

A FULLY COUPLED MODEL OF NONISOTHERMAL MULTIPHASE FLOW, GEOMECHANICS, AND CHEMISTRY DURING CO₂ SEQUESTRATION IN BRINE AQUIFERS

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ABSTRACT

The significance of thermal-hydrologic-mechanical-chemical (THMC) processes has been well recognized in the operation of CO₂ geosequestration and geothermal resource development. Geomechanical and geochemical effects may significantly change aqueous-phase composition, porosity, and permeability of the formation, as well as flow and transport. The TOUGHREACT simulator (Xu et al., 2004b) has the capability to quantitatively simulate the fluid flow, solute transport and geochemical reactions of these processes using sequential coupling. Using a mean stress formulation, we have simulated the stresses, displacements, and rock deformation due to fluid injection via the recently developed TOUGH2_CSM (Winterfeld and Wu, 2011) for modeling geomechanical effects in CO₂ flow and transport in brine aquifers. Based on these previously developed numerical simulators—ECO2N (Pruess, 2005), TOUGH2_MP (Zhang et al., 2008), TOUGHREACT, and TOUGH2_CSM—we present a fully coupled computational framework model to simulate reactive transport of CO₂ in porous and fractured media with complex chemical reactions that occur in gaseous, liquid, and solid phases. The framework is designed to keep a unified computational structure for different THMC processes. This fully coupled simulator focuses on: (1) fluid and heat flow, and aqueous-phase solute transport within a three-phase mixture; (2) the stresses and displacements related to the mean stress; (3) the nonisothermal effect on fluid properties and reaction processes, and (4) the equilibrium and kinetics of fluid-rock and gas-rock interactions. A system of partial differential equations is formed to represent the physical, mechanical, and chemical processes of reactive solute transport associated with CO₂ in aquifers. The fully coupled model is verified against the TOUGHREACT simulator, and we present

analytical solutions as well as a few practical examples related to CO₂ sequestration.

INTRODUCTION

Coupled THMC processes have been of increasing interest to researchers studying CO₂ geosequestration, which is regarded as a possible effective solution in preventing CO₂ generated from burning fossil fuels from entering the atmosphere. Saline aquifers have the largest capacity among the many options for long-term geological sequestration. They are large underground formations saturated with brine that are often rich in dissolved minerals. CO₂ is injected into these formations as a supercritical fluid with a liquid-like density and a gas-like viscosity. It is believed that the geomechanical effects during and after CO₂ injection, and the geochemical reactions between CO₂ and rock minerals, are very important for the safe injection and long-term fate of CO₂.

In this paper, we present a fully coupled model—to simulate fluid and heat flow, rock deformation due to fluid injection, and water-rock-gas interaction under chemical equilibrium and/or kinetic conditions—developed for CO₂ geosequestration. The development of this model is based on the algorithms of ECO2N (Pruess, 2005), TOUGHREACT (Xu et al., 2004b), TOUGH_MP (Zhang et al., 2008), and TOUGH_CSM (Winterfeld and Wu, 2011). The mean stress and geochemical reaction equations are fully coupled with fluid flow, heat flow, and mass transport equations. In this model, all the governing equations to describe the THMC process are solved simultaneously by Newton-Raphson iteration, which allows a larger time step to be applied. This fully coupled simulator has the following features: (1) the fluid and heat flow, aqueous-phase solute transport within a three-phase mixture, (2) the stresses and displacements related to the mean stress, (3) the

nonisothermal effect on fluid properties and reaction processes, and (4) the equilibrium and kinetics of fluid-rock and gas-rock interactions. The mathematical descriptions and implementation of the fully coupled model are addressed in detail.

To verify and validate the capabilities of the fully coupled simulator, we compare the simulation results with analytical solutions for the mineral dissolution under local equilibrium and chemical kinetics. Furthermore, a batch geochemical system, considering the chemical interaction of gas-liquid-mineral under the equilibrium state, is presented to verify the geochemical capability in the absence of flow and stress. Then, a 1D geochemical reaction system, subjected to the environment of supercritical CO₂ injection, is designed to validate coupled fluid flow and geochemistry. Finally, a complex batch system with both chemical equilibrium and kinetics is simulated to demonstrate the capability of the fully coupled model.

MATHEMATICAL DESCRIPTION

Governing Equations

The governing equations include mass conservation, energy conservation, momentum conservation, and chemical reaction equations. Table 1 provides a brief mathematical description and numerical implementation of the fully coupled THMC model. The fluid and heat flow equations are based on that of the ECO2N module of TOUGH2 (Pruess, 2005), which is a numerical simulator of multicomponent, multiphase fluid and heat flow in porous media and is designed for applications related to geologic sequestration of CO₂ in saline aquifers. Fluid advection is described with a multiphase extension of Darcy's law, and diffusive mass transport is included for all phases. Heat flow occurs by conduction and convection. Furthermore, the equations representing the geomechanical effect during CO₂ injection are based on that of TOUGH_CSM (Winterfeld and Wu, 2011), which is a modified version of TOUGH_MP (Zhang et al., 2008), to incorporate the geomechanical effects in the equation system through effective stress. The

detailed derivation of the momentum conservation equation is given by Winterfeld et al. (2011). The derived governing equation of mean stress is shown in Table 1. Equations describing the geochemistry are based on the TOUGHREACT simulator (Xu et al., 2004b), which employs a sequential coupling approach to solve reactive-solute-transport problems in subsurface porous media. The equations for chemical equilibrium and kinetics are now incorporated into the existing phase-behavior equation system to control the local combined phase-chemical equilibrium and kinetics. The mass gain/loss of each component and the associated energy change are then added as source/sink terms into the mass/energy-balance equations.

Time Discretization and Solution Method

By employing the fully coupled approach, the mathematical equations for fluid and heat flow, geomechanics and geochemical reactions are solved simultaneously. Based on the discretization at each grid cell, the entire governing equation system for the multicomponent reactive solute transport can be expressed as residual forms R and F . R 's are for the residual forms of mass, energy, and momentum conservation equations; F 's are for the residual forms of saturation index for minerals and gases. For each grid cell, there are N equations, including mass balance, energy balance, momentum balance, and chemical constraints for minerals and gases at equilibrium, so a fully coupled reactive solute transport system with NL gridblocks represents a total of $NL \times N$ coupled nonlinear equations. The unknowns are the $NL \times N$ independent primary variables, which completely define the state of the whole THMC system at time level t^{k+1} . These equations are solved by Newton-Raphson iteration. The Taylor series expansion of residual equation for each primary variable is shown in Table 1. By keeping only the terms up to first order, we obtain a set of $NL \times N$ linear equations for the increments. The entire set of linear equations for coupled processes is solved simultaneously until the prescribed convergence criteria are satisfied.

Table 1. Mathematical description for the fully coupled model of fluid and heat flow, Geomechanics, and chemical reactions.

<p><i>Mass conservation</i></p> $\frac{d}{dt} \int_{V_n} M^\kappa dV_n = \int_{\Gamma_n} \bar{F}^\kappa \cdot \hat{n} d\Gamma_n + \int_{V_n} q^\kappa dV_n + \int_{V_n} R_{\text{req}}^\kappa dV_n + \int_{V_n} R_r^\kappa dV_n$ <p><i>Energy conservation</i></p> $\frac{d}{dt} \int_{V_n} U dV_n = \int_{\Gamma_n} \bar{F} \cdot \hat{n} d\Gamma_n + \int_{V_n} q_h dV_n$ <p><i>Momentum conservation</i></p> $\frac{3(1-\nu)}{1+\nu} \nabla^2 \tau_m + \nabla \cdot \bar{F} - \frac{2(1-2\nu)}{1+\nu} (\alpha \nabla^2 p + 3\beta K \nabla^2 T) = 0$ <p><i>Chemical equilibrium for mineral</i></p> $F_m = \log \Omega_m = \log \left[X_m^{-1} \lambda_m^{-1} K_m^{-1} \prod_{j=1}^{N_c} c_j^{v_{mj}} \gamma_j^{v_{mj}} \right] = 0$ <p><i>Chemical equilibrium for CO₂ gas</i></p> $F_g = \log \Omega_g = \log \left[\Gamma_g^{-1} P_g^{-1} K_g^{-1} \prod_{j=1}^{N_c} c_j^{v_{gj}} \gamma_j^{v_{gj}} \right] = 0$	<p><i>Supplemental equations for mass conservation</i></p> $M^\kappa = \phi \sum_{\beta} S_{\beta} \rho_{\beta} x_{\beta}^{\kappa}$ $F^\kappa = F_{\text{adv}}^\kappa + F_{\text{dis}}^\kappa \quad F_{\text{adv}}^\kappa = \sum_{\beta} x_{\beta}^{\kappa} F_{\beta} \quad F_{\text{dis}}^\kappa = \sum_{\beta} \rho_{\beta} \bar{D}_{\beta}^{\kappa} \nabla x_{\beta}^{\kappa}$ <p><i>Supplemental Equations for energy conservation</i></p> $U = (1-\phi) \rho_R C_R T + \phi \sum_{\beta} S_{\beta} \rho_{\beta} h_{\beta} \quad F = -\lambda \nabla T + \sum_{\beta} h_{\beta} F_{\beta}$ <p><i>Total mass fraction of primary chemical species</i></p> $x^{\kappa} = \frac{C^{\kappa} M^{\kappa}}{\rho_l} \quad C_j = c_j + \sum_{k=1}^{N_c} v_{kj} c_k \quad j = 1, \dots, N_c$ <p><i>Aqueous complex</i></p> $c_k = K_k^{-1} \gamma_k^{-1} \prod_{j=1}^{N_c} c_j^{v_{kj}} \gamma_j^{v_{kj}}$ <p><i>Kinetic rate for mineral dissolution/precipitation</i></p> $r_n = f(c_1, c_2, \dots, c_{N_c}) = \pm k_n A_n 1 - \Omega_n^{\theta} \quad n = 1, \dots, N_q$ <p><i>Convergence Criteria</i></p> $\left \frac{\Delta c_{j,p+1}^{k+1}}{c_{j,p}^{k+1}} \right \leq \tau \quad j = 1, 2, \dots, L, N_c + N_p + N_g$
<p><i>Time Discretization and Solution Method</i></p> $\sum_{j=1}^{N_c + N_p + N_g} \left. \frac{\partial R_n^{k,k+1}}{\partial c_j} \right _p (c_{j,p+1} - c_{j,p}) = -R_n^{k,k+1}(c_{j,p})$ $\sum_{j=1}^{N_c + N_p + N_g} \left. \frac{\partial F_m^{k+1}}{\partial c_j} \right _p (c_{j,p+1} - c_{j,p}) = -F_m^{k+1}(c_{j,p})$ $\sum_{j=1}^{N_c + N_p + N_g} \left. \frac{\partial F_g^{k+1}}{\partial c_j} \right _p (c_{j,p+1} - c_{j,p}) = -F_g^{k+1}(c_{j,p})$	

Convergence Criteria

Referring to the TOUGHREACT simulator (Xu et al., 2004b), 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 mathematical expression of the convergence criteria is given in Table 1. The default value of the convergence criterion is $\tau = 10^{-4}$. In this fully coupled THMC simulator, we still use this convergence criterion to evaluate the convergence. The convergence is achieved when the absolute value of the ratio between the relative increment of primary variables and primary variables is less than a given convergence tolerance.

CODE STRUCTURE

In this fully coupled simulator, the code structure of the original TOUGH code is kept for consistency. The numerical scheme for solving fluid and heat flow, geomechanics, and geochemistry is a fully coupled solving procedure. The mass-balance equation for each primary component or chemical species, energy-balance equation, momentum-balance equation and chemical constraint equations are constructed simultaneously. These equations are highly nonlinear algebraic equations when taking the geochemical reaction into account. They are solved by the Newton-Raphson iteration method, and the Jacobin matrix coefficients are calculated by the numerical approach. The multi-module (subroutine multi) within the TOUGH family code are rewritten as a result of the increased number of governing equations, with the number of equations in the

equation system possibly being three to six times larger than that in the original equation system. The conjugate gradient solver will be used once to solve the fluid and heat flow, solute transport, geomechanical, and chemical reactions. In addition, for phase behavior and fluid-property calculation, the EOS module is also rebuilt to couple the phase equilibrium, geomechanics, and geochemistry.

Verification and validation

In this paper, we present only the verification of the geochemistry capability within the fully coupled simulator. A verification of mineral dissolution under the conditions of local equilibrium and kinetics is presented against analytical solutions. In addition, we present a batch reaction model and a 1D reactive solute transport model coupled with geochemical reactions under equilibrium conditions, to validate the fully coupled simulator.

Analytical Solution

The TOUGHREACT simulator was verified against analytical solutions (Xu and Pruess, 1998; Xu et al., 1999). These analytical solutions are employed here again to verify the geochemistry calculations of the fully coupled simulator. The initial conditions, boundary conditions, and the derivations of the analytical solutions are given by Xu (1996). The model is a semi-infinite fluid-saturated porous medium under a steady-state uniform velocity flow regime, in which mineral dissolution is considered under the local equilibrium and kinetics. The solution corresponds to 1D transport of two hypothetical species A and B, which originate from the dissolution of a mineral phase $AB(s)$: (1) $AB(s) \leftrightarrow A + B$ in local equilibrium, (2) $AB(s) \rightarrow A + B$ in kinetics. Fig. 1 shows the verification of 1D solute transport under local equilibrium, and Fig. 2 shows the verification of 1D solute transport under chemical kinetics. The numerical results for both conditions agree well with the analytical solutions.

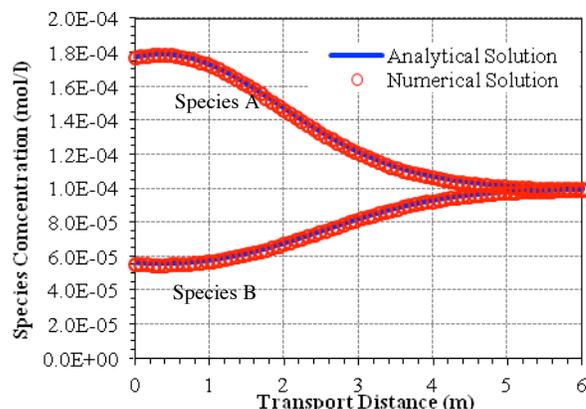


Figure 1. Concentration profiles for two species A and B in a problem involving dissolution of a mineral $AB(s)$ under conditions of local equilibrium

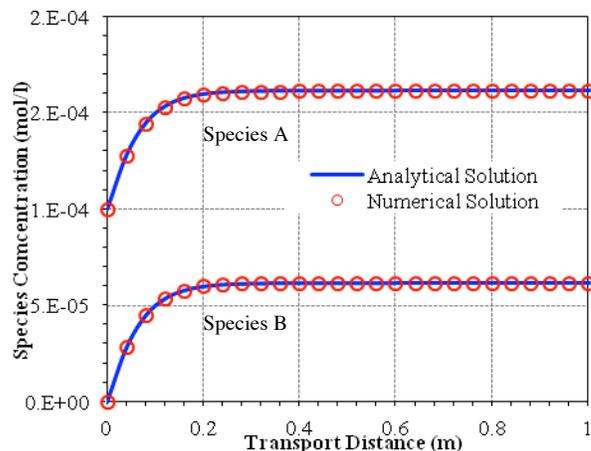


Figure 2. Concentration profiles for two species A and B in a problem involving dissolution of a mineral $AB(s)$ under conditions of kinetics.

Numerical Solution

Batch reaction system with local equilibrium

The batch reaction system includes saline water, $CO_2(g)$ and $CaCO_3(s)$. Based on the geochemical and thermodynamic database used in TOUGHREACT simulator, i.e., EQ3/6 (Wolery, 1992), the potential geochemical reactions in the batch reaction system includes twelve aqueous chemical reactions, one calcite dissolution, and one CO_2 gas dissolution. The chemical equations involved in the batch reaction system are listed in Table 2. All the chemical reactions are set in equilibrium. Three phases (aqueous, gaseous, and solid) are taken into account, i.e., the gaseous phase contains CO_2 and vaporized H_2O ; the aqueous phase includes aqueous chemical species; the mineral

species includes reactive calcite and nonreactive minerals exclusively. These chemical reactions are controlled by the chemical equilibrium constants, which can be calculated from the EQ3/6 database, and shown in Table 2.

Table 2. Equilibrium constants for chemical reactions in the batch system.

Chemical Reactions	log Keq at 75 °C
Aqueous complex	
$\text{OH}^- \rightleftharpoons \text{H}_2\text{O} - \text{H}^+$	12.706522
$\text{CaCl}^+ \rightleftharpoons \text{Ca}^{2+} + \text{Cl}^-$	0.5081909
$\text{CaCl}_2(\text{aq}) \rightleftharpoons \text{Ca}^{2+} + 2\text{Cl}^-$	0.5497973
$\text{NaCl}(\text{aq}) \rightleftharpoons \text{Na}^+ + \text{Cl}^-$	0.5826229
$\text{NaHCO}_3(\text{aq}) \rightleftharpoons \text{Na}^+ + \text{HCO}_3^-$	0.2380571
$\text{CaHCO}_3^+ \rightleftharpoons \text{Ca}^{2+} + \text{HCO}_3^-$	-1.2478107
$\text{CO}_2(\text{aq}) \rightleftharpoons \text{H}^+ + \text{HCO}_3^- - \text{H}_2\text{O}$	-6.2960791
$\text{CO}_3^{2-} \rightleftharpoons \text{HCO}_3^- - \text{H}^+$	10.098570
$\text{CaCO}_3(\text{aq}) \rightleftharpoons \text{Ca}^{2+} + \text{HCO}_3^- - \text{H}^+$	6.2485457
$\text{Ca}(\text{OH})^+ \rightleftharpoons \text{Ca}^{2+} + \text{H}_2\text{O} - \text{H}^+$	11.218291
$\text{Na}(\text{OH})(\text{aq}) \rightleftharpoons \text{Na}^+ + \text{H}_2\text{O} - \text{H}^+$	12.881724
$\text{NaCO}_3 \rightleftharpoons \text{Na}^+ + \text{HCO}_3^- - \text{H}^+$	10.262679
Calcite mineral dissolution	
$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+} + \text{HCO}_3^- - \text{H}^+$	1.1147844
Gaseous CO ₂ dissolution	
$\text{CO}_2(\text{g}) \rightleftharpoons \text{H}^+ + \text{HCO}_3^- - \text{H}_2\text{O}$	-8.168289

The selected primary components or species are CO₂(g), H₂O, H⁺, Na⁺, Ca²⁺, Cl⁻ and HCO₃⁻. All the other twelve aqueous complexes are defined as secondary species. The concentrations of the secondary species can be represented by the primary species. The total concentrations of the primary species can represent the compositions of the batch reaction system.

The geochemical reactions between aqueous and mineral phases result in mass generation, i.e., CO₂(g) dissolution and calcite dissolution. The source or sink terms in the mass-balance equation can be calculated from the dissolved

concentration of calcite ($C_{\text{CaCO}_3(\text{s})}$) and the dissolved concentration of CO₂ ($C_{\text{CO}_2(\text{g})}$). The algebraic relationships between them are shown by the chemical reaction equations in Table 2. The geochemical reaction between mineral and saline solution is dominated by the equilibrium constant. The chemical reaction between CO₂ (g) and aqueous phase is CO₂ dissolution. It is set to be under equilibrium conditions, and dominated by the partial pressure of CO₂ and the equilibrium constant. Therefore, nine governing equations are solved by Newton-Raphson iteration. Nine primary variables are selected in the batch reaction model, i.e., $P_{\text{CO}_2(\text{g})}$, C_{H^+} , $C_{\text{Ca}^{2+}}$, C_{Na^+} , $C_{\text{HCO}_3^-}$, C_{Cl^-} , S_{g} , $C_{\text{CaCO}_3(\text{s})}$ and $C_{\text{CO}_2(\text{g})}$.

The geochemical reaction system is in equilibrium, so the system reaches equilibrium conditions once CO₂ comes into contact with the aqueous phase. The initial input data for the batch reaction model are given in Table 3; the initial concentrations of aqueous species are given in the second column of Table 4. The simulation results by the fully coupled simulator and TOUGHREACT are given in the third and fourth columns of Table 4. We can see that the concentrations of CO₂(aq) and Ca²⁺ have dramatically increased, owing to the dissolutions of CO₂(g) and CaCO₃(s), which dominate the entire batch reaction system. By comparing the results from the two bunches, we see that the error is within 4%; we can then conclude that the simulation results from the two simulators agree well.

Table 3. Initial parameters of the batch system.

Parameter	Values
Gas Saturation	0.5
Initial Pressure	200 bar
Temperature	75 °C
Porosity	0.3
Volume fraction of calcite	0.5
Volume fraction of non-reactive	0.5

Table 4. Result comparison between the fully coupled simulator and TOUGHREACT.

Species	Initial data	Fully-coupled	TOUGHREAC	Errors (%)
H ⁺	3.0865518E-05	2.385574E-05	2.3200153E-05	2.82580
Ca ²⁺	4.4801997E-03	3.789724E-02	3.7248307E-02	1.74217
Na ⁺	0.9000024	0.8910427	0.8911388	0.01078
HCO ₃ ⁻	1.9974637E-03	6.469279E-02	6.3385779E-02	2.06199
Cl ⁻	0.9106334	0.9125819	0.9124661	0.01269
OH ⁻	1.4343495E-08	1.892241E-08	1.9503686E-08	2.98034
CaCl ⁺	1.7247709E-04	1.393002E-03	1.3709958E-03	1.60509
CaCl ₂ (aq)	5.9203653E-05	4.642690E-04	4.5762974E-04	1.45079
NaCl(aq)	8.9297867E-02	8.604993E-02	8.6185575E-02	0.15739
NaHCO ₃ (aq)	4.2996252E-04	1.336103E-02	1.3114010E-02	1.88363
CaHCO ₃ ⁺	2.1416910E-05	5.513980E-03	5.3798849E-03	2.49252
CO ₂ (aq)	4.3136821E-02	1.012978	0.98246	3.10628
CO ₃ ²⁻	3.7063587E-08	1.625055E-06	1.6483202E-06	1.41144
CaCO ₃ (aq)	2.1937727E-08	7.349152E-06	7.3491650E-06	0.00018
CaOH ⁺	2.7707266E-10	2.960948E-09	3.0037454E-09	1.42481
NaOH(aq)	3.6957495E-09	4.702559E-09	4.8647524E-09	3.33405
NaCO ₃ ⁻	3.1457201E-09	1.297723E-07	1.3184608E-07	1.57285
CaCO ₃ (s)	0.0	4.186248E-02	4.0960340E-02	2.20246
CO ₂ (g)	0.0	1.022362	1.009385	1.28559
P _{co2} (bar)	197.71524	173.2262	168.49643	2.80704

1D Reactive-solute-transport model under chemical equilibrium

A 1D reactive-solute-transport model under local chemical equilibrium is presented to verify the fully coupled simulator against the TOUGHREACT simulator. Sample Problem 5 in the TOUGHREACT manual (Xu et al., 2004b) is the reference for setting up the verification model. We assume that there is CO₂ gas saturated initially in the model ($S_g=0.2$), and that there are no chemical reactions in the system. The geochemical equilibrium is reached simultaneously at the beginning of CO₂ injection. The hydrogeological parameters for this model are in Table 5. (All the geochemical reactions involved in the model are shown in Table 2, above.) The model corresponds to a 1D reactive-solute-transport problem, and the calculation of nonisothermal and geomechanical effects are deactivated to verify the geochemical reaction calculation of the fully coupled simulator. This model is used to validate the effects of fluid flow mechanics on geochemistry.

Table 5. Parameters for the 1D transport problem.

Parameters	Value
Aquifer thickness	100 m
Permeability	10 ⁻¹³ m ²
Porosity	0.3
Compressibility	4.5×10 ⁻¹⁰
Temperature	75 °C
Pressure	200 bar
CO ₂ injection rate	5 kg/s
Injection time	365days
Original CO ₂ satu-	0.2
Number of grids	22
Aquifer length	500m

To validate the fluid flow, the model is run four times by TOUGH_CSM geomechanics, TOUGHREACT, the fully couple simulator, and the fully coupled simulator without geochemical reaction. Figures 4 and 5 show the saturation profiles and gas pressure profiles after one year's injection of CO₂ gas. In Figure 3, the saturation profiles are very close for TOUGH_CSM, TOUGHREACT, and the fully

coupled simulator without geochemical reactions. In the TOUGHREACT simulator, the fluid flow, solute transport, and geochemistry is treated in three separate systems, with the fluid flow part having no interaction with the other two parts. However, the saturation profile obtained by the fully coupled simulator is lower than the other simulations. The problem is the treatment of CO₂ dissolution. In TOUGH_CSM and TOUGHREACT, the dissolution of CO₂ gas in the aqueous phase is calculated by phase behavior, but in the fully coupled simulator, it is treated as a geochemical reaction involving the mass loss of CO₂ gas. The model instantly becomes equilibrated by geochemical reactions at the beginning of CO₂ injection, and the gas saturation decreases because of the dissolution reactions, shown by the green line in Fig. 3.

Fig. 4 indicates that the gas-pressure profiles obtained by TOUGH_CSM, TOUGHREACT, and the fully coupled simulator without geochemical reactions are close to each other. The pressure obtained by the fully coupled simulator is much lower than the others. The fully coupled procedure in the fully coupled simulator tracks the changes in gas pressure and related fluid flow due to the dissolution of gaseous reactants. However, the assumption is that chemical reactions and accompanying changes in partial pressures do not affect overall gas and liquid flow in TOUGHREACT (Xu et al., 2001). This might be a good approximation under some circumstances, but for the supercritical CO₂ geosequestration, this might not reflect the real conditions when fluid flow interacts with geochemical reactions.

Fig. 5 shows the gas partial-pressure evolution in the injection grid cell during one year's CO₂ injection by TOUGHREACT and the fully coupled simulator: the CO₂ gas partial pressure obtained by the fully coupled simulator is much lower than that obtained by TOUGHREACT. As we know, the CO₂ partial pressure is proportional to the quantity of CO₂ dissolved into the aqueous phase. The partial pressure of CO₂ gas dominates the geochemical reaction path of the entire system. CO₂ dissolution decreases the partial pressure, which is quantitatively simulated by the fully coupled simulator. Figures 6–8 show the pH value, the accumulative CaCO₃(s) dissolved concentration, and the accumulated CO₂ (g) dissolved

concentration after one year's CO₂ injection. The larger partial pressure results in a lower pH value, higher dissolved concentrations of CaCO₃(s), and CO₂(gas) simulated by TOUGHREACT.

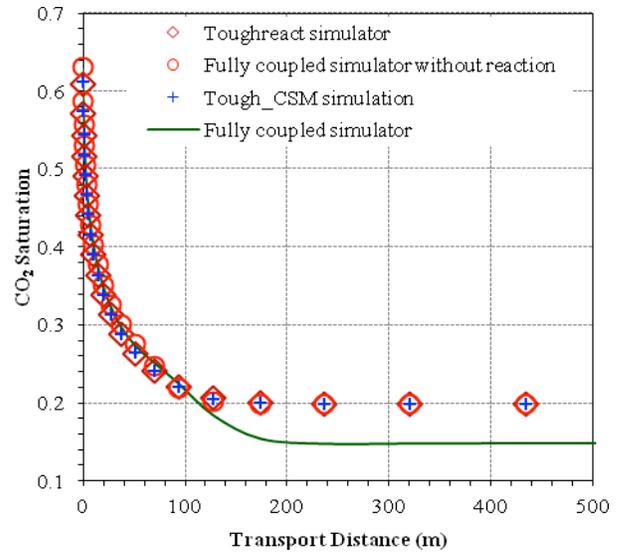


Figure 3. CO₂ saturation profiles after one year's injection simulated by different simulator.

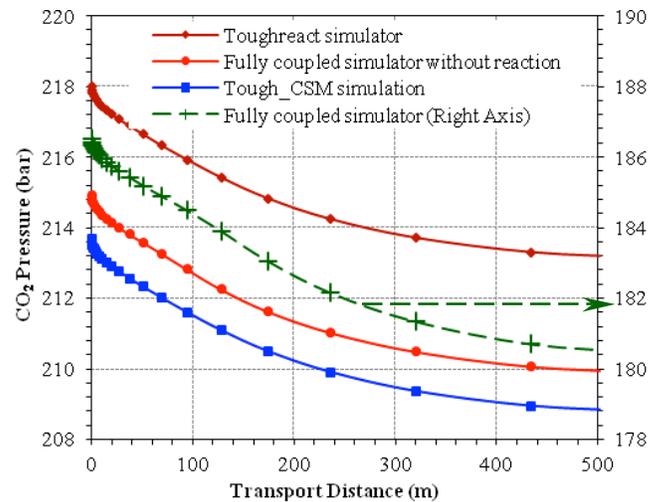


Figure 4. CO₂ pressure profiles after one year's injection simulated by different simulator.

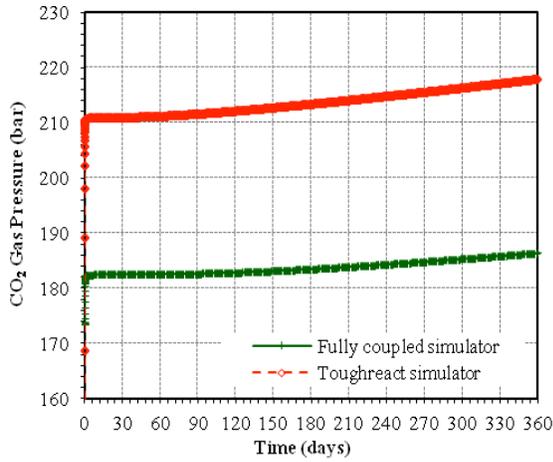


Figure 5. CO₂(g) partial pressure evolution profiles at the CO₂ injection grid cell.

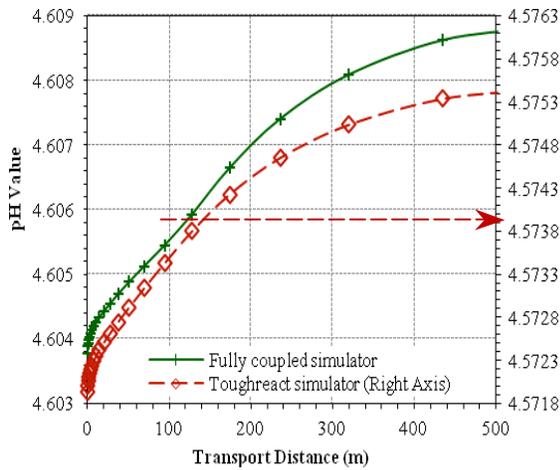


Figure 6. pH value profiles simulated by the fully coupled simulator and TOUGHREACT simulator.

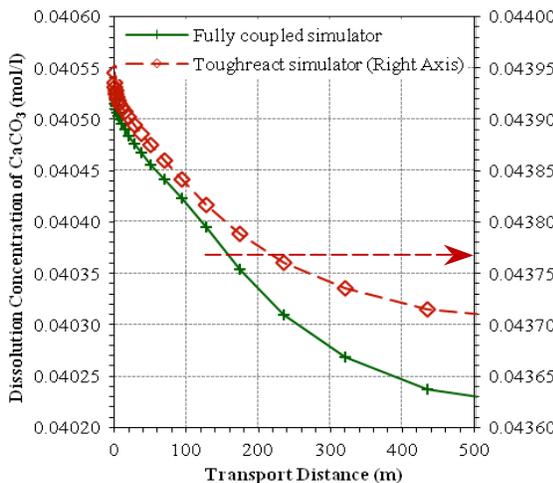


Figure 7. Dissolved concentration of CaCO₃(s) by the fully coupled simulator and TOUGHREACT simulator.

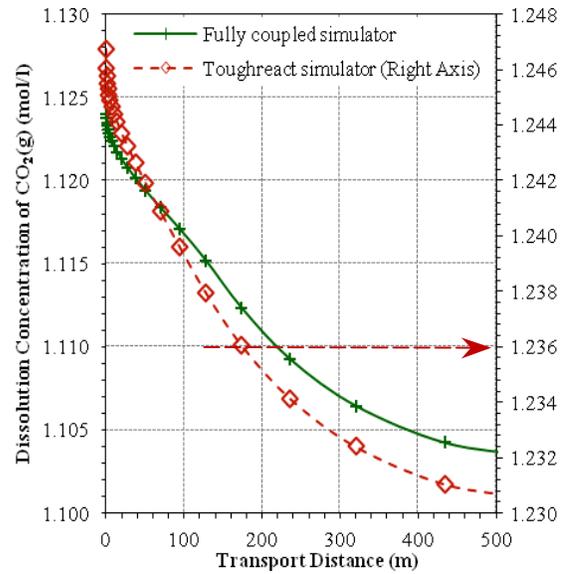


Figure 8. Dissolved concentration of CO₂(g) by the fully coupled simulator and TOUGHREACT simulator.

APPLICATION: BATCH REACTION SYSTEM OF COMPLEX CHEMICAL KINETICS

The fully coupled simulator can be applied to simulate a system that considers the equilibrium and kinetic minerals simultaneously. The initial mineral abundances used in the current batch reaction system are refined from the geochemical modeling study by Xu et al. (2004a) and geochemical reaction modeling Example 5 in the TOUGHREACT manual (Xu et al., 2004b). The initial conditions for this batch are the same as with the previous batch system under equilibrium conditions, as shown in Table 3. The reactive minerals are redefined here, with the initial mineral volume fraction and the distribution of the original mineral shown in Fig. 9. The mineralogy in this problem is similar to that commonly encountered in sedimentary basins (e. g., Gulf Coast sediments).

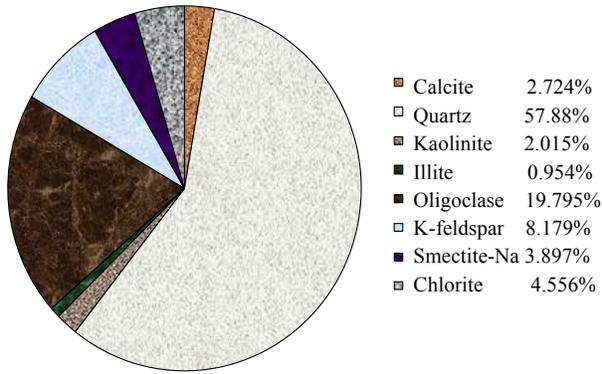


Figure 9. The original rock mineral compositions.

In this complex geochemical reaction system, calcite was assumed to react with aqueous species at local equilibrium, because its reaction rate is typically quite rapid. Dissolution and precipitation of other minerals are kinetically controlled. The equilibrium constants and kinetic-rate constants are again those from the study by Xu et al. (2004a and 2004b). There are four kinds of geochemical reactions, i.e., aqueous equilibrium reactions, kinetic mineral dissolution and precipitation, equilibrium gas dissolution, and equilibrium mineral dissolution. Twelve chemical species are selected as primary species. Thirty aqueous equilibrium chemical reactions form thirty secondary aqueous chemical species, which can be represented by the primary chemical species selected. Fourteen chemical reactions for kinetic mineral dissolution and precipitation are controlled by kinetic reaction rates. All the chemical reaction parameters are from the database of EQ3/6.

From the simulation results, we find that the majority of the CO_2 gas is dissolved into aqueous phase after 3,680 years. During the dissolution of the acid CO_2 gas, the pH value continues to buffer from 4.6 to 7.6, which is shown in Fig. 10. The majority of the calcite is dissolved into aqueous phase, as shown in Fig. 11. Among the original mineral compositions, the oligoclase has an almost 50% volume fraction change, while the Na-smectite and illite have minor precipitations, as shown in Fig. 12. Fig. 13 shows the potential precipitated minerals: significant ankerite and albite-low precipitate due to CO_2 injection and dissolution of aluminosilicate minerals. Minor smectite-Ca and very slight dawsonite precipitation occurs. No dolomite precipitation is observed in the

simulation. The redistribution of volume fractions for the rock minerals after 3,680 years' reaction with CO_2 is shown in Fig. 14, with the area enclosed by the red lines representing the newly precipitated minerals after long-term geo-sequestration of CO_2 .

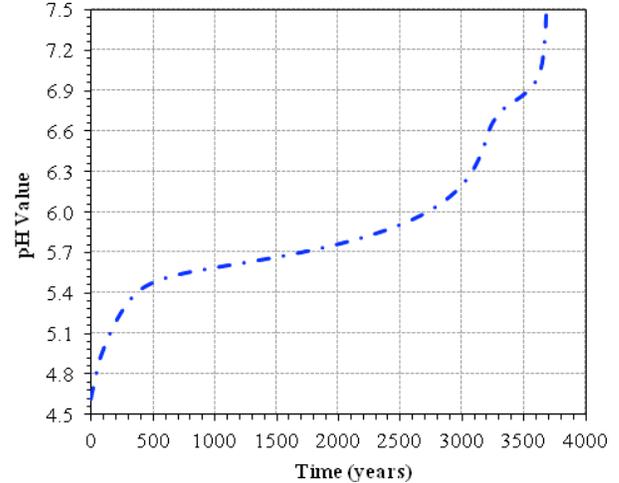


Figure 10. The evolution of pH value during CO_2 geo-sequestration.

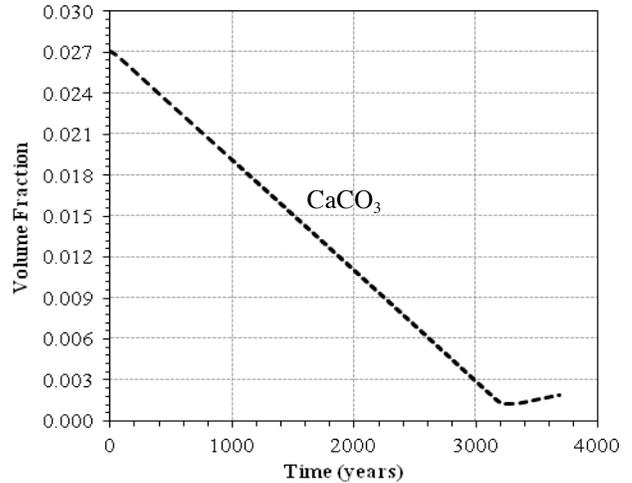


Figure 11. The volume fraction change of CaCO_3 in the rock matrix.

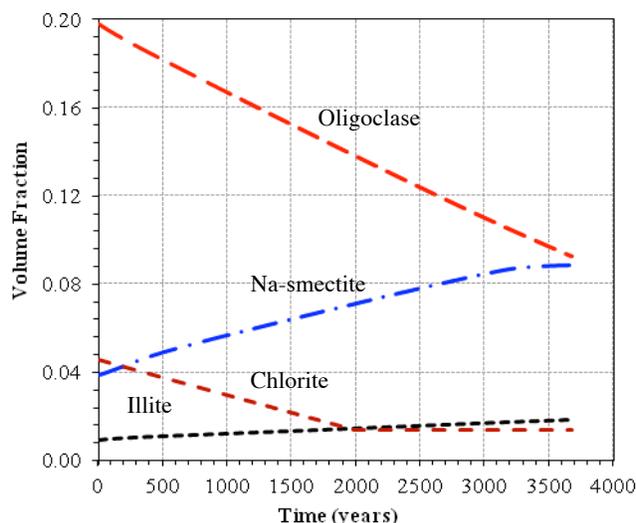


Figure 12. The volume fraction change of rock minerals in the rock matrix.

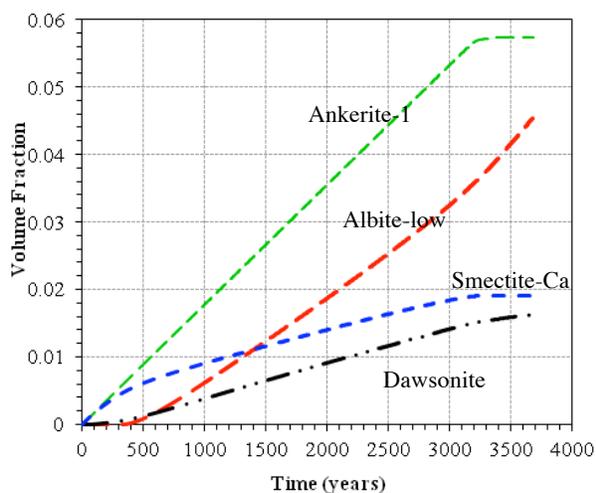


Figure 13. The volume fraction change of precipitated minerals in the rock matrix.

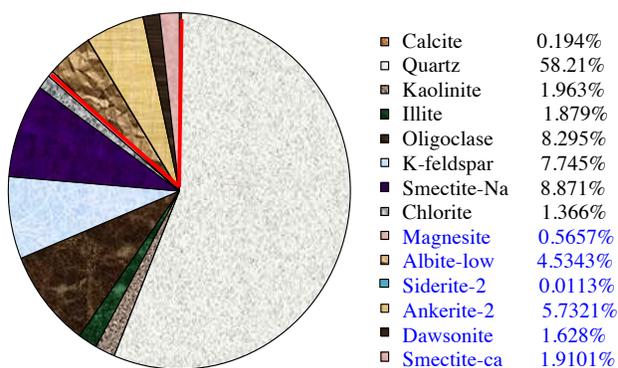


Figure 14. The mineral compositions after CO₂ sequestration.

CONCLUDING REMARKS

The transport phenomena subjected to CO₂ geological sequestration is a THMC process, one that includes fluid and heat flow, rock deformation, a mix of equilibrium and kinetic reactions, as well as an enormous range of aqueous concentrations. This poses great challenges for numerical simulation. Based on TOUGH family simulators, we have developed an efficient fully coupled model, in which the geochemical reactions are quantitatively embedded into the fluid- and heat-flow equations, while pore pressure and temperature are directly related to the rock deformation equation. We presented the fundamental equations describing mean stress, various gas-water-rock interactions in porous media, chemical equilibrium constraint equations relating chemical species' concentration, partial pressure, and temperature—and incorporated them together with the mass and energy conservation equations of primary chemical components or species, which are already embedded in the fully coupled code.

The model was verified against analytical solutions for mineral dissolution under local equilibrium and chemical kinetics. Then a batch system (CO₂, H₂O, NaCl, and CaCO₃) under chemical equilibrium was taken as the second validation to compare with the TOUGHREACT simulator. We obtained good matches for the two validations. Furthermore, a 1D transport model with chemical equilibrium was performed as the third validation to simulate the mutual interaction between fluid flow and geochemical reaction. It was indicated that the gas partial pressure dominates the whole THMC process. This pressure directly corresponds to the dissolution quantity of CO₂ gas in aqueous phase, further affecting the chemical reaction path and long-term fate of CO₂ in the saline aquifer. The fully coupled approach has an improved estimate of the CO₂ partial pressure and the geochemistry system. Finally, a complex geochemical batch reaction system, considering the chemical equilibrium and kinetics simultaneously, was simulated to demonstrate its handling capability for complex geochemical reactions in the fully coupled simulator.

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