure 34: Volume fraction change of calcite subjected to supercritical CO₂ injection

Figure 35: Volume fraction change of kaolinite subjected to low temperature supercritical CO₂ injection

Figure 36: Volume fraction change of kaolinite subjected to supercritical CO₂ injection

Figure 37: Kinetic reaction rate of anorthite subjected to low temperature supercritical CO₂ injection

Figure 38: Kinetic reaction rate of anorthite subjected to supercritical CO₂ injection

Figure 39: Kinetic reaction rate of kaolinite subjected to low temperature supercritical CO₂ injection

Figure 40: Kinetic reaction rate of kaolinite subjected to supercritical CO₂ injection

Figure 41: Dissolution concentration of $\text{CO}_2(\text{g})$ subjected to low temperature supercritical CO_2 injection

Figure 42: Dissolution concentration of $\text{CO}_2(\text{g})$ subjected to supercritical CO_2 injection

4. Concluding Marks

- A novel mathematical model of the THMC processes is developed. The
860 fully coupled computational framework is proposed and used to simulate reactive transport of supercritical CO₂ in subsurface formation with geo-mechanics. The novel framework is designed to keep a generalized computational structure, which can be easily applied for the numerical simulation of other THMC processes. Applications of THMC transport
865 models are presented to analyze the THMC process 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.
- For the coupled THMC processes during the CO₂ geo-sequestration, the
870 geochemical reactions do not have significant impact on pore pressure, mean stress and temperature. But, the thermal energy transport affects the mean stress and geochemical reactions in the saline aquifer, especially for cold CO₂ injection into deep saline aquifer. Low temperature accelerates equilibrium dissolution of gas and mineral, but slows down kinetic
875 dissolution/precipitation of minerals, such as anorthite and kaolinite.
- After cold supercritical CO₂ (32 °C) injection into saline aquifer (75 °C), the area within 600 m become low temperature zone. In the low temperature zone, the dissolved concentration of CO₂ increases by 30 percent under equilibrium condition, and the dissolved concentration of calcite
880 increases by 100 percent under equilibrium condition. During long term CO₂ geo-sequestration, the kinetic chemical reactions dominate the chemical reaction pathway for supercritical CO₂. The kinetic reaction rates for mineral dissolution and precipitation become lower and lower with time increasing during storage period, because the geochemical reaction system
885 reach equilibrium within long term period. The rock minerals at the interface of two phase zone and water zone react significantly and rapidly

under kinetic conditions. When anorthite (a typical mineral of plagioclase group) and kaolinite (a typical mineral of clay minerals) are present in the formation, the dissolution of anorthite leads to kaolinite precipitation.

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1130 Appendix A. Derivation for THMC Model with Chemical Kinetic Reactions

There are six primary chemical species (H_2O , H^+ , HCO_3^- , Ca^{2+} , SiO_2 and AlO_2^-) that can represent the total mass or mole in the chemical reaction system of gaseous CO_2 dissolution and mineral dissolution/precipitation, in which
1135 there are twelve aqueous equilibrium reactions, one gas dissolution into aqueous phase under equilibrium condition, one mineral dissolution into aqueous phase under equilibrium condition, and two mineral dissolution or precipitation into aqueous phase under kinetic condition. The twelve aqueous chemical complex chemical reactions are controlled by aqueous equilibrium constant, the CO_2 gas
1140 dissolution is controlled by partial pressure and fugacity coefficient, and the calcite dissolution is controlled by equilibrium constant for mineral dissolution, the kaolinite dissolution/precipitation and the anorthite dissolution/precipitation are controlled by kinetic reaction rate. These fourteen chemical reactions can be expressed by Eqs. A.1 - A.18:

$$c_{\text{OH}^-} = K_{\text{OH}^-}^{-1} \gamma_{\text{OH}^-}^{-1} \left[\frac{c_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}}{c_{\text{H}^+} \gamma_{\text{H}^+}} \right] \quad (\text{A.1})$$

$$c_{\text{CO}_3^{2-}} = K_{\text{CO}_3^{2-}}^{-1} \gamma_{\text{CO}_3^{2-}}^{-1} \left[\frac{c_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-}}{c_{\text{H}^+} \gamma_{\text{H}^+}} \right] \quad (\text{A.2})$$

$$c_{\text{CO}_2(\text{aq})} = K_{\text{CO}_2(\text{aq})}^{-1} \gamma_{\text{CO}_2(\text{aq})}^{-1} \left[\frac{c_{\text{H}^+} \gamma_{\text{H}^+} \cdot c_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-}}{c_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}} \right] \quad (\text{A.3})$$

$$c_{\text{CaCO}_3(\text{aq})} = K_{\text{CaCO}_3(\text{aq})}^{-1} \gamma_{\text{CaCO}_3(\text{aq})}^{-1} \left[\frac{c_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}} \cdot c_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-}}{c_{\text{H}^+} \gamma_{\text{H}^+}} \right] \quad (\text{A.4})$$

$$c_{\text{CaHCO}_3^-} = K_{\text{CaHCO}_3^-}^{-1} \gamma_{\text{CaHCO}_3^-}^{-1} \left[\frac{c_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-} \cdot c_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}}}{1} \right] \quad (\text{A.5})$$

$$c_{\text{CaOH}^+} = K_{\text{CaOH}^+}^{-1} \gamma_{\text{CaOH}^+}^{-1} \left[\frac{c_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}} \cdot c_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}}{c_{\text{H}^+} \gamma_{\text{H}^+}} \right] \quad (\text{A.6})$$

$$c_{\text{Al}^{3+}} = K_{\text{Al}^{3+}}^{-1} \gamma_{\text{Al}^{3+}}^{-1} \left[\frac{c_{\text{H}^+}^4 \gamma_{\text{H}^+}^4 \cdot c_{\text{AlO}_2^-} \gamma_{\text{AlO}_2^-}}{c_{\text{H}_2\text{O}}^2 \gamma_{\text{H}_2\text{O}}^2} \right] \quad (\text{A.7})$$

$$c_{\text{HAlO}_2(\text{aq})} = K_{\text{HAlO}_2(\text{aq})}^{-1} \gamma_{\text{HAlO}_2(\text{aq})}^{-1} \left[\frac{c_{\text{H}^+} \gamma_{\text{H}^+} \cdot c_{\text{AlO}_2^-} \gamma_{\text{AlO}_2^-}}{1} \right] \quad (\text{A.8})$$

$$c_{\text{AlOH}^{2+}} = K_{\text{AlOH}^{2+}}^{-1} \gamma_{\text{AlOH}^{2+}}^{-1} \left[\frac{c_{\text{H}^+}^3 \gamma_{\text{H}^+}^3 \cdot c_{\text{AlO}_2^-} \gamma_{\text{AlO}_2^-}}{c_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}} \right] \quad (\text{A.9})$$

$$c_{\text{Al}(\text{OH})_2^+} = K_{\text{Al}(\text{OH})_2^+}^{-1} \gamma_{\text{Al}(\text{OH})_2^+}^{-1} \left[\frac{c_{\text{H}^+}^2 \gamma_{\text{H}^+}^2 \cdot c_{\text{AlO}_2^-} \gamma_{\text{AlO}_2^-}}{1} \right] \quad (\text{A.10})$$

$$c_{\text{Al}(\text{OH})_3(\text{aq})} = K_{\text{Al}(\text{OH})_3(\text{aq})}^{-1} \gamma_{\text{Al}(\text{OH})_3(\text{aq})}^{-1} \left[\frac{c_{\text{H}^+} \gamma_{\text{H}^+} \cdot c_{\text{AlO}_2^-} \gamma_{\text{AlO}_2^-}}{c_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}} \right] \quad (\text{A.11})$$

$$c_{\text{H}_3\text{SiO}_4^-} = K_{\text{H}_3\text{SiO}_4^-}^{-1} \gamma_{\text{H}_3\text{SiO}_4^-}^{-1} \left[\frac{c_{\text{H}_2\text{O}}^2 \gamma_{\text{H}_2\text{O}}^2 \cdot c_{\text{SiO}_2(\text{aq})} \gamma_{\text{SiO}_2(\text{aq})}}{c_{\text{H}^+} \gamma_{\text{H}^+}} \right] \quad (\text{A.12})$$

$$P_{\text{CO}_2(\text{g})} = K_{\text{CO}_2(\text{g})}^{-1} \Gamma_{\text{CO}_2(\text{g})}^{-1} \left[\frac{c_{\text{H}^+} \gamma_{\text{H}^+} c_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-}}{c_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}} \right] \quad (\text{A.13})$$

$$K_{\text{CaCO}_3(\text{s})} = \frac{c_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}} c_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-}}{c_{\text{H}^+} \gamma_{\text{H}^+}} \quad (\text{A.14})$$

$$r_{\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(\text{s})} = \pm K_{\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(\text{s})} A_{\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(\text{s})} \left| 1 - \Omega_{\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(\text{s})} \right| \quad (\text{A.15})$$

$$\Omega_{\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(\text{s})} = K_{\text{m}}^{-1} \left[\frac{c_{\text{H}^+}^2 \gamma_{\text{H}^+}^2 \cdot c_{\text{SiO}_2(\text{aq})}^2 \gamma_{\text{SiO}_2(\text{aq})}^2 \cdot c_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}} \cdot c_{\text{AlO}_2^-}^2 \gamma_{\text{AlO}_2^-}^2}{1} \right] \quad (\text{A.16})$$

$$r_{\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)(\text{s})} = \pm K_{\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)(\text{s})} A_{\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)(\text{s})} \left| 1 - \Omega_{\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)(\text{s})} \right| \quad (\text{A.17})$$

$$\Omega_{\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)(\text{s})} = K_{\text{m}}^{-1} \left[\frac{c_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}} \cdot c_{\text{SiO}_2(\text{aq})}^2 \gamma_{\text{SiO}_2(\text{aq})}^2 \cdot c_{\text{AlO}_2^-}^2 \gamma_{\text{AlO}_2^-}^2}{1} \right] \quad (\text{A.18})$$

1145 The mass or mole of the secondary aqueous complex can be represented
by the primary species, as shown in the chemical reaction equations. The total
mass or mole of each primary species can represent the total compositions of the
aqueous phase. The mass or mole of the twelve secondary aqueous complexes
in the aqueous phase can be added to that of the four primary chemical species.
1150 The mathematical formula for the total mass or mole of each primary species
can be expressed as:

$$\begin{aligned} C_{\text{H}_2\text{O}} &= c_{\text{H}_2\text{O}} - K_{\text{CO}_2(\text{aq})}^{-1} \gamma_{\text{CO}_2(\text{aq})}^{-1} \left[\frac{c_{\text{H}^+} \gamma_{\text{H}^+} \cdot c_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-}}{c_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}} \right] \\ &+ K_{\text{OH}^-}^{-1} \gamma_{\text{OH}^-}^{-1} \left[\frac{c_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}}{c_{\text{H}^+} \gamma_{\text{H}^+}} \right] \\ &+ K_{\text{CaOH}^+}^{-1} \gamma_{\text{CaOH}^+}^{-1} \left[\frac{c_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}} \cdot c_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}}{c_{\text{H}^+} \gamma_{\text{H}^+}} \right] \\ &- 2K_{\text{Al}^{3+}}^{-1} \gamma_{\text{Al}^{3+}}^{-1} \left[\frac{c_{\text{H}^+}^4 \gamma_{\text{H}^+}^4 \cdot c_{\text{AlO}_2^-} \gamma_{\text{AlO}_2^-}}{c_{\text{H}_2\text{O}}^2 \gamma_{\text{H}_2\text{O}}^2} \right] \end{aligned}$$

$$\begin{aligned}
& -K_{\text{AlOH}^2+}^{-1} \gamma_{\text{AlOH}^2+}^{-1} \left[\frac{c_{\text{H}^+}^3 \gamma_{\text{H}^+}^3 \cdot c_{\text{AlO}_2^-} \gamma_{\text{AlO}_2^-}}{c_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}} \right] \\
& -K_{\text{Al}(\text{OH})_3(\text{aq})}^{-1} \gamma_{\text{Al}(\text{OH})_3(\text{aq})}^{-1} \left[\frac{c_{\text{H}^+} \gamma_{\text{H}^+} \cdot c_{\text{AlO}_2^-} \gamma_{\text{AlO}_2^-}}{c_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}} \right] \\
& +2K_{\text{H}_3\text{SiO}_4^-}^{-1} \gamma_{\text{H}_3\text{SiO}_4^-}^{-1} \left[\frac{c_{\text{H}_2\text{O}}^2 \gamma_{\text{H}_2\text{O}}^2 \cdot c_{\text{SiO}_2(\text{aq})} \gamma_{\text{SiO}_2(\text{aq})}}{c_{\text{H}^+} \gamma_{\text{H}^+}} \right]
\end{aligned} \tag{A.19}$$

$$\begin{aligned}
C_{\text{H}^+} &= c_{\text{H}^+} + K_{\text{CO}_2(\text{aq})}^{-1} \gamma_{\text{CO}_2(\text{aq})}^{-1} \left[\frac{c_{\text{H}^+} \gamma_{\text{H}^+} \cdot c_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-}}{c_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}} \right] \\
& -K_{\text{OH}^-}^{-1} \gamma_{\text{OH}^-}^{-1} \left[\frac{c_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}}{c_{\text{H}^+} \gamma_{\text{H}^+}} \right] \\
& -K_{\text{CaOH}^+}^{-1} \gamma_{\text{CaOH}^+}^{-1} \left[\frac{c_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}} \cdot c_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}}{c_{\text{H}^+} \gamma_{\text{H}^+}} \right] \\
& -K_{\text{CaCO}_3(\text{aq})}^{-1} \gamma_{\text{CaCO}_3(\text{aq})}^{-1} \left[\frac{c_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}} \cdot c_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-}}{c_{\text{H}^+} \gamma_{\text{H}^+}} \right] \\
& -K_{\text{CO}_3^{2-}}^{-1} \gamma_{\text{CO}_3^{2-}}^{-1} \left[\frac{c_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-}}{c_{\text{H}^+} \gamma_{\text{H}^+}} \right] \\
& +4K_{\text{Al}^{3+}}^{-1} \gamma_{\text{Al}^{3+}}^{-1} \left[\frac{c_{\text{H}^+}^4 \gamma_{\text{H}^+}^4 \cdot c_{\text{AlO}_2^-} \gamma_{\text{AlO}_2^-}}{c_{\text{H}_2\text{O}}^2 \gamma_{\text{H}_2\text{O}}^2} \right] \\
& +K_{\text{HAlO}_2(\text{aq})}^{-1} \gamma_{\text{HAlO}_2(\text{aq})}^{-1} \left[\frac{c_{\text{H}^+} \gamma_{\text{H}^+} \cdot c_{\text{AlO}_2^-} \gamma_{\text{AlO}_2^-}}{1} \right] \\
& +3K_{\text{AlOH}^2+}^{-1} \gamma_{\text{AlOH}^2+}^{-1} \left[\frac{c_{\text{H}^+}^3 \gamma_{\text{H}^+}^3 \cdot c_{\text{AlO}_2^-} \gamma_{\text{AlO}_2^-}}{c_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}} \right] \\
& +2K_{\text{Al}(\text{OH})_2^+}^{-1} \gamma_{\text{Al}(\text{OH})_2^+}^{-1} \left[\frac{c_{\text{H}^+}^2 \gamma_{\text{H}^+}^2 \cdot c_{\text{AlO}_2^-} \gamma_{\text{AlO}_2^-}}{1} \right] \\
& +K_{\text{Al}(\text{OH})_3(\text{aq})}^{-1} \gamma_{\text{Al}(\text{OH})_3(\text{aq})}^{-1} \left[\frac{c_{\text{H}^+} \gamma_{\text{H}^+} \cdot c_{\text{AlO}_2^-} \gamma_{\text{AlO}_2^-}}{c_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}} \right] \\
& -K_{\text{H}_3\text{SiO}_4^-}^{-1} \gamma_{\text{H}_3\text{SiO}_4^-}^{-1} \left[\frac{c_{\text{H}_2\text{O}}^2 \gamma_{\text{H}_2\text{O}}^2 \cdot c_{\text{SiO}_2(\text{aq})} \gamma_{\text{SiO}_2(\text{aq})}}{c_{\text{H}^+} \gamma_{\text{H}^+}} \right]
\end{aligned} \tag{A.20}$$

$$\begin{aligned}
C_{\text{Ca}^{2+}} &= c_{\text{Ca}^{2+}} + K_{\text{CaHCO}_3^-}^{-1} \gamma_{\text{CaHCO}_3^-}^{-1} \left[\frac{c_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-} \cdot c_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}}}{1} \right] \\
& +K_{\text{CaOH}^+}^{-1} \gamma_{\text{CaOH}^+}^{-1} \left[\frac{c_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}} \cdot c_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}}{c_{\text{H}^+} \gamma_{\text{H}^+}} \right] \\
& +K_{\text{CaCO}_3(\text{aq})}^{-1} \gamma_{\text{CaCO}_3(\text{aq})}^{-1} \left[\frac{c_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}} \cdot c_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-}}{c_{\text{H}^+} \gamma_{\text{H}^+}} \right]
\end{aligned} \tag{A.21}$$

$$\begin{aligned}
C_{\text{HCO}_3^-} &= c_{\text{HCO}_3^-} + K_{\text{CO}_2(\text{aq})}^{-1} \gamma_{\text{CO}_2(\text{aq})}^{-1} \left[\frac{c_{\text{H}^+} \gamma_{\text{H}^+} \cdot c_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-}}{c_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}} \right] \\
&+ K_{\text{CO}_3^{2-}}^{-1} \gamma_{\text{CO}_3^{2-}}^{-1} \left[\frac{c_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-}}{c_{\text{H}^+} \gamma_{\text{H}^+}} \right] \\
&+ K_{\text{CaCO}_3(\text{aq})}^{-1} \gamma_{\text{CaCO}_3(\text{aq})}^{-1} \left[\frac{c_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}} \cdot c_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-}}{c_{\text{H}^+} \gamma_{\text{H}^+}} \right] \\
&+ K_{\text{CaHCO}_3}^{-1} \gamma_{\text{CaHCO}_3}^{-1} \left[\frac{c_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-} \cdot c_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}}}{1} \right]
\end{aligned} \tag{A.22}$$

$$\begin{aligned}
C_{\text{AlO}_2^-} &= c_{\text{AlO}_2^-} + K_{\text{Al}^{3+}}^{-1} \gamma_{\text{Al}^{3+}}^{-1} \left[\frac{c_{\text{H}^+}^4 \gamma_{\text{H}^+}^4 \cdot c_{\text{AlO}_2^-} \gamma_{\text{AlO}_2^-}}{c_{\text{H}_2\text{O}}^2 \gamma_{\text{H}_2\text{O}}^2} \right] \\
&+ K_{\text{HAlO}_2(\text{aq})}^{-1} \gamma_{\text{HAlO}_2(\text{aq})}^{-1} \left[\frac{c_{\text{H}^+} \gamma_{\text{H}^+} \cdot c_{\text{AlO}_2^-} \gamma_{\text{AlO}_2^-}}{1} \right] \\
&+ K_{\text{AlOH}^{2+}}^{-1} \gamma_{\text{AlOH}^{2+}}^{-1} \left[\frac{c_{\text{H}^+}^3 \gamma_{\text{H}^+}^3 \cdot c_{\text{AlO}_2^-} \gamma_{\text{AlO}_2^-}}{c_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}} \right] \\
&+ K_{\text{Al}(\text{OH})_2^+}^{-1} \gamma_{\text{Al}(\text{OH})_2^+}^{-1} \left[\frac{c_{\text{H}^+}^2 \gamma_{\text{H}^+}^2 \cdot c_{\text{AlO}_2^-} \gamma_{\text{AlO}_2^-}}{1} \right] \\
&+ K_{\text{Al}(\text{OH})_3(\text{aq})}^{-1} \gamma_{\text{Al}(\text{OH})_3(\text{aq})}^{-1} \left[\frac{c_{\text{H}^+} \gamma_{\text{H}^+} \cdot c_{\text{AlO}_2^-} \gamma_{\text{AlO}_2^-}}{c_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}} \right]
\end{aligned} \tag{A.23}$$

$$C_{\text{SiO}_2(\text{aq})} = c_{\text{SiO}_2(\text{aq})} + K_{\text{H}_3\text{SiO}_4^-}^{-1} \gamma_{\text{H}_3\text{SiO}_4^-}^{-1} \left[\frac{c_{\text{H}_2\text{O}}^2 \gamma_{\text{H}_2\text{O}}^2 \cdot c_{\text{SiO}_2(\text{aq})} \gamma_{\text{SiO}_2(\text{aq})}}{c_{\text{H}^+} \gamma_{\text{H}^+}} \right] \tag{A.24}$$

The mass fraction of primary chemical species can be calculated from their concentrations:

$$X^\kappa = \frac{C^\kappa M^\kappa}{\rho_l} \quad \kappa = 1, \dots, N_C \tag{A.25}$$

Then, the fluid and heat flow, solute transport, geomechanics and geochemistry during CO₂ sequestration will be simulated in the fully coupled numerical model. The geochemical system is a kinetic reaction system (H₂O(l)-CO₂(g)-CaCO₃(s)-Al₂Si₂O₅(OH)₄(s)-Ca(Al₂Si₂O₈)(s)), including the equilibrium and kinetic reactions among three phases. Geochemical reactions are fully accounted for by including speciation in the aqueous phase, CO₂ gas and cal-

cite dissolutions into the aqueous phase, and kaolinite and anorthite dissolution/precipitation into aqueous phase. All of the potential chemical reactions
 1160 occurring in aqueous phase are set to be equilibrium. The six primary aqueous
 species (H_2O , H^+ , HCO_3^- , Ca^{2+} , SiO_2 and AlO_2^-), one primary gaseous species
 ($\text{CO}_2(\text{g})$) and three primary mineral species ($\text{CaCO}_3(\text{s})$, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(\text{s})$, and
 $\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)(\text{s})$) have been selected to dominate this chemical reaction system,
 there should be nine equations, of which seven mass balance equations for all the
 1165 primary chemical species, one gas saturation index equation to solve dissolution
 concentration of CO_2 gas, and one mineral saturation index equation to solve
 dissolution concentration of $\text{CaCO}_3(\text{s})$. In addition, one energy balance equation
 is to solve temperature, and one momentum balance equation to solve mean
 stress. Therefore, the equation system includes eleven main equations which can
 1170 represent the THMC system (CO_2 dissolution + calcite dissolution + Kaolinite
 dissolution/precipitation + anorthite dissolution/precipitation) numerically.
 The equation system is given by Eqs. A.26 - A.36.

$$\nabla \cdot \left\{ \rho_1 X_1^{\text{H}_2\text{O}} \frac{KK_{rl}}{\mu_1} (\nabla P_1 - \rho_1 g \nabla z) \right\} + \frac{\partial}{\partial t} \left\{ \phi S_1 \rho_1 X_1^{\text{H}_2\text{O}} \right\} + R^{\text{H}_2\text{O}} = 0 \quad (\text{A.26})$$

$$\nabla \cdot \left\{ \rho_1 X_1^{\text{H}^+} \frac{KK_{rl}}{\mu_1} (\nabla P_1 - \rho_1 g \nabla z) \right\} + \frac{\partial}{\partial t} \left\{ \phi S_1 \rho_1 X_1^{\text{H}^+} \right\} + R^{\text{H}^+} = 0 \quad (\text{A.27})$$

$$\nabla \cdot \left\{ \rho_1 X_1^{\text{HCO}_3^-} \frac{KK_{rl}}{\mu_1} (\nabla P_1 - \rho_1 g \nabla z) \right\} + \frac{\partial}{\partial t} \left\{ \phi S_1 \rho_1 X_1^{\text{HCO}_3^-} \right\} + R^{\text{HCO}_3^-} = 0 \quad (\text{A.28})$$

$$\nabla \cdot \left\{ \rho_1 X_1^{\text{Ca}^{2+}} \frac{KK_{rl}}{\mu_1} (\nabla P_1 - \rho_1 g \nabla z) \right\} + \frac{\partial}{\partial t} \left\{ \phi S_1 \rho_1 X_1^{\text{Ca}^{2+}} \right\} + R^{\text{Ca}^{2+}} = 0 \quad (\text{A.29})$$

$$\nabla \cdot \left\{ \rho_1 X_1^{\text{SiO}_2} \frac{KK_{rl}}{\mu_1} (\nabla P_1 - \rho_1 g \nabla z) \right\} + \frac{\partial}{\partial t} \left\{ \phi S_1 \rho_1 X_1^{\text{SiO}_2} \right\} + R^{\text{SiO}_2} = 0 \quad (\text{A.30})$$

$$\nabla \cdot \left\{ \rho_1 X_1^{\text{AlO}_2^-} \frac{KK_{rl}}{\mu_1} (\nabla P_1 - \rho_1 g \nabla z) \right\} + \frac{\partial}{\partial t} \left\{ \phi S_1 \rho_1 X_1^{\text{AlO}_2^-} \right\} + R^{\text{AlO}_2^-} = 0 \quad (\text{A.31})$$

$$\nabla \cdot \left\{ \rho_g X_g^{\text{CO}_2} \frac{KK_{rg}}{\mu_g} (\nabla P_g - \rho_g g \nabla z) \right\} + \frac{\partial}{\partial t} \left\{ \phi S_g \rho_g X_g^{\text{CO}_2} \right\} + R^{\text{CO}_2} + q_{\text{CO}_2} = 0 \quad (\text{A.32})$$

$$F_g = \log \Omega_g = \log \left[\Gamma_g^{-1} P_g^{-1} K_g^{-1} \frac{c_{\text{H}^+} \gamma_{\text{H}^+} c_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-}}{c_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}} \right] = 0 \quad (\text{A.33})$$

$$F_m = \log \Omega_m = \log \left[X_m^{-1} \lambda_m^{-1} K_m^{-1} \frac{c_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}} c_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-}}{c_{\text{H}^+} \gamma_{\text{H}^+}} \right] = 0 \quad (\text{A.34})$$

$$\sum_{\beta} \nabla \cdot \left\{ h_{\beta} \rho_{\beta} \frac{KK_{r\beta}}{\mu_{\beta}} (\nabla P_{\beta} - \rho_{\beta} g \nabla z) \right\} - \lambda \nabla T + \frac{\partial U}{\partial t} = 0 \quad (\text{A.35})$$

$$\frac{3(1-v)}{1+v} \nabla \tau - \frac{2(1-2v)}{1+v} (\alpha \nabla p + 3\beta K \nabla T) + \bar{F} = 0 \quad (\text{A.36})$$

In the equation system of this THMC model (CO₂ dissolution + calcite dissolution + Kaolinite dissolution/precipitation + anorthite dissolution/precipitation)

1175 for CO₂ injection, seven mass balance equations are present for six primary aqueous chemical species (H₂O, H⁺, HCO₃⁻, Ca²⁺, SiO₂ and AlO₂⁻) and one primary gaseous chemical species (CO₂(g)). Every mass balance equation has a generation term (R) due to mass gain or loss by chemical reaction between different phases, especially mineral dissolution and precipitation, which are under equilibrium or kinetic condition. Therefore, the source or sink term due to

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chemical reaction can be expressed mathematically as follows:

$$R^{\text{H}_2\text{O}} = -c_{\text{CO}_2(\text{g})} + r_{\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(\text{s})}\Delta t \quad (\text{A.37})$$

$$R^{\text{H}^+} = c_{\text{CO}_2(\text{g})} - c_{\text{CaCO}_3(\text{s})} + 2r_{\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(\text{s})}\Delta t \quad (\text{A.38})$$

$$R^{\text{HCO}_3^-} = c_{\text{CO}_2(\text{g})} + c_{\text{CaCO}_3(\text{s})} \quad (\text{A.39})$$

$$R^{\text{Ca}^{2+}} = c_{\text{CaCO}_3(\text{s})} + r_{\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)(\text{s})}\Delta t \quad (\text{A.40})$$

$$R^{\text{SiO}_2} = 2r_{\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(\text{s})}\Delta t + 2r_{\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)(\text{s})}\Delta t \quad (\text{A.41})$$

$$R^{\text{AlO}_2^-} = 2r_{\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(\text{s})}\Delta t + 2r_{\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)(\text{s})}\Delta t \quad (\text{A.42})$$

$$R^{\text{CO}_2} = c_{\text{CO}_2(\text{g})} \quad (\text{A.43})$$

Eleven unknown variables are selected as the primary variable for the fully coupled reactive solute transport model, i.e., P , c_{H^+} , $c_{\text{HCO}_3^-}$, $c_{\text{Ca}^{2+}}$, c_{SiO_2} , $c_{\text{AlO}_2^-}$, S_{g} , $c_{\text{CO}_2(\text{g})}$, $c_{\text{CaCO}_3(\text{s})}$, T and τ . Newton-Raphson iteration method is used to solve the equation system of the fully coupled reactive solute transport model. The numerical derivatives of mass balance equations by each primary variable forms Jacobian matrix of the equation system. The incident matrix of one grid cell is taken as an example to illustrate the Jacobian matrix setup, which is shown in Eq. A.44.