



Modeling Supercritical CO₂ Flow and Mineralization in Reactive Host Rocks with PFLOTRAN v7.0

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Abstract. Understanding the flow and reactivity of CO₂ injected into geologic reservoirs is important for many subsurface applications including secure geologic carbon storage (GCS), critical mineral extraction, enhanced geothermal systems (EGS), and enhanced oil recovery (EOR). Traditionally, subsurface CO₂ injection for GCS applications has focused on geologic formations with favorable subsurface configurations for CO₂ migration and trapping through non-reactive mechanisms such as structural, solubility, and petrophysical trapping to isolate CO₂ in the subsurface. Recently, CO₂-reactive rocks such as mafic and ultramafic basalts have been investigated for their potential to react with injected CO₂ in situ to simultaneously dissolve host rock minerals and mineralize CO₂ as carbonates. Engineering rapid CO₂ mineralization in the subsurface is attractive because of the increased density of stored CO₂, the additional safety factors associated with solidification, and the potential to extract valuable critical minerals. However, the limited availability of tools that are capable of modeling the associated coupled multiphase flow and reactive transport processes, especially at scale, makes it difficult to predict the long term behavior of a commercial-scale CO₂ injection into a reactive host rock. Here we present recent developments in the parallel flow and reactive transport simulator PFLOTRAN to model coupled CO₂-brine flow and reactive transport for a wide range of injection and production applications involving reactive CO₂-brine systems. These developments are based on the well established and trusted CO₂ flow capabilities in the STOMP-CO2 simulator. New capabilities added to PFLOTRAN include new CO₂-brine equations of state with optional thermal coupling, several new constitutive relationships like capillary pressure smoothing and scanning path hysteresis, a fully implicit well model, and native linkage with PFLOTRAN's well-established reactive transport libraries. A series of numerical benchmarks between PFLOTRAN and STOMP-CO2 verify the newly developed CO₂-brine flow capabilities, and demonstrations of coupled CO₂-brine flow modeling and reactive transport show how CO₂ mineralization can be engineered in reactive host rocks. Finally, an example use case involving copper leaching by CO₂ and critical mineral extraction is presented to showcase the strengths of this new implementation. Several limitations still remain, including limited availability of field data to parameterize models. Future work should constrain the evolution of mineral surface area during mineralization and the temperature/pH dependence of geochemical reactions for specific systems of interest.



1 Introduction

The fate of CO₂ injected into the subsurface has been of interest for several decades because of its potential utility to a variety of subsurface energy engineering challenges, including enhanced oil recovery and geologic carbon storage. More recently, CO₂ has been proposed as a potential working fluid for extracting heat from geothermal energy reservoirs using novel well configurations and for producing heat from enhanced geothermal systems (Pruess, 2008; Wu and Li, 2020). It has also been shown that in highly CO₂-reactive reservoirs composed of, e.g., mafic and ultramafic basalts, CO₂ can mineralize as carbonates on much shorter timescales than in traditional non-reactive reservoirs (McGrail et al., 2017; Pogge von Strandmann et al., 2019). The geochemistry of these reactions is also such that the dissolution of the host rock that is promoted by enhanced brine acidity could release valuable critical minerals; CO₂ has therefore been proposed as a working fluid to promote critical mineral recovery with the added benefit of storing CO₂ (Stanfield et al., 2024).

To predict the transient behavior of CO₂ injected into the subsurface for any of these applications and to engineer optimal injection strategies, reservoir simulation tools are required. Such tools have matured over the past few decades; recently, the Society of Petroleum Engineers (SPE) concluded its 11th international Comparative Solution Project, which benchmarked state-of-the-art industry and research simulators on a series of CO₂ storage challenge problems in 2D and 3D (Nordbotten et al., 2024). However, many of these tools are limited in their capacity to model coupled multiphase flow and reactive transport in reactive host reservoirs. Lacking these capabilities makes it difficult to predict the long term behavior of a commercial-scale CO₂ injection into a reactive host rock, let alone model enhanced critical mineral dissolution and extraction using CO₂ as the working fluid.

The parallel flow and reactive transport simulator PFLOTRAN has been extended to model coupled CO₂-brine flow and reactive transport for a wide range of injection and production applications involving reactive CO₂-brine-mineral systems. These developments are based on the well established and trusted CO₂-brine flow capabilities in the STOMP-CO2 simulator. New capabilities added to PFLOTRAN include new CO₂-brine equations of state with optional thermal coupling, several new constitutive relationships like capillary pressure smoothing and scanning path hysteresis, a fully implicit well model, and native linkage with PFLOTRAN's well-established reactive transport libraries. We first present the theory behind all of this newly-implemented functionality. Then we discuss how to invoke these capabilities in a PFLOTRAN input deck, and we present a suite of benchmark exercises and verification tests to demonstrate how our implementation compares to other well-established simulators like STOMP-CO2 and TOUGH2. Finally, we demonstrate the capabilities on a copper extraction problem using CO₂ to induce copper leaching for critical mineral extraction.

2 Theory

Simulating CO₂ injection into reactive subsurface reservoirs requires solving systems of nonlinear partial differential equations describing the transport of water, CO₂, and salt; heat transfer; and chemical reactions through porous media at large scales. These equations are strongly coupled: for instance, the dissolved concentration of CO₂ affects liquid water density, viscosity, enthalpy and pH among other state variables, which in turn affect the transport and reactivity of other species. In



PFLOTTRAN, SCO2 Mode has been developed to fully implicitly solve a set of "flow" governing equations. Those equations include conservation of water mass, conservation of CO₂ mass, conservation of salt mass, conservation of energy, and well mass flux conservation. Water, CO₂, and salt components partition between three phases (liquid [aqueous], gas [CO₂-rich], and salt precipitate); water is miscible in the CO₂ phase, and CO₂ and salt are miscible in the aqueous phase. Transport of mass in the SCO2 flow mode occurs as the result of pressure gradients within each phase, concentration gradients within each phase, buoyancy, and component sources/sinks. These equations are all solved fully implicitly within SCO2 Mode; some equations, like the energy equation and the well equation, are optional. The governing partial differential equations, constitutive relationships, equations of state, and fully implicit well model formulation were designed with base functionality that emulates the STOMP-CO2 simulator (White et al., 2012) and expands beyond those capabilities.

Modeling transport and reaction of dissolved aqueous species also requires solving a coupled system of mass action equations. We refer to this as the "reactive transport" step. To model multicomponent geochemistry in addition to multiphase CO₂-brine flow, PFLOTTRAN's SCO2 flow mode has been designed to sequentially couple to PFLOTTRAN's global implicit reactive transport (GIRT) mode, a mature and comprehensive reactive transport code (Hammond et al., 2014). SCO2 Mode first solves its set of governing equations for mass and energy fluxes over a given time step. Then, it passes certain variables like Darcy fluxes, porosity, and gas phase saturation to reactive transport. Reactive transport then takes as many sub-steps as are required to complete one "flow" step. If CO₂ is produced or consumed through mineralization reactions in reactive transport, transport passes a source/sink term of CO₂ back to flow. Flow and reactive transport hand this information off at every flow time step for the duration of the simulation.

2.1 Flow Governing Equations

PFLOTTRAN's SCO2 Mode solves a fully coupled system of three component mass conservation equations and one energy conservation equation. The energy conservation equation can be optionally disabled in favor of isothermal simulations at user-defined initial temperature conditions (including temperatures read from a restart file). Additionally, an arbitrary number of fully coupled well mass conservation equations can be solved corresponding to each well in the domain with or without thermal coupling. The default mass and energy conservation equations consider conservation of water, CO₂, salt, and system internal energy. The equations take the following form:

$$\frac{\partial \phi (s_1 \rho_l X_w^l + s_g \rho_g X_w^g)}{\partial t} = -\nabla \cdot (\rho_l X_w^l \mathbf{q}_l + \rho_g X_w^g \mathbf{q}_g + \mathbf{J}_w^l + \mathbf{J}_w^g) + q_w \quad (1)$$

$$\frac{\partial \phi (s_1 \rho_l X_{CO_2}^l + s_g \rho_g X_{CO_2}^g)}{\partial t} = -\nabla \cdot (\rho_l X_{CO_2}^l \mathbf{q}_l + \rho_g X_{CO_2}^g \mathbf{q}_g + \mathbf{J}_{CO_2}^l + \mathbf{J}_{CO_2}^g) + q_{CO_2} \quad (2)$$

$$\frac{\partial \phi (s_1 \rho_l X_{salt}^l + s_s \rho_s)}{\partial t} = -\nabla \cdot (\rho_l X_{salt}^l \mathbf{q}_l + \mathbf{J}_{salt}^l) + q_{salt} \quad (3)$$

$$\frac{\partial \phi (s_\alpha \rho_\alpha U_\alpha) + (1 - \phi) C_p^{rock} \rho_{rock} T}{\partial t} = -\nabla \cdot (\rho_l H_l \mathbf{q}_l + \rho_g H_g \mathbf{q}_g - \kappa_{eff} \nabla T) + q_e \quad (4)$$



85 where ϕ is porosity, s_α is the saturation of phase α , ρ_α is the mass density of phase α , X_β^α is the mass fraction of component β in phase α , q_α is the Darcy flux of phase α , J_β^α is the diffusive flux of component β in phase α , q_β are the sources and sinks of component β , U_α is the internal energy of phase α , C_p^{rock} is the heat capacity of the rock, ρ_{rock} is the solid rock density, T is temperature, H_α is the enthalpy of phase α , κ_{eff} is the effective thermal conductivity of the medium, and q_e are the energy sources and sinks.

90 Three phases are considered in this formulation: liquid phase, CO₂-rich phase, and salt precipitate phase. Within the CO₂-rich phase, trapped and free-phase saturations are tracked separately for performing optional hysteresis calculations. The salt precipitate phase contains only the salt component; the salt component can also partition into the aqueous phase, but it cannot exist in the CO₂-rich phase. The state of the CO₂-rich phase can be either liquid, gaseous, or supercritical CO₂. For convenience, the CO₂-rich phase will be labeled the "gas" phase throughout this document. This phase can contain both CO₂ and
95 water components.

2.2 Constitutive Relationships

Advective fluxes of the mobile phases are modeled using Darcy's equation:

$$\mathbf{q}_\alpha = -\frac{k k_{r\alpha}}{\mu_\alpha} \nabla (p_\alpha - \gamma_\alpha z) \quad (5)$$

100 where k is the permeability of the medium, $k_{r\alpha}$ is the relative permeability of phase α , μ_α is the viscosity of phase α , p_α is the pressure of phase α , γ_α is the specific gravity of phase α , and z is vertical elevation.

Relative permeability is computed as a function of pore fluid saturations through one of several available relative permeability function options. Please see the PFLOTRAN Documentation for a comprehensive list of available relative permeability functions for liquid and gas phases. When considering effects of hysteresis on gas trapping, SCO2 Mode removes trapped gas from the mobile gas phase saturation used in gas relative permeability computations.

105 Diffusive fluxes in the aqueous phase are modeled using Fick's Law:

$$\mathbf{J}_{\text{CO}_2}^l = D_{\text{CO}_2}^l \nabla c_{\text{CO}_2} \quad (6)$$

$$\mathbf{J}_{\text{salt}}^l = D_{\text{salt}}^l \nabla c_{\text{salt}} \quad (7)$$

$$\mathbf{J}_w^l = 1 - \mathbf{J}_{\text{CO}_2}^l - \mathbf{J}_{\text{salt}}^l \quad (8)$$

where D_β^l is the diffusivity of component β in the liquid and ∇c_β is the gradient in dissolved concentration of component β .

110 Transport of dissolved salt through the aqueous phase is additionally weighted using the Patankar method (Patankar, 2018).

Likewise, gas phase diffusive flux is modeled as follows:

$$\mathbf{J}_{\text{CO}_2}^g = D_{\text{CO}_2}^g \nabla c_{\text{CO}_2} \quad (9)$$

$$\mathbf{J}_w^g = 1 - \mathbf{J}_{\text{CO}_2}^g \quad (10)$$

115 where D_β^g is the diffusivity of component β in the gas, ∇c_β is the gradient in mass fraction of component β in the gas, and the salt component is not present in the gas phase.



2.3 Equations of State

Several options exist in PFLOTRAN to customize the set of equations of state (EOS) used in a simulation to fit a desired application. Here we describe the default options available in SCO2 Mode. We refer the user to the PFLOTRAN Documentation for more information on EOS options.

120 2.3.1 Density

With the exception of the salt precipitate phase, the composite density of each phase is computed by correcting the pure phase density as a function of component concentrations. The salt precipitate is considered to be a pure "salt" component phase. The default density equation for salt is a function of temperature and pressure and assumes that salt is composed entirely of NaCl (Battistelli et al., 1997).

125 For the aqueous liquid (non CO₂-rich) phase, the density of pure water is first computed as a function of pressure and temperature (Meyer et al., 1993). Brine density is then computed as a function of pure water density and salt mass fraction (Phillips et al., 1981). Finally, the composite mixture density is calculated as a function of pure water density, brine density, and mass fractions of salt and CO₂ components (Alendal and Drange, 2001).

In the gas phase, a similar approach is taken with the exception that there is no dissolved salt in the gas phase. Pure gas phase
130 density (Span and Wagner, 1996) and water vapor density (Meyer et al., 1993) are first calculated as functions of pressure and temperature. Then, the gas mixture density is computed as a weighted average of the two densities weighted by gas phase component mass fractions. Pure CO₂ thermodynamic properties (density, viscosity, internal energy, and enthalpy) can either be computed or read in through a database for greater efficiency. A generic CO₂ thermodynamic property table based off of the Span-Wagner EOS is included in the PFLOTRAN database directory and it is recommended to use this lookup table for CO₂
135 simulations.

2.3.2 Vapor Pressure

The liquid vapor pressure is computed as a function of temperature, salinity, and capillary pressure. Pure water saturation pressure is first computed as a function of temperature (Meyer et al., 1993), and then an adjustment is applied to include the effect of salinity (Haas, 1976). The Kelvin equation is then applied to calculate the reduced vapor pressure as a function of
140 capillarity (Nitao, 1988).

2.3.3 Viscosity

Similar to density, the viscosity of each mobile phase is computed as a function of temperature, pressure, and phase composition. For the liquid phase, the viscosity of pure water is computed as a function of temperature and pressure (Meyer et al., 1993). This pure water viscosity is then adjusted as a function of temperature and salinity (Phillips et al., 1981) to get the
145 brine viscosity. The viscosity of CO₂ is separately calculated as a function of temperature and density (Fenghour et al., 1998), and the final composite liquid viscosity is computed as a function of CO₂ mass fraction, CO₂ viscosity, and brine viscosity.



In the gas phase, viscosity is calculated as a function of pure water viscosity, pure CO₂ viscosity, and mass fractions of each component in the gas phase (Poling et al., 2001).

2.3.4 Diffusion Coefficients

150 Diffusion drives fluxes of dissolved CO₂ and dissolved salt in the aqueous phase, and it drives water vapor diffusion in the gas phase. Diffusive flux is governed by concentration gradients and molecular diffusion coefficients of each component in each phase. In the aqueous phase, the diffusion coefficient of CO₂ is computed as a function of temperature (Cadogan et al., 2014) and dissolved salt mass fraction (Belgodere et al., 2015). The molecular diffusion coefficient of salt in the aqueous phase is computed using the Gordon method (Poling et al., 2001) and as a function of mean ionic activity (Bromley, 1973). The
155 diffusivity of water vapor in the gas phase is computed as a function of temperature and pressure via the method of Wilke and Lee (Poling et al., 2001).

2.3.5 Two-Phase Equilibrium

When dissolved CO₂ exceeds its solubility in the aqueous phase, or when water vapor condenses from the CO₂-rich phase, a two-phase state can arise in a model. That is, in a given cell/location, both the liquid (water-rich) and gas (CO₂-rich) phases can
160 coexist. In SCO2 Mode, the transition from single- to two-phase is treated as an equilibrium process. Two-phase coexistence therefore requires an equilibrium partitioning model to determine how CO₂ and water partition between phases at a given pressure, temperature, and salinity. This equilibrium partitioning is used to determine the solubility of CO₂ dissolved in water and the partial pressure of water vapor in the gas; these are used as conditions for determining the transition between the single-phase aqueous state and the two-phase state or the single phase gas state and the two phase state, respectively. At temperatures
165 below 100°C, the method of (Spycher et al., 2003) is used. Above 100°C, the method of (Spycher and Pruess, 2010) with salinity correction is used.

2.3.6 Internal Energy and Enthalpy

Enthalpy of the liquid phase is computed as a function of temperature, pressure, dissolved CO₂ concentration, dissolved salt concentration, and individual pure component enthalpies (Battistelli et al., 1997). Pure liquid water enthalpy is computed from
170 the pure water EOS (Meyer et al., 1993) and then adjusted as a function of salinity (Michaelides, 1981). Pure CO₂ enthalpy is computed from the CO₂ EOS (Span and Wagner, 1996). In the gas phase, the composite gas phase enthalpy is computed as a weighted average of water vapor enthalpy and pure CO₂ enthalpy, weighted by the mass fraction of each component in the gas. Finally, the internal energy of each phase is computed by taking phase enthalpy and subtracting cell pressure divided by phase density.



175 2.4 Fluid-Rock Properties

Several fluid-rock properties are computed as functions of the state of the pore fluids in the system. Separate gas phase and liquid phase tortuosities are computed as functions of rock porosity, liquid saturation, and gas saturation (Millington and Quirk, 1959). When dissolved salt mass becomes supersaturated in the aqueous phase, it precipitates as a solid and changes both the effective porosity and the absolute permeability of the medium (Verma and Pruess, 1988). Relative permeability of each mobile
180 phase is computed as a function of phase saturations; when modeling trapped gas hysteresis, the liquid-saturated end point of the gas phase relative permeability model adapts as a function of trapped gas saturation. The CO₂-brine-rock interfacial tension is computed as a function of salt concentration and temperature (Abramzon and Gaukhberg, 1994). This results in a decrease in capillary pressure with decreasing interfacial tension.

2.4.1 Unsaturated Capillary Pressure Extensions

185 At the unsaturated end of a typical capillary pressure function (e.g., Van Genuchten or Brooks-Corey), there can exist a non-zero residual liquid saturation toward which the capillary pressure increases asymptotically. This is due to the fact that drainage of the wetting (aqueous) phase by the non-wetting (gas) phase is limited by the connectivity of the liquid phase in the porous medium. When the liquid phase is completely disconnected, the gas phase is unable to displace any more liquid and therefore capillary pressure can theoretically become infinite. However, under miscible two-phase flow conditions where both the water
190 and the CO₂ components can dissolve into both phases, it is possible to drive water saturation below the residual saturation without displacing fluid. In the case of dry CO₂ injection, continuous pumping of a pure CO₂ phase into a brine-saturated reservoir can cause desaturation of the rock through desiccation, where water molecules evaporate from the liquid phase into the free CO₂ phase.

Capturing this phenomenon requires extending the capillary pressure past the residual liquid saturation. Using the approach
195 of Webb (2000), the capillary pressure function is divided into two regimes: above and below the matching point aqueous saturation. The matching point saturation is the point at which the capillary pressure curve transitions between its original form and its extension to low aqueous saturation conditions. The matching point is computed by finding the aqueous saturation at which the slope of the original capillary pressure curve matches that of the extended curve given a specified capillary pressure at zero liquid saturation (i.e., the oven-dried capillary pressure) and a specified extension shape. In PFLOTRAN,
200 several types of unsaturated extensions are available for the standard Van Genuchten capillary pressure model. Additionally, this work developed a capillary head-based Van Genuchten model with a logarithmic extension (Fayer and Simmons, 1995) and a Brooks-Corey capillary pressure with a logarithmic extension, both of which are compatible with the scanning path hysteresis model.

2.4.2 Gas Trapping Hysteresis

205 Gas trapping occurs when an aqueous phase imbibes through a medium that is partially saturated with a gas phase. The gas phase can become disconnected and therefore immobilized (though, analogous to the desiccation process, CO₂ can continue to



dissolve into water and diffuse through the aqueous phase) as aqueous phase saturation increases throughout the medium. The extent to which the free gas phase can be trapped depends on the degree to which the medium was saturated with gas prior to imbibition. The process of gas trapping can therefore be formulated as a hysteretic phenomenon via a scanning path hysteresis model (Parker and Lenhard, 1987). In PFLOTTRAN, the simplified Parker and Lenhard model is implemented (Kaluarachchi and Parker, 1992). This model is compatible with the Brooks-Corey capillary pressure model and the capillary head-based Van Genuchten model, as well as any choice of relative permeability functions.

2.5 Fully Implicit Well Model

An optional fully coupled well model can inject CO₂ or produce reservoir fluids in user-specified portions of a model domain and dynamically adapt to changes in pressure along the wellbore, pressure in the reservoir, and physical properties of the formation. The well model is solved on an embedded sub-domain of the reservoir grid; where a well segment passes through a reservoir cell, the associated flux from well to reservoir is incorporated into the residual and Jacobian calculations.

To construct a well, the well trajectory is first defined by the user in terms of line segments and curves. The wellbore is then discretized as a function of the reservoir grid discretization, and finally individual well segments are each coupled to their corresponding reservoir grid cells.

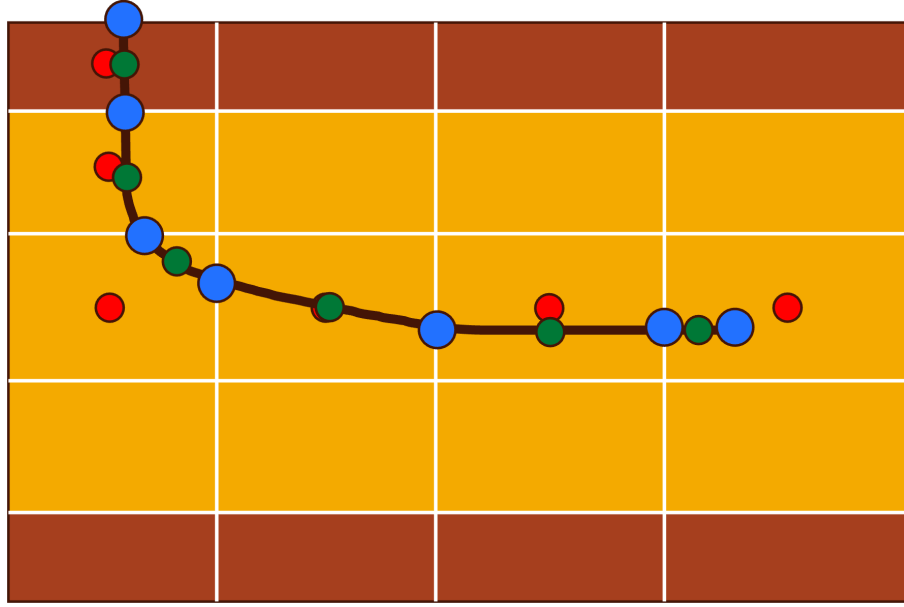


Figure 1. Discretized well model embedded in a layered reservoir. Blue dots mark the ends of each well segment, green dots mark well segment centers, and red dots mark reservoir cell centers.

When embedded into a discrete reservoir, a well model is defined in terms of well segments, well segment centers, and the reservoir cell center through which each well segment passes. In Figure 1, well segments are defined by the intervals between blue circles. Green circles denote the well segment centers, which are defined by their centroids. Red circles denote the center of each reservoir cell through which the well passes.

Invoking the well model adds one extra equation to the set of governing equations in the following form:

$$\sum_i Q_{w,\alpha}^i = q_{w,\alpha} \quad (11)$$

where Q_w is the mass flow rate of phase α between the reservoir and the well in well segment i , and q_w is the top hole mass flow rate of phase α into or out of the well. The fluid flux in or out of the well at a given well segment is computed as a function of the pressure difference between the center of each well segment and the reservoir cell that the segment occupies, where the cell-centered reservoir pressure is adjusted by a hydrostatic correction to the same depth as the well segment:

$$Q_{w,\alpha}^i = -\frac{WI\rho_\alpha}{\mu_\alpha}(P_w^i - (P_r^i + \rho_\alpha g z_{w-r})) \quad (12)$$

where ρ_α is the density of phase α , μ_α is the viscosity of phase α , P_w is the wellbore pressure at the center of well segment i , P_r^i is the pressure in the reservoir cell occupied by well segment i , g is the gravity vector, and z_{w-r} is the vertical offset between well cell center and reservoir cell center. The well index, WI , is computed as a function of the directional permeability



235 of the reservoir in addition to well properties like well orientation, skin factor, casing, and wellbore radius through a modified 3D anisotropic Peaceman equation (Peaceman, 1978, 1983) using the projection of an arbitrarily oriented well segment onto the principal axes of the domain (Shu, 2005; White et al., 2013).

In the fully implicit formulation, bottomhole pressure is solved as a primary solution variable in addition to the reservoir primary variables. Wellbore pressure in each segment is then computed as a function of well bottomhole pressure by assuming 240 hydrostatic pressure conditions along the well. Fluid densities in each segment of the well are computed as functions of pressure and temperature; the elevations of well segment centers are fixed at the beginning of a simulation.

Well pressure control can be imposed individually upon each well either through a specified fracture pressure (injection wells) or through a minimum pressure (extraction wells). Wells are initialized as rate-controlled until the well pressure hits either the fracture pressure or the minimum pressure. If one of these pressure bounds is exceeded, the well switches to pressure 245 controlled, whereby the pressure in the well is fixed and flow rates are computed accordingly. This can be used to prevent either injection wells from injecting at pressures that would fracture the host rock or extraction wells from generating non-physical suction. Note that when a well is pressure-controlled, Equation 11 will not be satisfied until the well returns to rate-controlled (i.e., the well pressure falls within the user-specified bounds again).

2.6 Primary Variables and Phase States

250 In addition to modeling miscible coupled flow of CO₂-rich and aqueous phases, SCO2 Mode also models phase appearance and disappearance. Depending on the phase state of the system, PFLOTTRAN solves its system of governing equations for different primary variables. When phase state changes, those primary variables are also changed accordingly. For example, if a grid cell begins a simulation in the aqueous state, only liquid water, dissolved CO₂, and dissolved salt exist in that grid cell. In this state, the primary variables are liquid pressure, CO₂ mass fraction, salt mass fraction per unit mass brine, and (optionally) 255 temperature. If CO₂ is injected into the cell, dissolved CO₂ mass fraction increases until it exceeds the solubility of CO₂. Once this happens, dissolved CO₂ mass fraction becomes fixed and another primary variable must be used to solve the system of equations. The cell therefore transitions to the two-phase state and updates its primary variables. The transition from aqueous to two-phase state requires only one primary variable to change: CO₂ mass fraction to gas phase pressure. SCO2 Mode considers four phase states: an aqueous state with no free-phase CO₂, a two-phase state with both aqueous and free-phase CO₂, a gas 260 state with only free-phase CO₂, and a trapped gas state with only aqueous liquid phase and immobile trapped gas phase (Table 1). When designing a model, care should be taken to identify which phase state the grid cells should be assigned at initialization and choose the set of primary variable constraints accordingly (see Section 3.2 for more discussion).



Table 1. Primary Variables and Phase States

Phase State	Primary Variables
Aqueous State	$P_l, X_{CO_2}^l, m_{NaCl}^b, T^*$.
Two-Phase State	$P_l, P_g, m_{NaCl}^b, T^*$.
Gas State	$P_g, P_{CO_2}, M_{NaCl}^b, T^*$.
Trapped Gas State	$P_l, s_{tg}, m_{NaCl}^b, T^*$.

Temperature is only required for thermal models.

2.7 Reactive Transport Governing Equations

PFLOTRAN's reactive transport process model couples multiphase, multicomponent transport and biogeochemical reaction through the governing mass conservation equation:

$$\sum_{\alpha} \left(\frac{\partial \phi s_{\alpha} \psi_j^{\alpha}}{\partial t} + \nabla \cdot (\mathbf{q}_{\alpha} - \phi s_{\alpha} \tau_{\alpha} \mathbf{D}_{\alpha} \nabla) \psi_j^{\alpha} \right) = q_j - \sum_r \nu_{j,r} I_r \quad (13)$$

with porosity ϕ , saturation s , total component concentration ψ , Darcy velocity \mathbf{q} , tortuosity τ , hydrodynamic dispersion tensor \mathbf{D} , and source/sink term q for primary species j in phase α . Kinetic rates are scaled by the stoichiometry of species j in each reaction r . The total component concentrations for the liquid and gas phases are defined, respectively, as

$$\psi_j^l = c_j + \sum_i \nu_{ji} \chi_i, \quad (14)$$

$$\psi_j^g = \sum_{i'} \nu_{ji'}^g C_{i'}^g. \quad (15)$$

with aqueous free ion concentration c , secondary aqueous complex concentration χ , and gas concentration C^g . ν_{ji} and $\nu_{ji'}^g$ are the stoichiometric contribution of the free ion species j to each secondary aqueous complex and gas.

Secondary aqueous complex and gas concentrations are defined, respectively, by the expressions

$$\chi_i = \frac{K_i}{\gamma_i} \prod_j (\gamma_j c_j)^{\nu_{ji}}, \quad (16)$$

$$C_{i'}^g = \frac{K_{i'}^g}{\gamma_{i'}} \prod_j (\gamma_j c_j)^{\nu_{ji'}} \quad (17)$$

through the law of mass action (Lichtner, 1985).

2.7.1 Solubility of CO₂ in the Aqueous Phase

Following Duan and Sun (2003), equilibrium is defined as equality of the chemical potential (μ) of CO₂ in liquid and gas phases

$$\mu_{CO_2}^l = \mu_{CO_2}^g. \quad (18)$$



For multi-component systems where $\text{CO}_{2(\text{aq})}$ may not be the primary species for the CO_2 component (e.g., use of HCO_3^- instead of $\text{CO}_{2(\text{aq})}$), equilibrium is generalized to

$$\sum_j \nu_{ji'} \mu_j^1 = \mu_{i'}^g, \quad (19)$$

285 where the sum j is over all primary species and $\nu_{ji'}$ is the stoichiometric contribution of each primary free ion species to the secondary $\text{CO}_{2(\text{aq})}$ species. Substituting the expressions for the chemical potentials equating liquid and gas potentials

$$\mu_j^1 = \mu_j^{1(0)} + RT \ln \gamma_j m_j, \quad (20)$$

$$\mu_{i'}^g = \mu_{i'}^{g(0)} + RT \ln \varphi_{i'} p_{i'}^g, \quad (21)$$

290 where $\varphi_{i'}$ and $p_{i'}^g$ are respectively the fugacity coefficient and partial pressure for species i' in the gas phase. Substituting Eqs. 20–21 into Eq. 19 yields

$$\sum_j \nu_{ji'}^g \left(\mu_j^{1(0)} + RT \ln \gamma_j m_j \right) = \mu_{i'}^{g(0)} + RT \ln \varphi_{i'} p_{i'}^g, \quad (22)$$

and alternatively,

$$-\frac{1}{RT} \left(\mu_{i'}^{g(0)} - \sum_j \nu_{ji'}^g \mu_j^{1(0)} \right) = \ln \varphi_{i'} p_{i'}^g - \sum_j \nu_{ji'}^g \ln \gamma_j m_j. \quad (23)$$

295 Or in terms the gas equilibrium constant $K_{i'}^g$

$$K_{i'}^g = \frac{\varphi_{i'} p_{i'}^g}{Q_{i'}^g}, \quad (24)$$

with the equilibrium constant related to the standard state chemical potentials by the equation

$$\ln K_{i'}^g = -\frac{1}{RT} \left(\mu_{i'}^{g(0)} - \sum_j \nu_{ji'}^g \mu_j^{1(0)} \right) \quad (25)$$

and

$$300 \quad Q_{i'}^g = \prod_j (\gamma_j m_j)^{\nu_{ji'}^g}. \quad (26)$$

Substituting Eq. 26 and the exponential of Eq. 25 into Eq. 24 results in

$$\frac{\varphi_{i'} p_{i'}^g}{\prod_j (\gamma_j m_j)^{\nu_{ji'}^g}} = \exp \left(-\frac{1}{RT} \left(\mu_{i'}^{g(0)} - \sum_j \nu_{ji'}^g \mu_j^{1(0)} \right) \right) \quad (27)$$



2.7.2 Contribution to CO₂ Residual Equation

For grid cells with a nonzero CO₂ gas saturation (i.e., $s_g > 0$), the governing mass conservation equation (i.e., Eq. 13) for CO₂ is replaced by a residual equation that constrains the CO_{2(aq)} concentration against the solubility of CO₂. The residual equation for the primary CO₂ species (i.e., CO_{2(aq)}, HCO₃⁻ or CO₃²⁻) is then based on Eq. 27, i.e.,

$$f_{\text{CO}_2} = \prod_j (\gamma_j m_j)^{\nu_{j\text{CO}_2}^g} - \frac{\varphi_{\text{CO}_2} p_{\text{CO}_2}^g}{\exp\left(-\frac{1}{RT} \left(\mu_{\text{CO}_2}^{g(0)} - \sum_j \nu_{j\text{CO}_2}^g \mu_j^{l(0)}\right)\right)} = 0 \quad (28)$$

with Jacobian entries

$$\frac{\partial f_{\text{CO}_2}}{\partial m_{j'}} = \frac{\partial \left(\prod_j (\gamma_j m_j)^{\nu_{j\text{CO}_2}^g} \right)}{\partial m_{j'}} \quad \forall j' \quad (29)$$

where f_{CO_2} is the residual equation for the CO₂ component and j' represents the primary species.



3 Usage

The following section describes new input parameters specific to SCO2 Mode, the well model, and coupling with reactive transport. All other base PFLOTRAN functionality (e.g., gridding, material property definition, output options, dataset I/O, etc) can be used with SCO2 Mode just like all other flow modes (see the PFLOTRAN Documentation for more details).

315 Running models with SCO2 Mode requires invoking the flow mode through the input deck and then choosing from a variety of input options specific to SCO2 Mode. Several new options have been added to the input deck that allow the user to choose the functionality they desire and parameterize accordingly. The following sections provide the user with a description of new input options, associated keywords, and snapshots of input decks providing context on where those keywords are used.

3.1 New Inputs

320 The two highest-level input blocks required to run a subsurface model with SCO2 Mode are the SIMULATION and SUBSURFACE blocks. In the SIMULATION block, the user chooses which process models they would like to simulate. Those can include any combination of flow modes, transport modes, geomechanics, well models, and more. PFLOTRAN will couple these processes together according to their default coupling schemes and provide coupling options where available. To select SCO2 Mode, the user would invoke MODE SCO2 under SUBSURFACE_FLOW within the PROCESS_MODELS sub-block
325 of SIMULATION.

Additionally, an OPTIONS block within SUBSURFACE_FLOW can be used to define certain refinements to the process model. Most notably, this is where the user would decide whether to run an isothermal simulation or a non-isothermal simulation. To run isothermal, the user has two options: first, ISOTHERMAL_TEMPERATURE <temperature value> sets a single constant temperature equal to <temperature value> throughout the entire model domain. Second, the user could invoke
330 FIXED_TEMPERATURE_GRADIENT to specify initial temperature conditions in the model and keep those temperatures fixed over time. Use of the FIXED_TEMPERATURE_GRADIENT keyword requires including thermal state variables in the FLOW_CONDITIONs and then setting cell temperatures through an INITIAL_CONDITION.

Other options in the OPTIONS block include:

- UPDATE_SURFACE_TENSION scales the CO₂-brine-rock interfacial tension as a function of temperature and brine
335 saturation, which in turn affects capillary pressure. Otherwise, no interfacial tension scaling is used.
- MIXTURE_DENSITY provides options for computing CO₂-brine mixture density.
- UPWIND_VISCOSITY fully upwinds the viscosity for use in flux calculations.
- PHASE_PARTITIONING can select the CO₂-brine equilibrium phase partitioning calculation method.
- NO_H2O_SOURCE_UPDATE_FROM_TRANS turns off water source/sink due to mineralization reactions if reactive
340 transport is being used



Another option in the PROCESS_MODELS block is to invoke the WELL_MODEL. The WELL_MODEL then expects a TYPE. Currently, TYPE HYDROSTATIC is supported by SCO2 Mode, and the well model coupling strategy is fully implicit. The PROCESS_MODELS block is also where a user would request the SUBSURFACE_TRANSPORT for coupling flow, a well model, and/or reactive geochemical transport. A list of new keywords can be found in Table 2.

Table 2. Input Deck Keywords.

Keyword(s)	Parent Block(s)	Description
MODE SCO2	SUBSURFACE_FLOW	Invokes the SCO2 flow mode.
WELL_MODEL	SUBSURFACE_FLOW	Invokes the well model.
ISOTHERMAL_TEMPERATURE	MODE SCO2, OPTIONS	Sets a single model temperature.
FIXED_TEMPERATURE_GRADIENT	MODE SCO2, OPTIONS	Sets a constant temperature distribution. ^(a)
UPDATE_SURFACE_TENSION	MODE SCO2, OPTIONS	Turns on surface tension scaling.
MIXTURE_DENSITY	MODE SCO2, OPTIONS	Sets CO ₂ -brine mixture density. ^(b)
UPWIND_VISCOSITY	MODE SCO2, OPTIONS	Fully upwinds viscosity. ^(c)
PHASE_PARTITIONING	MODE SCO2, OPTIONS	Sets CO ₂ -brine phase partitioning model. ^(d)
NO_H2O_SOURCE_UPDATE_FROM_TRANS	MODE SCO2, OPTIONS	Turns off H ₂ O source/sink from reaction.
TYPE	WELL_MODEL	Sets the well model type. ^(e)
WELLBORE_MODEL	SUBSURFACE	Opens the Wellbore model input block. ^(f)
WELL_MODEL_OUTPUT	SUBSURFACE	Sets well variables to output. ^(g)

^(a) Temperature distribution is read in through an INITIAL_CONDITION the same way as a thermal model, and it is held constant throughout the simulation.

^(b) Options: GARCIA (default is Alendal and Drange, 2001).

^(c) Default is a harmonic average.

^(d) Options: SPYCHER_SIMPLE. Default is Spycher and Pruess, 2010.

^(e) Options: HYDROSTATIC is the only supported option with SCO2 Mode.

^(f) This is where the user defines all well properties including well trajectory, geometry, flow rate, and well index relationship. Use multiple WELLBORE_MODEL blocks to define multiple wells.

^(g) Options: WELL_LIQ_PRESSURE, WELL_GAS_PRESSURE, WELL_LIQ_Q, WELL_GAS_Q.

345 Within the SUBSURFACE block, several new options have been added to simulate injection and production wells. The WELLBORE_MODEL block is used to begin defining the properties of a well. Multiple WELLBORE_MODEL blocks can be used to define multiple wells, each with different properties. Each WELLBORE_MODEL block requires a name (e.g., WELLBORE_MODEL well-1, WELLBORE_MODEL well-2). Within a WELLBORE_MODEL block, several sub-blocks are used to build different parts of the well and apply specific constraints. The first sub-block is the WELL_GRID block, which is used to define the orientation and trajectory of a particular well. The WELL block defines properties of the wellbore itself, like diameter and skin factor. Pressure limitations can be imposed by the FRACTURE_PRESSURE and MINIMUM_PRESSURE keywords. A list of keywords can be found in Table 4, and more information on well model construction can be found in Section 3.3.

350



3.1.1 New Characteristic Curve Options

355 A new, head-based Van Genuchten characteristic curve option is now available. This model takes the following form:

$$\bar{s}_l = (1 + (\alpha \beta_{gl} h_{gl})^n)^{-m}, \quad (30)$$

$$\bar{s}_l = \frac{s_l - s_{lr}}{1 - s_{lr}}, \quad (31)$$

$$h_{gl} = \frac{P_g - P_l}{\rho_l^* g} \quad (32)$$

360 where h_{gl} is the gas-liquid capillary head in meters, α is the inverse of the capillary entry head in m^{-1} , β_{gl} is the interfacial tension scaling factor, and ρ_l^* is a liquid reference density, which by default is set to 998.32 kg/m³.

This new capillary head-based saturation function is invoked with keyword VG_STOMP. Both the Van Genuchten capillary head function and the default Brooks-Corey capillary pressure function can now be optionally extended into the region below residual liquid saturation by using the UNSATURATED_EXTENSION keyword. Both functions are also now compatible with the scanning path hysteresis model for gas trapping.

Table 3. Characteristic Curve Keywords

Keyword	Description
UNSATURATED_EXTENSION	Extends the capillary pressure function below residual saturation.
MAX_TRAPPED_GAS_SAT	Sets $s_{gt,max}$ for the hysteresis model.
VG_STOMP	Selects the Van Genuchten capillary head model.
OVEN_DRIED_CAP_HEAD	Sets head value at $s_l = 0$. *

* Applies to Van Genuchten capillary head function only, used when extending the capillary head curve below residual saturation.



Table 4. Well Model Keywords

Keyword(s)	Parent Block(s)	Description
WELL_GRID	WELLBORE_MODEL	Defines well orientation and casing.
WELL	WELLBORE_MODEL	Defines well geometric properties.
USE_WELL_COUPLER	WELLBORE_MODEL	Sets rate through a WELL_COUPLER. ^(a)
FRACTURE_PRESSURE	WELLBORE_MODEL	Fracture pressure limit. ^(b)
MINIMUM_PRESSURE	WELLBORE_MODEL	Minimum pressure limit. ^(c)
PRINT_WELL_FILE	WELLBORE_MODEL	Prints a .well file
WELL_TRAJECTORY	WELL_GRID	Defines well trajectory. ^(d)
SURFACE_ORIGIN	WELL_TRAJECTORY	Center of the top of the well.
SEGMENT_LIST	WELL_TRAJECTORY	Reads well segment information. ^(e)
SEGMENT_DXYZ	WELL_TRAJECTORY	Define well by line segments. ^(f)
SEGMENT_RADIUS_TO_HORIZONTAL_X	WELL_TRAJECTORY	Define a kickoff radius. ^(g)
SEGMENT_RADIUS_TO_HORIZONTAL_Y	WELL_TRAJECTORY	Define a kickoff radius. ^(h)
SEGMENT_RADIUS_TO_HORIZONTAL_ANGLE	WELL_TRAJECTORY	Define a kickoff radius. ⁽ⁱ⁾
DIAMETER	WELL	Sets wellbore diameter.
FRICTION_COEFFICIENT	WELL	Sets axial friction coefficient.
SKIN_FACTOR	WELL	Sets well skin factor.
WELL_INDEX_MODEL	WELL	Sets well index model. ^(j)

^(a) A WELL_COUPLER block links FLOW_CONDITIONS and TRANSPORT_CONDITIONS to WELLS in the same manner as INITIAL_CONDITIONS and BOUNDARY_CONDITIONS link FLOW_CONDITIONS and REGIONS.

^(b) The well model switches to pressure-controlled if pressures exceed the FRACTURE_PRESSURE anywhere in the well (for injection wells).

^(c) The well model switches to pressure-controlled if pressures drop below MINIMUM_PRESSURE anywhere in the well (for extraction wells).

^(d) Other options exist (i.e., TOP_OF_HOLE / BOTTOM_OF_HOLE for vertical wells, CASING for cell-by-cell casing specification). Please see the PFLOTRAN Documentation for alternative keywords for defining well trajectory.

^(e) This can be written into the input deck or read from a FILE

^(f) This marks a change in <dx,dy,dz> from the reference point, starting at SURFACE_ORIGIN and updating with each segment. Each segment must be defined as CASED or SCREENED/PERFORATED/UNCASED. This is used instead of the SEGMENT_LIST keyword. PFLOTRAN will determine segment lengths and centers based off of the model geometry and save a segment list file for future use. Use in combination with multiple SEGMENT_DXYZ keywords and/or SEGMENT_RADIUS_TO_HORIZONTAL_X / Y / ANGLE.

^(g) Ends in a horizontal leg in the x-direction.

^(h) Ends in a horizontal leg in the y-direction.

⁽ⁱ⁾ Ends in a horizontal leg at an angle between the x- and y- axes.

^(j) Options: PEACEMAN_ISO, PEACEMAN_2D, PEACEMAN_3D, SCALE_BY_PERM. Default is PEACEMAN_3D.

365 3.2 Isothermal Injection

Setting up an isothermal model with a CO₂ injection requires first invoking the SCO2 flow mode, providing an isothermal temperature in the SUBSURFACE_FLOW OPTIONS block, providing SCO2 Mode-specific initial flow conditions, and setting



an SCO2 Mode-specific injection flow condition. Setting up the grid, specifying material properties/characteristic curves, labeling regions, etc can all be performed using standard PFLOTRAN input deck formatting. An example of some minimum requirements for setting up an isothermal CO₂ injection model are shown below.

The following example contains sections of an input deck that can be used to set up a simple CO₂ injection. Complete input decks corresponding to more complex benchmark problems can be found in the supplementary material.

SCO2 Mode is invoked in the SUBSURFACE_FLOW block with keywords MODE SCO2. To make the model isothermal, the keyword ISOTHERMAL_TEMPERATURE is used in the OPTIONS block. This model will run at a constant isothermal temperature of 45 C.

```

SIMULATION
  SIMULATION_TYPE SUBSURFACE
  PROCESS_MODELS
380    SUBSURFACE_FLOW flow
        MODE SCO2
        OPTIONS
            ISOTHERMAL_TEMPERATURE 45.d0
        /
385    /
        /
END

```

Flow conditions for the isothermal version of SCO2 Mode require three constraints. Constraints should be selected depending on the phase state of the flow condition. For example, if the model is to be initialized at fully aqueous-saturated conditions, a FLOW_CONDITION must be specified with LIQUID_PRESSURE, CO₂ MASS_FRACTION, and SALT_MASS_FRACTION. Likewise, if an initial or boundary condition were to be in the two-phase state, a GAS_PRESSURE, LIQUID_PRESSURE, and SALT_MASS_FRACTION would be required. That is, to achieve a particular phase state for a flow condition, the constraints requested in the flow conditions must match the primary variables associated with that phase state (Table 1).



SUBSURFACE

...

```
400 FLOW_CONDITION initial
      TYPE
      LIQUID_PRESSURE HYDROSTATIC
      CO2_MASS_FRACTION DIRICHLET
      SALT_MASS_FRACTION DIRICHLET
405 /
      DATUM 0.d0 0.d0 1.d2
      LIQUID_PRESSURE 5.0d6
      CO2_MASS_FRACTION 0.d0
      SALT_MASS_FRACTION 1.d-2
410 END
      ...
```

The CO₂ injection is defined through a RATE type flow condition, where water mass rate, CO₂ mass rate, and salt mass rate are specified followed by their corresponding units. More information on options for specifying injection/extraction rates can

415 be found in Section 3.3.

```
FLOW_CONDITION injection
      TYPE
      RATE MASS_RATE
420 /
      RATE 0.d0 12.5d0 0.d0 kg/s kg/s kg/s
      END
      ...
```



425 3.3 Well Model

Defining a well trajectory in PFLOTTRAN can take several forms (see Table 4). The most general form invokes the WELL_TRAJECTORY keyword and allows the user to employ an arbitrary combination well path segments (lines and curves) to construct a well geometry of their choice. Since the well trajectory is defined first by a set of lines and curves in 3 dimensions, using this option ensures that if reservoir grid resolution is refined, the well trajectory will be refined accordingly and that well segments will properly map to reservoir cells. Defining the well trajectory always begins at the surface $\langle x, y, z \rangle$ location of the wellhead and proceeds downward through a sequence of well intervals.

As an example, constructing the well shown in Figure 2 would require four entries to the WELL_TRAJECTORY block: first, the SURFACE_ORIGIN would be defined (red circle in Figure 2). Then, well interval 1 would be defined by SEGMENT_DXYZ and the corresponding dx , dy , and dz of that interval (green in Figure 2). Next, the well transitions to horizontal in the x -dimension over a particular radius. This is achieved by using the SEGMENT_RADIUS_TO_HORIZONTAL_X keyword and the desired radius r (green in Figure 2). Finally, a horizontal leg extending in the x -direction can be constructed with another SEGMENT_DXYZ entry. Note, this interval definition is independent of the reservoir mesh. PFLOTTRAN will split each interval into its corresponding discrete well segment form (i.e., the representation in Figure 1) internally as a function of the mesh. For curved intervals or intervals that do not move strictly in one principal direction, this can result in stair-stepping on structured grids, so users should keep this in mind when building wells. Each well interval is additionally defined as being either CASED or SCREENED; separate well intervals need to be defined accordingly. CASED intervals are disconnected from the reservoir cells through which they pass (i.e., well-reservoir flux is 0); SCREENED intervals are hydraulically connected to their reservoir cells.

On very large unstructured grids, the algorithm for constructing discrete well segments and mapping well segments to reservoir cells can be computationally costly. Therefore, whenever a well is constructed using the WELL_TRAJECTORY keyword, PFLOTTRAN outputs a $\langle \text{well-name} \rangle_ \text{well-segments.dat}$ text file containing all of the necessary information to import the discretized well back into the simulator for future runs. It is recommended that the user read in a well trajectory by invoking the keywords SEGMENT_LIST FILE $\langle \text{well-name} \rangle_ \text{well-segments.dat}$ when running multiple models on the same reservoir mesh with the same well or wells, to speed up model runs. If the reservoir discretization changes, or if the well trajectories are adjusted, these files must be regenerated.

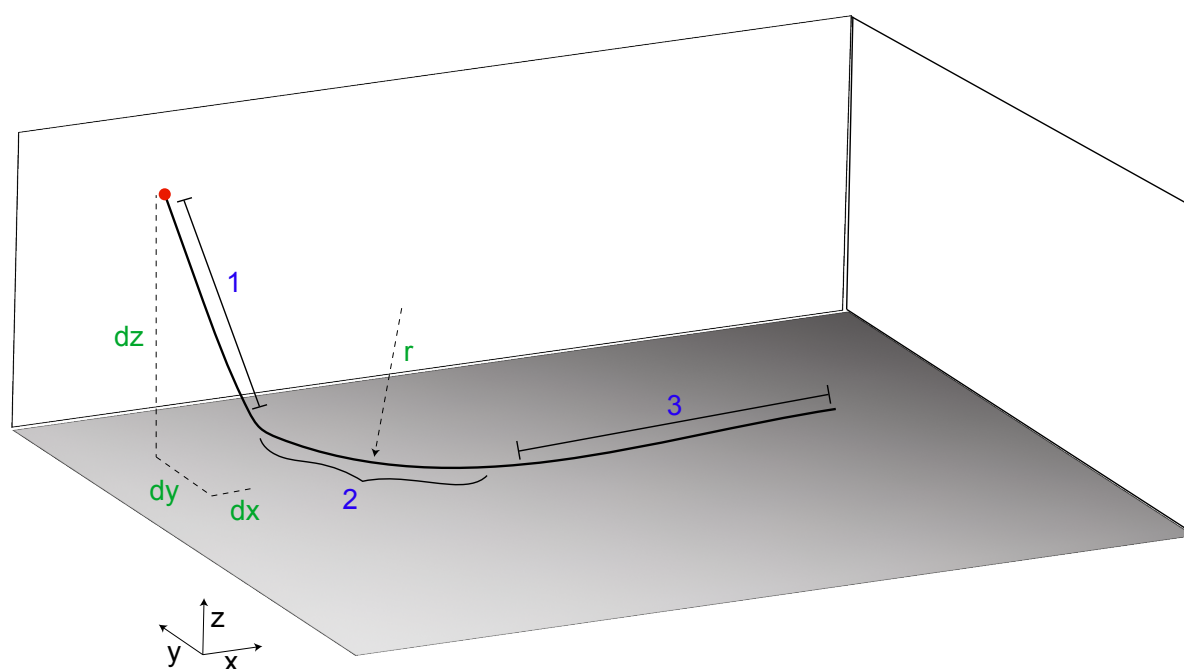


Figure 2. Example well trajectory. Red: the location of the wellhead; blue: example ordering of well intervals; green: example input types



The wellbore itself is defined by several parameters. Those include the wellbore diameter, wellbore axial friction coefficient, skin factor, and well index model. The default well index model is the 3D anisotropic Peaceman model (PEACEMAN_3D). To define an upper pressure threshold, beyond which the well is treated as pressure controlled, the keyword `FRAC-`
455 `TURE_PRESSURE` must be invoked followed by a value for fracture pressure. Likewise, a minimum threshold pressure can be assigned using the keyword `MINIMUM_PRESSURE`.

It is recommended that the user define well flow rate and composition for `SCO2` Mode using a `WELL_COUPLER`. By invoking the `USE_WELL_COUPLER` keyword in the `WELLBORE_MODEL` block, the user can then subsequently define a `FLOW_CONDITION` to be applied to the well vis-a-vis the `WELL_COUPLER` block. Just as a `BOUNDARY_CONDITION/INITIAL_CONDITION/SOURCE_SINK` block links `FLOW_CONDITIONs` (and `TRAN-`
460 `SPORT_CONDITIONs`) to `REGIONs`, a `WELL_COUPLER` links `FLOW_CONDITIONs` (and `TRANSPORT_CONDITIONs`) to `WELLs`. A `FLOW_CONDITION` for a well contains at minimum a `TYPE RATE MASS_RATE` constraint, where the `RATE` can be defined by a single set of values or a time-dependent list of values (see `PFLOTRAN` Documentation for a more detailed description of flow conditions and rate options, including interpolation options).

The `RATE` keyword expects the same number of entries as there are reservoir degrees of freedom. That means that for
465 isothermal simulations, `RATE` expects 3 entries followed by 3 units. The order matters: the first entry is a water source or sink, the second entry is a CO_2 source or sink, and the third entry is a salt source or sink. Units are mass per time. Positive numbers indicate injection. Therefore, to inject 1000 kg/s of pure CO_2 , the `RATE` would appear as follows:

```
RATE 0.0 1000.0 0.0 kg/s kg/s kg/s
```

If thermal effects are being considered, the `RATE` keyword expects an additional entry for energy flux. Note that this also
470 applies to `FIXED_TEMPERATURE_GRADIENT`, and that the energy source term is added on top of the enthalpy of the fluid being injected. Therefore, it is most common for the energy source/sink to be 0. Units also need to be provided, typically in MW. For example, a modified `RATE` when running thermal simulations looks as follows:

```
RATE 0.0 1000.0 0.0 0.0 kg/s kg/s kg/s MW
```

By default, injection temperature is set equal to the reservoir temperature at the location of the injection. Injection temper-
475 ature can optionally be modified by including an additional `TEMPERATURE DIRICHLET` constraint in the `TYPE` block of the `FLOW_CONDITION`. Also, `RATEs` are treated by default as pure component mass rates. The user can optionally invoke the `CO2_MASS_FRACTION DIRICHLET` and `RELATIVE_HUMIDITY DIRICHLET` constraint types. By invoking these, `PFLOTRAN` will treat water mass source terms as liquid phase mass sources and partition between CO_2 and H_2O mass according to the `CO2_MASS_FRACTION` provided; likewise, a CO_2 mass source will be treated as a CO_2 phase mass source and
480 partition between components according to the `RELATIVE_HUMIDITY` fraction. This could also be achieved by supplying two component mass rates without the need to invoke the `CO2_MASS_FRACTION` or `RELATIVE_HUMIDITY` keywords.

Negative `RATE` values extract mass from the reservoir through the well. Reservoir fluid temperature and composition are always used with extraction wells. Thus, the values provided are always total mass rates. Any values provided to the mass rate



terms are summed, and PFLOTTRAN applies that value as the total mass extraction rate applied to the model. Therefore it is
485 recommended that users supply total mass extraction rates to the first entry of each RATE for simplicity. To extract 1000 kg/s
of total mass in an isothermal simulation, a RATE would look as follows:

```
RATE -1000.0 0.0 0.0 kg/s kg/s kg/s
```

For example, if the reservoir contains only liquid water with dissolved salt and dissolved CO₂, applying this rate will extract
water, CO₂, and salt components where the sum of the component mass rates equals the total production rate. On the other
490 hand, if free-phase CO₂ and liquid water both coexist in the reservoir cell where the extraction is taking place, individual phase
mass rates are weighted by their mobility ratios (i.e., if gas phase exists but it is immobile, only liquid phase will be extracted,
and vice versa). PFLOTTRAN then solves for well bottomhole pressure such that sum of total mass of water and CO₂ extracted
from both phases equals the user-specified extraction rate.

When running models with reactive transport, a TRANSPORT_CONDITION will define the constraints on dissolved aque-
495 ous species that are not CO₂. For instance, if the user wishes to inject 1000 kg/s of water with a tracer in an isothermal model,
the FLOW_CONDITION would read as follows:

```
RATE 1000.0 0.0 0.0 kg/s kg/s kg/s
```

where the water component is being injected at 1000 kg/s. A separate TRANSPORT_CONDITION would prescribe the tracer
concentration in the water.

500 The following example contains sections of an input deck that invoke certain well model options. Complete input decks
corresponding to more complex benchmark problems can be found in the supplementary material.

The well model is first requested by invoking WELL_MODEL in the PROCESS_MODELS block of SIMULATION:

```
SIMULATION
505 SIMULATION_TYPE SUBSURFACE
    PROCESS_MODELS
        SUBSURFACE_FLOW flow
        MODE SCO2
    /
510 WELL_MODEL well1
    TYPE HYDROSTATIC
    END
    /
END
```

515



In the WELLBORE_MODEL block in SUBSURFACE, the WELL_GRID and WELL properties must be defined. Optionally, USE_WELL_COUPLER links a well to flow/transport conditions and FRACTURE_PRESSURE sets a maximum pressure threshold for pressure control:

```
520 SUBSURFACE
    ...

    WELLBORE_MODEL well1
        PRINT_WELL_FILE
525     WELL_GRID
        WELL_TRAJECTORY
            SURFACE_ORIGIN 50.d0 50.d0 1000.d0
            SEGMENT_DXYZ CASED 0.d0 0.d0 -200.d0
            SEGMENT_DXYZ SCREENED 0.d0 0.d0 -100.d0
530     /
        /

        WELL
            DIAMETER 0.25
535     FRICTION_COEFFICIENT 1.d0
            WELL_INDEX_MODEL PEACEMAN_3D
            SKIN_FACTOR 0.d0
        /

540     USE_WELL_COUPLER

        FRACTURE_PRESSURE 15.0d6

    END
545     ...
```

A separate WELL_MODEL_OUTPUT block defines certain well variables to include in output files.

```
WELL_MODEL_OUTPUT
```



```
550  WELL_LIQ_PRESSURE
      WELL_GAS_PRESSURE
      WELL_LIQ_Q
      WELL_GAS_Q
```

/

```
555  ...
```

Injection/extraction rates and schedules are defined in a FLOW_CONDITION and then coupled to any/all wells through a WELL_COUPLER.

```
560  FLOW_CONDITION inject_extract
      SYNC_TIMESTEP_WITH_UPDATE
      TYPE
      RATE MASS_RATE
```

/

```
565  RATE LIST
      TIME_UNITS y
      DATA_UNITS kg/y kg/y kg/y
      0.d0 0.d0 1.d9 0.d0
      2.d0 0.d0 0.d0 0.d0
570  3.d0 1.d7 0.d0 0.d0
      4.d0 -1.d8 0.d0 0.d0
```

/

END

...

```
575  WELL_COUPLER injection-extraction
      FLOW_CONDITION inject_extract
      WELL well1
```

END

```
580  ...
```




3.4 Non-isothermal Flow

Running non-isothermal models is the default behavior of SCO2 Mode. Therefore to set up a CO₂ model that considers thermal effects, no additional OPTIONS are required in the SUBSURFACE_FLOW block. However, in addition to the three mass
585 degree of freedom constraints, an additional constraint for the energy equation is also required. The fourth primary variable for all phase states is temperature; therefore, a temperature Dirichlet constraint (or energy flux Neumann constraint) is required in each FLOW_CONDITION. An example of some minimum requirements for setting up a thermal CO₂ injection model are shown below.

The following example contains sections of an input deck that can be used to set up a simple CO₂ injection considering
590 thermal effects. Complete input decks corresponding to more complex benchmark problems can be found in the supplementary material.

SCO2 Mode is invoked in the SUBSURFACE_FLOW block with keywords MODE SCO2. No additional options are required for a thermal model.

```
595 SIMULATION
      SIMULATION_TYPE SUBSURFACE
      PROCESS_MODELS
        SUBSURFACE_FLOW flow
        MODE SCO2
600    /
    /
END
```



In each FLOW_CONDITION, a thermal constraint must be added. For temperature constraints of TYPE DIRICHLET,
605 the user can either specify a constant temperature or the temperature at a reference datum in conjunction with a geothermal
gradient. Here, the initial condition specifies a geothermal temperature gradient and a temperature at a specified datum. In an
injection well, a constant temperature is specified.

SUBSURFACE

610 ...

FLOW_CONDITION initial

TYPE

LIQUID_PRESSURE HYDROSTATIC

615 CO2_MASS_FRACTION DIRICHLET

SALT_MASS_FRACTION DIRICHLET

TEMPERATURE DIRICHLET

/

DATUM 0.d0 0.d0 1.d2

620 GRADIENT

TEMPERATURE 0.d0 0.d0 -2.d-2

/

LIQUID_PRESSURE 5.0d6

CO2_MASS_FRACTION 0.d0

625 SALT_MASS_FRACTION 1.d-2

TEMPERATURE 45.d0

END

...

630 FLOW_CONDITION injection_well

SYNC_Timestep_WITH_UPDATE

TYPE

RATE MASS_RATE

TEMPERATURE DIRICHLET

635 /

TEMPERATURE 30.d0

RATE LIST

TIME_UNITS y



```

DATA_UNITS kg/y kg/y kg/y MW
640 0.d0 0.d0 5.d8 0.d0 0.d0
    3.d0 1.d8 0.d0 0.d0 0.d0
    10.d0 0.d0 0.d0 0.d0 0.d0
/
END
645 ...

```

3.5 Reactive Transport Coupling

SCO2 Mode has been designed to couple with PFLOTRAN's reactive transport libraries for modeling coupled multiphase flow and CO₂ reactivity. Invoking this coupling only requires adding a SUBSURFACE_TRANSPORT block to the PROCESS_MODELS list and including CO₂ species in additional input blocks associated with reactive transport.

650 The following example contains sections of an input deck that can be used to set up reaction coupling with CO₂ flow. Complete input decks corresponding to more complex example problems, including problems that involve geochemistry coupling, can be found in the supplementary material.

Here, SCO2 Mode is invoked in the SUBSURFACE_FLOW block, and GIRT Mode is invoked through the SUBSURFACE_TRANSPORT block. No additional options are required for reactive transport coupling, but the
655 FIXED_TEMPERATURE_GRADIENT option and the WELL_MODEL block are included here as an example of possible combinations of process models.

```

SIMULATION
  SIMULATION_TYPE SUBSURFACE
660  PROCESS_MODELS
    SUBSURFACE_FLOW flow
      MODE SCO2
      OPTIONS
        FIXED_TEMPERATURE_GRADIENT
665  /
  /
  SUBSURFACE_TRANSPORT
    MODE GIRT
  /
670  WELL_MODEL well1
      TYPE HYDROSTATIC
END

```



/

END

675

The CHEMISTRY block and associated constraints must include CO₂(aq) in order to properly enable coupling between SCO₂ Mode and reactive transport. CO₂(g) must also be included as an ACTIVE_GAS_SPECIES. This example includes the mineral calcite in its chemistry block, which is defined in a chemistry database. Specific combinations of minerals and aqueous species will depend on the desired application. The PFLOTRAN Documentation contains more information on setting up reactive transport models, including a description of the structure of a geochemical database.

680

SUBSURFACE

...

685 CHEMISTRY

PRIMARY_SPECIES

Al+++

Ca++

Fe++

690 CO₂ (aq)

...

/

SECONDARY_SPECIES

695 HCO₃⁻

OH⁻

CO₃⁻⁻

CaCO₃ (aq)

...

700 /

ACTIVE_GAS_SPECIES

GAS_TRANSPORT_IS_UNVETTED

CO₂ (g)

705 ...

/



MINERALS

Calcite

...

710 /

...

/

...

715 WELL_COUPLER injection

FLOW_CONDITION injection

TRANSPORT_CONDITION background_conc

WELL well1

END

720 ...



4 Benchmarks

Five benchmark test cases were built to demonstrate the capability of SCO2 Mode to simulate multiple coupled processes related to subsurface CO₂ injection, brine mixing, multiphase miscible flow with hysteresis, well modeling, and reactivity.

725 These models were constructed from STOMP-CO2 short course material to directly compare PFLOTRAN's results with those produced by STOMP-CO2.

4.1 Radial Flow of Supercritical CO₂

This benchmark problem is equivalent to STOMP-CO2 Short Course Example Problem CO2-1. In this problem, originally developed for the GeoSeq Project (Pruess et al., 2002), a 1D radial domain is initialized to a constant pressure of 12 MPa and a temperature of 45 C. The domain is initially water-saturated; at the beginning of the simulation a constant scCO₂ injection rate of 12.5 kg/s is applied at $r = 0$ m and held constant throughout the simulation. The aquifer is homogeneous and isotropic, and the far edge of the model is placed such that the domain is essentially infinite. Gravity effects are ignored.

735 This benchmark test was designed to evaluate the ability of simulators to properly model two-phase flow of CO₂ and brine under capillary and relative permeability effects; to adequately account for temperature, pressure, and salinity dependent phase properties like density, viscosity, and CO₂ solubility; and to appropriately handle phase behavior like CO₂ bubbling and salt precipitation during desiccation. This problem has two variants: first, the CO₂ injection occurs in a freshwater aquifer; second, CO₂ is injected into a brine aquifer. Injection is simulated using a simple source term in the first grid cell (not a well model). Table 5 summarizes key properties of the model.

Table 5. Radial Flow of Supercritical CO₂: Model Properties

Property	Value	Units	Description
ϕ	0.12	-	porosity
k	1.0E-13	m^2	permeability
T	45	C	temperature
α	0.5	1/m	inverse entry head
n	1.84162	-	Van Genuchten n
m	0.457	-	Van Genuchten m
S_{rl}	0.3	-	residual liquid saturation
S_{rg}	0.05	-	residual gas saturation
P_l	12	MPa	initial liquid pressure
$x_{CO_2}^l$	0	kg/kg	initial CO ₂ mass fraction
m_{NaCl}	0.15	kg/kg	initial salt mass fraction*
q_{CO_2}	12.5	kg/s	CO ₂ mass injection rate

* Salt mass fraction is zero for the first problem variant.



4.1.1 Zero Salinity

740 In this variant of the Radial Flow of Supercritical CO₂ benchmark problem, CO₂ is injected into a freshwater aquifer (no dissolved salt). Both PFLOTTRAN and STOMP-CO₂ simulators were run with the same model setup; plots of a select set of output variables vs radial distance from the wellbore are shown below. These output variables include gas pressure, gas saturation, and dissolved CO₂ mass fraction (Figure 3). For this problem, PFLOTTRAN and STOMP-CO₂ results are nearly indistinguishable, indicating very strong agreement between the two simulators and verifying the implementation in PFLOTTRAN.

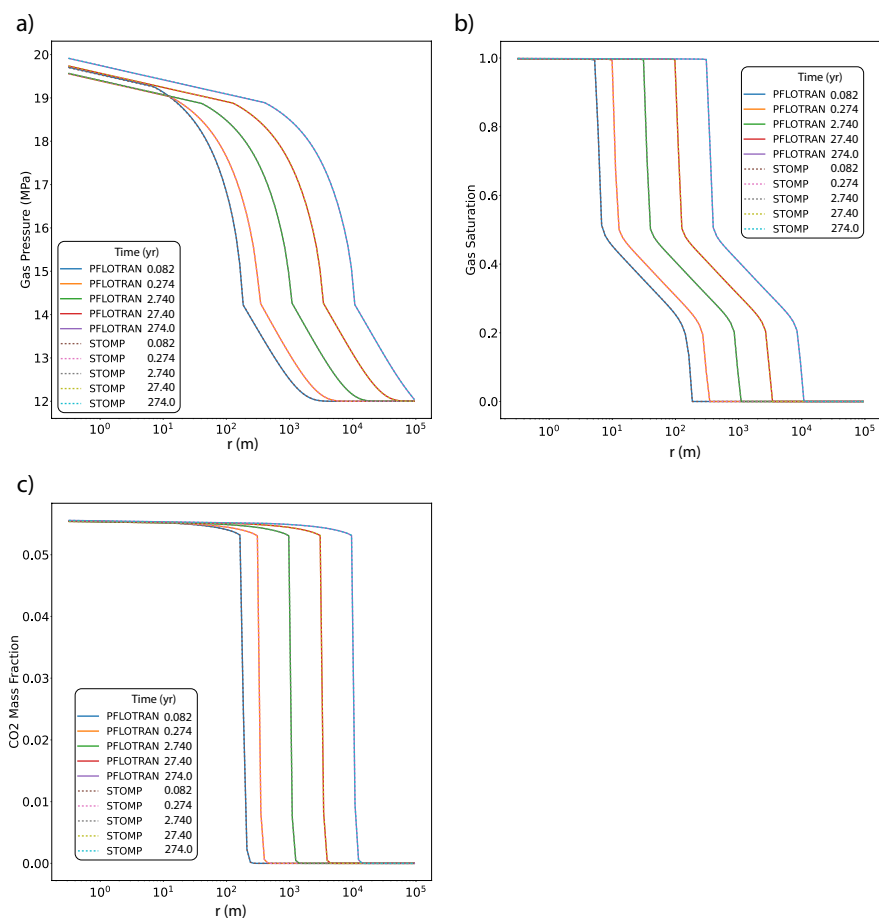


Figure 3. Radial Flow of Supercritical CO₂ without salt: a) Gas Pressure, b) Gas Saturation, c) CO₂ Aqueous Dissolved Mass Fraction.



745 4.1.2 With Salinity

In this variant of the Radial Flow of Supercritical CO₂ benchmark problem, CO₂ is injected into a brine aquifer characterized by an initial constant dissolved salt mass fraction. Both PFLOTRAN and STOMP-CO₂ simulators were run with the same model setup; plots of a select set of output variables vs radial distance from the wellbore are shown below. These output variables include gas pressure, gas saturation, dissolved CO₂ mass fraction, and salt precipitate saturation (Figure 4). For this problem, 750 PFLOTRAN and STOMP-CO₂ results are very close for all variables, indicating very strong agreement between the two simulators and verifying the implementation in PFLOTRAN. PFLOTRAN and STOMP-CO₂ differ slightly in their reporting of precipitate saturation very close to the wellbore; here, both simulators show a small amount of numerical oscillation. Under strict time step control to small time steps, this numerical oscillation can be eliminated.

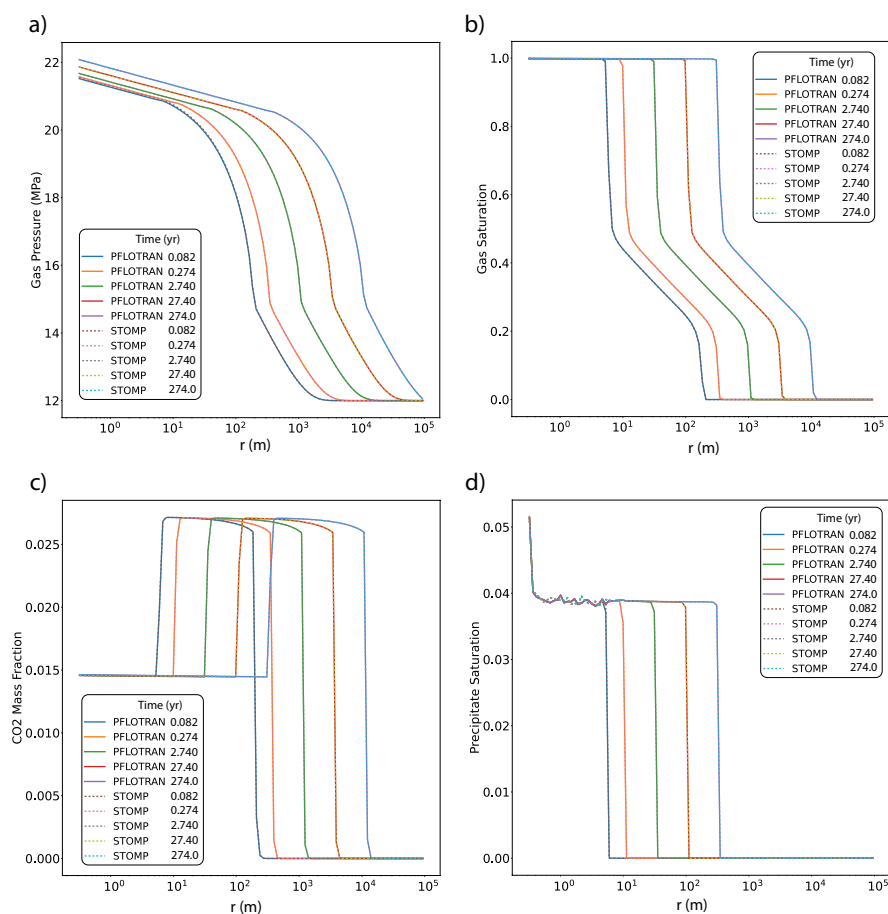


Figure 4. Radial Flow of Supercritical CO₂ with salt: a) Gas Pressure, b) Gas Saturation, c) CO₂ Aqueous Dissolved Mass Fraction, d) Salt Precipitate Saturation.



4.2 Discharge of CO₂ Along a Fault

755 This benchmark problem is equivalent to STOMP-CO₂ Short Course Example Problem CO₂-2. Like the Radial Flow of Supercritical CO₂ benchmark problem, this problem was also introduced as part of the GeoSeq Project (Pruess et al., 2002). The focus here is on modeling buoyant vertical flow rather than radial flow. Here, a 1D vertical Cartesian domain is initialized to hydrostatic conditions with pure water (no dissolved salt). This vertical model is meant to emulate loss of stored CO₂ into a freshwater aquifer along a leaky fault. This problem tests the ability of simulators to model displacement of water by buoyant

760 CO₂ migration, dissolution of CO₂ at the gas-water interface, hydrostatic water pressure and a Dirichlet top water pressure boundary, and a bottom gas pressure boundary that drives CO₂ flow into the domain.

Pressure at the top of the domain (500 m) is set to 10 MPa, and temperature everywhere is set to 45°C. The model is isothermal. The model is run in two stages: first, an equilibration step obtains an initial pressure distribution (though the keyword HYDROSTATIC in PFLOTTRAN can also be used to apply a hydrostatic pressure distribution); second, the model is

765 restarted with a gas phase boundary condition imposed on the bottom boundary and characterized by a gas pressure of 24 MPa. Table 7 summarizes key properties of the model.

Table 6. Buoyant CO₂ Flow: Model Properties

Property	Value	Units	Description
ϕ	0.35	-	porosity
k	1.0E-13	m^2	permeability
T	45	C	temperature
α	0.5	1/m	inverse entry head
n	1.84162	-	Van Genuchten n
m	0.457	-	Van Genuchten m
S_{rl}	0.3	-	residual liquid saturation
S_{rg}	0.05	-	residual gas saturation
P_l	10	MPa	initial liquid pressure at the top of the model
$x_{CO_2}^l$	0	kg/kg	initial CO ₂ mass fraction
m_{NaCl}	0	kg/kg	initial salt mass fraction
P_g	24	MPa	gas pressure applied at the base of the model

Both PFLOTTRAN and STOMP-CO₂ simulators were run with the same model setup; plots of a select set of output variables versus height of the column are shown below. These output variables include gas pressure, gas saturation, aqueous dissolved CO₂ mass fraction, and mass fraction of CO₂ in the gas phase (Figure 5). For this problem, PFLOTTRAN and STOMP-CO₂

770 results are nearly indistinguishable, indicating very strong agreement between the two simulators and verifying the implementation in PFLOTTRAN.

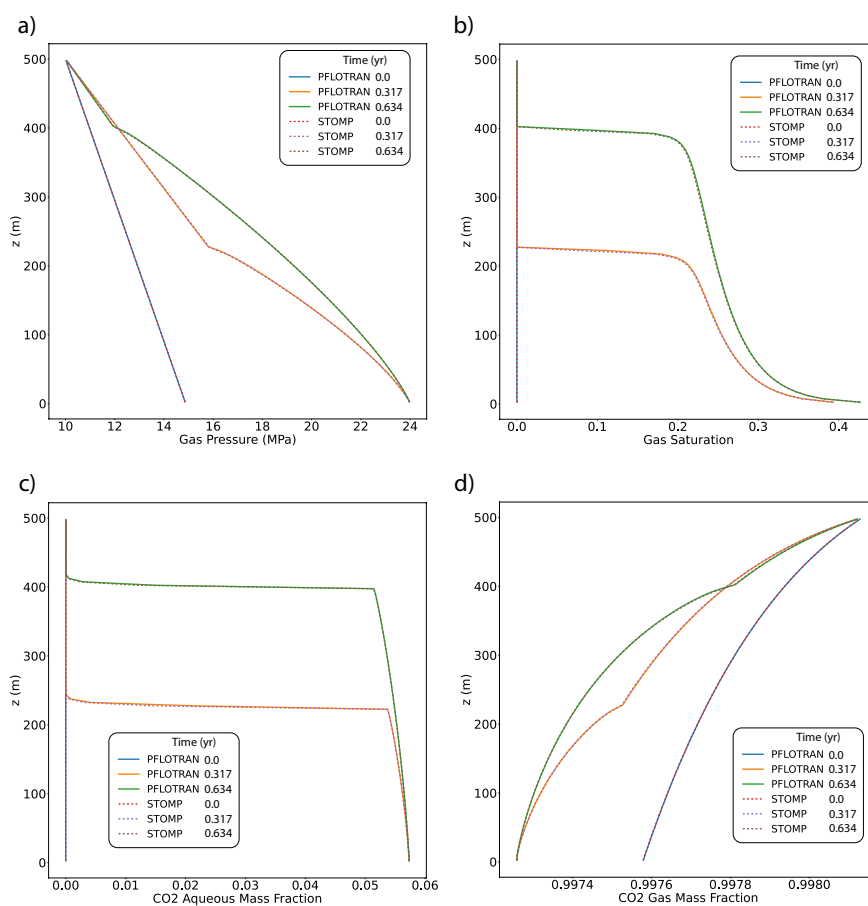


Figure 5. CO₂ Discharge Along a Fault: a) Gas Pressure, b) Gas Saturation, c) CO₂ Aqueous Dissolved Mass Fraction, and d) Free-phase CO₂ Gas Mass Fraction.



4.3 CO₂ Injection into a 2D Layered Formation

This benchmark problem is equivalent to STOMP-CO₂ Short Course Example Problem CO₂-3. This problem was originally developed for the GeoSeq project (Pruess et al., 2002). Here, a 2D Cartesian layered model was designed to be representative of the Sleipner Vest field in the Norwegian North Sea. The problem contains alternating sand and shale sequences in a marine environment (i.e., saline pore water).

The problem is isothermal at 37°C, and a source term injects scCO₂ into the bottom left corner of a sandy reservoir unit beneath the deepest shale layer. The model is initialized to hydrostatic liquid pressure with a pressure of 11.20525 MPa at the elevation of the injection well, 22 m from the bottom of the domain. No flow boundary conditions are applied on the left as a symmetry boundary, top as an impermeable shale seal, and bottom as another impermeable seal. The right boundary is a Dirichlet boundary at hydrostatic conditions. The domain spans 6 km horizontally and 184 m vertically, with a series of four 3-m thick horizontal shale units at different depths and spanning the entire length of the domain.

The sand layers and shale layers are characterized by different lithologic properties, adding heterogeneity to the model. They have different permeabilities, porosities, and capillary entry pressures. ScCO₂ is injected for a period of 2 years at a single well location in the model and at a constant rate of 0.1585 kg/s. Table 7 summarizes key properties of the model.

Table 7. 2D CO₂ Injection into a Layered Formation: Model Properties

Property	Value	Units	Description
ϕ_{sand}	0.35	-	sand porosity
k_{sand}	3.0E-12	m^2	sand permeability
α_{sand}	2.735	1/m	sand inverse entry head
ϕ_{shale}	0.1025	-	shale porosity
k_{shale}	1.0E-14	m^2	shale permeability
α_{shale}	0.158	1/m	shale inverse entry head
T	37	C	temperature
n	1.667	-	Van Genuchten n
m	0.4	-	Van Genuchten m
S_{rl}	0.2	-	residual liquid saturation
S_{rg}	0.05	-	residual gas saturation
P_l	11.20525	MPa	initial liquid pressure at the well elevation
$x_{CO_2}^l$	0	kg/kg	initial CO ₂ mass fraction
m_{NaCl}	0.032	kg/kg	initial salt mass fraction
q_{CO_2}	0.1585	kg/s	CO ₂ injection rate at the well
z_{well}	22	m	elevation of the well



790 This problem was used to test the ability of SCO2 Mode to simulate the coupled processes described in the previous benchmarks but in 2D and with lithologic heterogeneity. Simulation results are shown for PFLOTTRAN, STOMP-CO2, and published results using TOUGH2 (Pruess et al., 2002) at 30 days, 1 year, and 2 years (Figure 6). ScCO₂ initially migrates buoyantly upward from the injection site through the sand reservoir until it reaches a lower permeability shale layer, where it begins to spread laterally. Over time, due to capillary entry pressure and permeability contrasts, free-phase CO₂ accumulates at the interface between layers in the model. Overall, there is good agreement between PFLOTTRAN, STOMP-CO2, and TOUGH2, verifying the implementation in PFLOTTRAN (Figure 6). PFLOTTRAN exhibits slightly more curvature in the the free-phase CO₂ plume than STOMP-CO2, which is more plug-like. The PFLOTTRAN model more closely matches TOUGH2 in this regard.

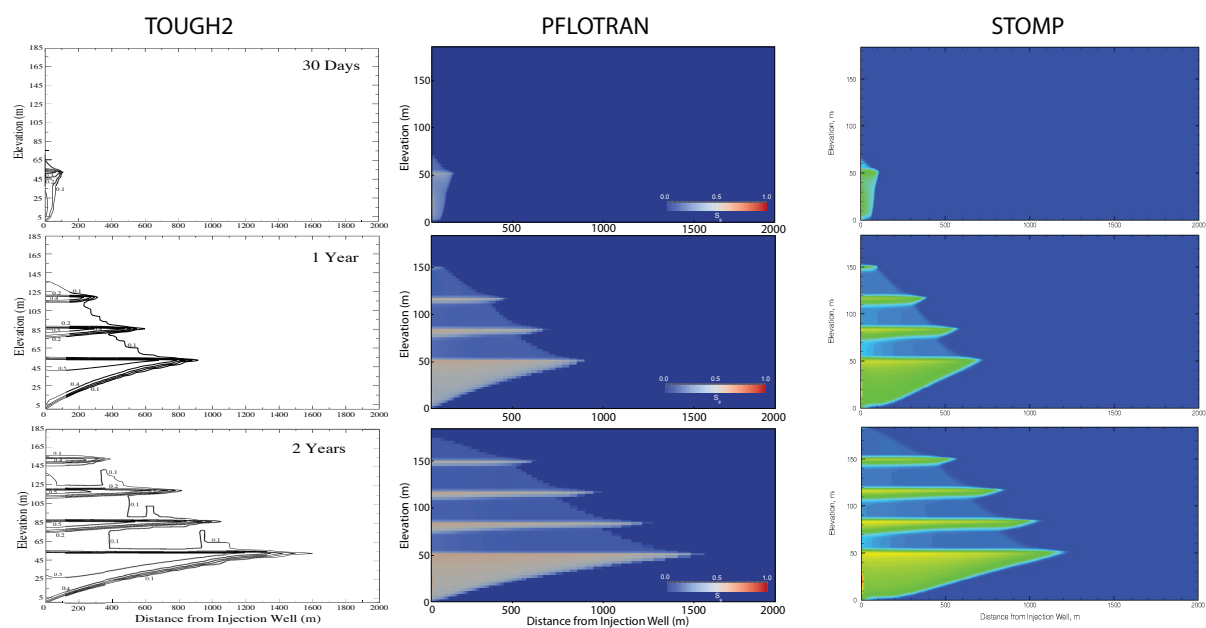


Figure 6. TOUGH2, PFLTRAN, and STOMP-CO2 Comparison. TOUGH2 results adopted from (Pruess et al., 2002), and STOMP-CO2 results adopted from STOMP-CO2 Short Course Problem CO2-3.



4.4 2D Cylindrical Injection with a Fully Coupled Well Model

795 This benchmark problem is equivalent to STOMP-CO₂ Short Course Example Problem CO₂-4. In addition to the coupled processes verified by the first three benchmark test cases, this problem also tests the ability of SCO₂ Mode to model fully coupled wells with pressure control, unsaturated capillary pressure curve extensions, trapped gas hysteresis, permeability anisotropy, fixed temperature gradient, and gravity in a 2D cylindrical domain. Here, a well model is used to inject scCO₂ into a layered brine reservoir with heterogeneous permeability and capillary entry pressure.

800 The model consists of 1 caprock layer at the top of the domain and 24 reservoir layers of varying thickness (Table 8). The original model, developed for STOMP-CO₂, uses a mixture of Imperial and SI units; here, all units were converted to SI units. Maximum trapped gas saturation for trapped gas hysteresis calculations is set at 0.2 for all layers in the domain. The model is initialized to hydrostatic pressure and a geothermal gradient of 20°C/km, with a pressure of 12.34 MPa and temperature of 43.75 °C at an elevation of -1040 m. Initial salt mass fraction in the brine is set to 0.0475 kg/kg. The fracture pressure of the
805 reservoir is set to 16.4 MPa; if pressures in the wellbore exceed this pressure, the well becomes rate-controlled. The wellbore diameter is set to 0.2286 m with no well skin. The well injects CO₂ at a constant rate of 1.0 MMT/year for the first 2 years. Then the injection well switches off and the model continues to run for a total simulation time of 10 years. The cylindrical grid increases in the radial direction from a cell radius of 5.2 m in the innermost cell to 551.2 m at the far edge for a total of 20 cells in the radial direction. In the vertical dimension, cell thickness varies from 1.2 m to 24.99 m in thickness over a total of
810 25 cells.

PFLOTRAN and STOMP-CO₂ results are nearly identical (Figure 7). They show slight differences in the radial extent of the CO₂ plume in a few of the cells at the outer edge of the plume. Other than this, the magnitude and distribution of free phase CO₂ saturation match between the two simulators, verifying the implementation of the well model with pressure control, trapped gas hysteresis, and capillary pressure extensions in PFLOTRAN.



Table 8. 2D Cylindrical Injection: Model Properties

Material Name	ϕ	$k(m^2)$	Anisotropy*	Compressibility (Pa^{-1})**	$P_{c,entry}$ (kPa)	λ	S_{rl}
Caprock	0.07	5.63E-20	1.0	1.08E-13	98	0.8311	0.0597
Reservoir24	0.13	1.91E-14	1.0	5.38E-14	11.76	0.8311	0.0597
Reservoir23	0.18	1.73E-13	1.0	5.38E-14	4.90	0.6215	0.0810
Reservoir22	0.09	1.75E-15	0.1	5.38E-14	35.28	0.8311	0.0597
Reservoir21	0.10	4.66E-15	1.0	5.38E-14	19.60	0.8311	0.0597
Reservoir20	0.08	7.03E-16	0.1	5.38E-14	49.00	0.8311	0.0597
Reservoir19	0.11	1.53E-14	1.0	5.38E-14	12.74	0.8311	0.0597
Reservoir18	0.09	2.71E-16	0.1	5.38E-14	67.62	0.8311	0.0597
Reservoir17	0.11	7.17E-15	1.0	5.38E-14	16.66	0.8311	0.0597
Reservoir16	0.08	3.75E-16	0.1	5.38E-14	60.76	0.8311	0.0597
Reservoir15	0.10	5.02E-15	1.0	5.38E-14	18.62	0.8311	0.0597
Reservoir14	0.08	1.32E-15	1.0	5.38E-14	30.38	0.8311	0.0597
Reservoir13	0.10	5.26E-15	1.0	5.38E-14	18.62	0.8311	0.0597
Reservoir12	0.12	1.57E-14	1.0	5.38E-14	11.76	0.8311	0.0597
Reservoir11	0.19	2.07E-13	1.0	5.38E-14	3.92	1.1663	0.0708
Reservoir10	0.12	1.37E-14	1.0	5.38E-14	12.74	0.8311	0.0597
Reservoir9	0.12	1.37E-14	1.0	5.38E-14	12.74	0.8311	0.0597
Reservoir8	0.13	2.07E-14	1.0	5.38E-14	10.78	0.8311	0.0597
Reservoir7	0.11	6.42E-15	1.0	5.38E-14	16.66	0.8311	0.0597
Reservoir6	0.09	2.23E-15	1.0	5.38E-14	25.48	0.8311	0.0597
Reservoir5	0.12	1.78E-16	1.0	5.38E-14	63.70	0.8311	0.0597
Reservoir4	0.12	4.69E-17	1.0	5.38E-14	104.86	0.8311	0.0597
Reservoir3	0.15	1.23E-14	1.0	5.38E-14	13.72	0.8311	0.0597
Reservoir2	0.11	2.83E-15	1.0	5.38E-14	22.54	0.8311	0.0597
Reservoir1	0.11	2.83E-15	1.0	5.38E-14	22.54	0.8311	0.0597

* Vertical : Horizontal permeability anisotropy ratio

** linear porosity compressibility

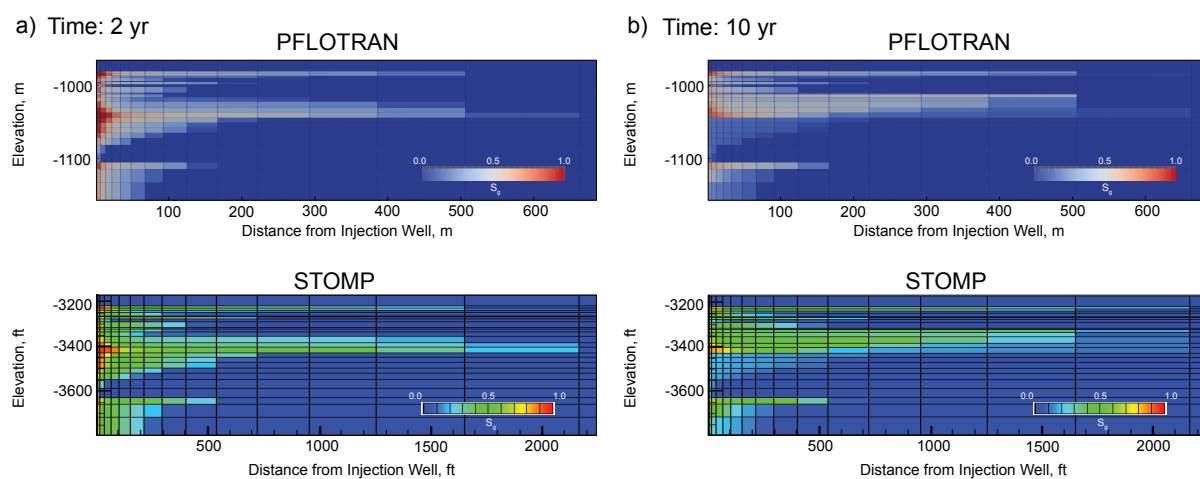


Figure 7. Well Model with Gas Trapping Hysteresis: a) 2 years and b) 10 years. STOMP-CO2 results adopted from STOMP-CO2 Short Course Problem CO2-4.



815 4.5 Mineral Trapping in Basalts

This benchmark problem is equivalent to STOMP-CO₂ Short Course Example Problem CO₂-6. This problem simulates injection of CO₂ into a reactive basalt reservoir by coupling SCO₂ Mode with the GIRT reactive transport mode in PFLOTTRAN. The physical and geochemical properties in this scenario are designed to emulate those of the Grande Ronde continental flood basalts of the Columbia Plateau province in southeastern Washington state. In this system, high permeability basalt flow tops
820 have been targeted as potential reactive reservoirs for CO₂ storage; these flow tops are sandwiched between low permeability flow interiors which serve as confining layers and create a stacked reservoir. The Wallula Basalt Pilot Project, which injected roughly 1,000 MT of CO₂ into one such reservoir system in 2013, demonstrated the ability of highly reactive basalts to rapidly mineralize CO₂ in the subsurface (McGrail et al., 2017).

Here, a 2D radial injection of CO₂ into a single flow top reservoir unit is modeled. No flow boundaries are applied at the top
825 and bottom to simulate a flow top confined between two impermeable flow interiors. The model is initialized with a hydrostatic brine pressure distribution and temperature following a geothermal gradient of 26.8 °C/km, with a brine pressure of 10 MPa and temperature of 39.83 °C at a datum of -1087.53 m elevation. Salt mass fraction is initially set to 0.01 kg/kg everywhere. CO₂ is injected along the entire span of the reservoir unit at $r = 0$ m at a total mass injection rate of 0.827 kg/s for a total of 1,000 Mt of CO₂ injected after 14 days. At the end of 14 days, the CO₂ source is shut off and the model is run to a total
830 simulation time of 10 years.

PFLOTTRAN and STOMP-CO₂ results show good agreement. The pH distribution in the reservoir is controlled by the movement of dissolved CO₂ through the system (Figure 8); pH profiles after 10 years show similar distributions and magnitudes between STOMP-CO₂ and PFLOTTRAN. STOMP-CO₂ shows a bit more spread in the pH plume than PFLOTTRAN, and the pH decrease reaches slightly further in the radial direction. This is consistent with results obtained from previous benchmarks, but
835 it also is likely affected by stronger mineralization reported by PFLOTTRAN (Figure 9). The differences could be due to several factors: first, there are likely differences in PFLOTTRAN's GIRT mode implementation of the reactive transport equations as compared to STOMP. Second, just like in previous benchmarks, STOMP-CO₂ used a combination of imperial, field, and SI units. These values (depths, pressures, temperatures, etc) were converted to SI units for use in PFLOTTRAN. Finally, STOMP-CO₂ allows the user to specify a hydrostatic gradient to initialize the model, while PFLOTTRAN computes hydrostatic pressure
840 internally relative to a datum. The pressure solution will evolve in response to boundary conditions as well as the evolution of CO₂ and salt mass distributions; final pressures could be sensitive to initialization and the far-field boundary pressure.

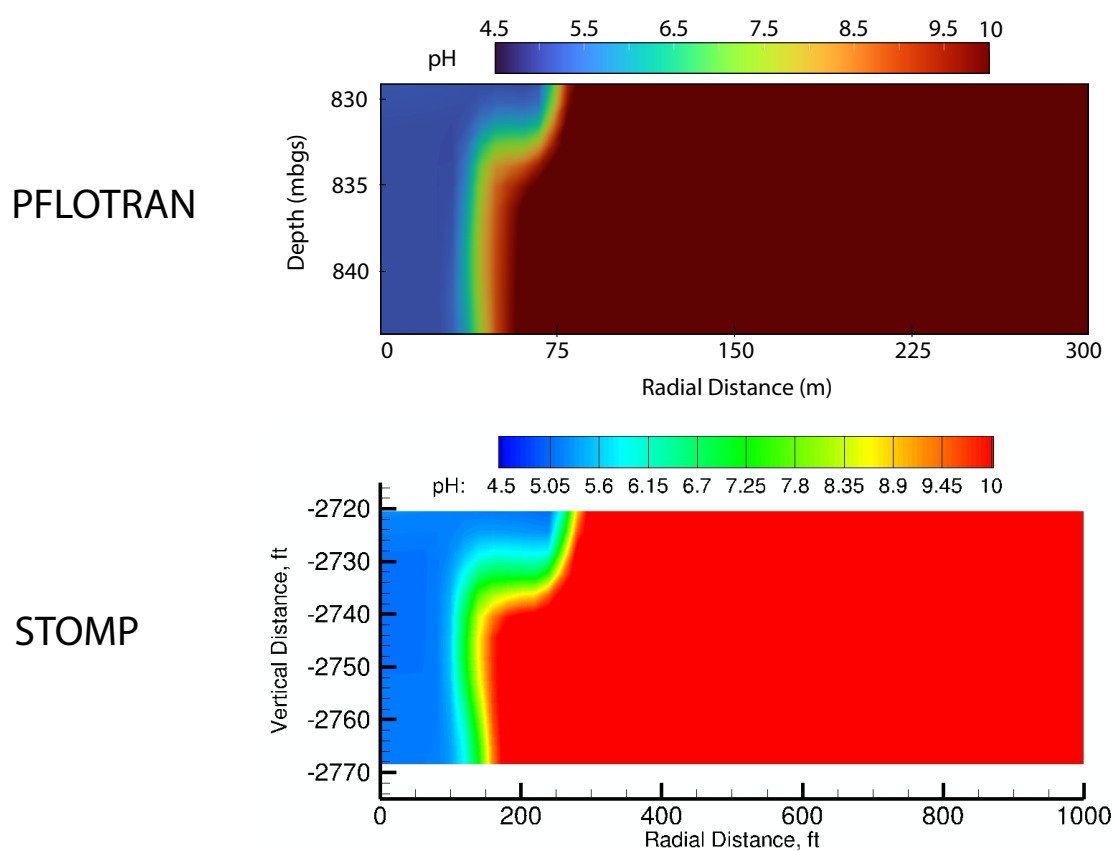


Figure 8. pH after 10 years: PFLOTRAN and STOMP-CO₂. STOMP-CO₂ results adopted from STOMP-CO₂ Short Course Problem CO₂-6.



There is good agreement between PFLOTRAN and STOMP-CO₂ with respect to the evolution of primary and secondary mineralogy in the system (Figure 9). Both simulations agree in terms of order of magnitude of dissolution and precipitation, as well as mineral order of importance. For both models, glass was the most dominant primary mineral to dissolve, followed by clinopyroxene, plagioclase, and magnetite. Likewise, dolomite was the most dominant secondary carbonate mineral formed, followed by calcite, beidellite-Ca, beidellite-Mg, and then the others. In addition to the differences noted above and in previous benchmark tests, differences in mineral volumes could also have to do with kinetic reaction rates in STOMP-CO₂ being supplied at different reference temperatures; reaction rates were adjusted to a common reference temperature of 25°C for PFLOTRAN.

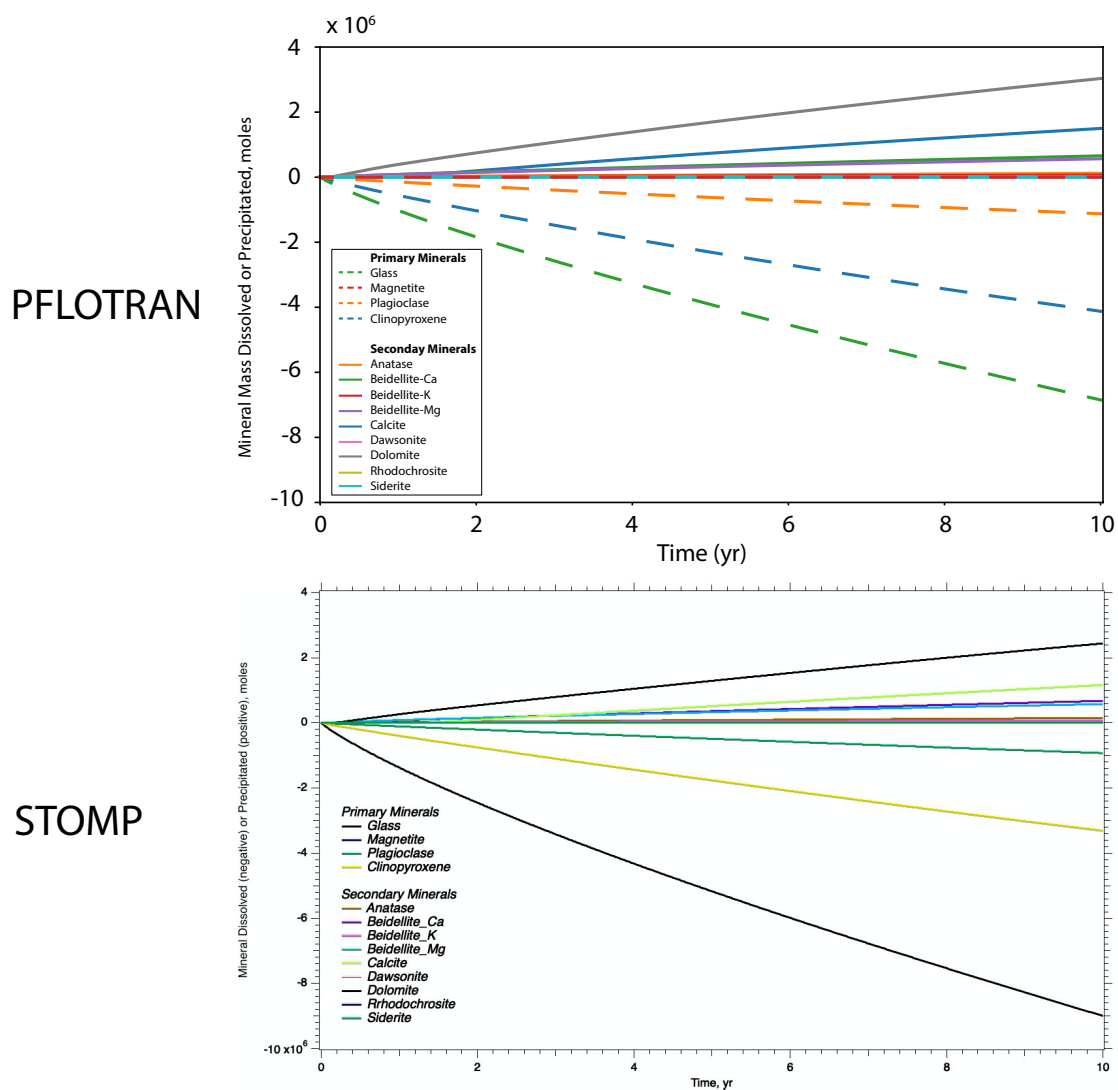


Figure 9. Minerals: PFLOTRAN and STOMP-CO₂. Negative indicates mineral dissolution, positive indicates mineral precipitation. STOMP-CO₂ results adopted from STOMP-CO₂ Short Course Problem CO₂-6.



850 The global CO₂ mass balance tells a similar story (Figure 10). Both PFLOTRAN and STOMP-CO₂ report roughly the same
total amount of dissolved CO₂ in the whole model, but they differ slightly in the amount of free-phase CO₂. This is likely
attributable to PFLOTRAN reporting slightly higher amounts of carbonate mineralization in comparison to STOMP-CO₂,
particularly dolomite mineralization. Mineralization could be retarding the movement of CO₂ through the system, which is also
expressed in the pH plume. Total free CO₂ mass (the sum of dissolved and free gas mass) is consistent between both simulators
855 at the end of the injection period, and by 10 years PFLOTRAN reports slightly lower total free CO₂ mass; the difference
is attributable to differences in total mineralization (negligible amounts of CO₂ leave the far-field boundary). Overall, good
agreement between the two simulators verifies the implementation of CO₂ flow coupled to mineral dissolution/precipitation
and aqueous reaction networks in PFLOTRAN.

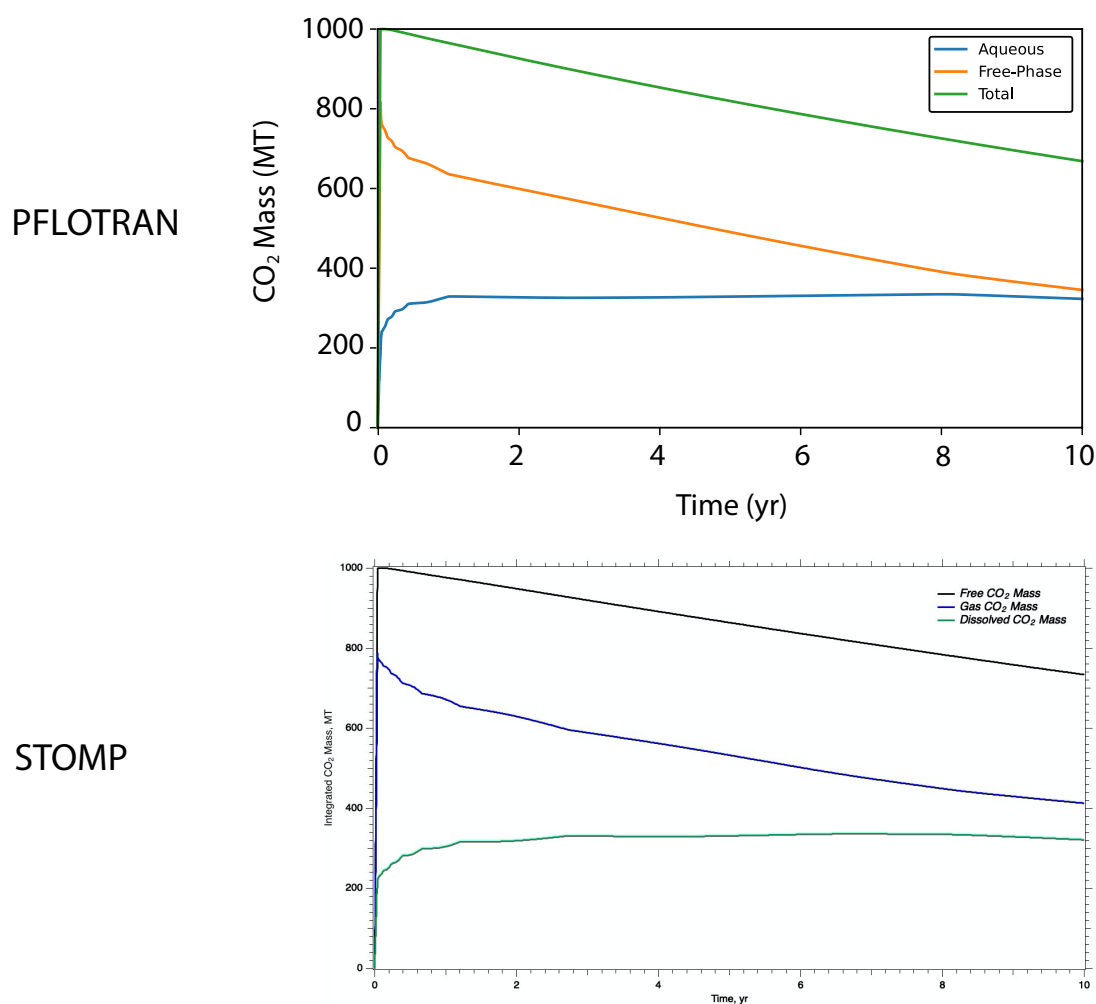


Figure 10. Total free (non-mineralized) CO₂ mass, aqueous dissolved CO₂ mass, and free phase CO₂ mass. Total free CO₂ mass decreases over time due to mineralization. STOMP-CO₂ results adopted from STOMP-CO₂ Short Course Problem CO₂-6.



5 Critical Mineral Extraction

860 As shown previously, injecting CO₂ into subsurface reservoirs naturally acidifies the formation water. In highly reactive basalt rocks, this can dissolve a host rock rich in cations that then react with dissolved CO₂ to form secondary carbonate minerals. However, in addition to promoting carbonate reactions in basalts, acidic solutions can also promote leaching of critical minerals from ore deposits; in situ leach mining is an established technique to recover metals from ores in situ such as uranium, gold, copper, and others (Bartlett, 2013). Here we demonstrate how CO₂ could be used to promote leaching and in situ production
865 of a copper ore deposit. This process has the dual benefit of storing CO₂ and producing valuable critical minerals.

In this example, a horizontal well is drilled through a hypothetical copper ore deposit. The domain measures 750 m in both lateral directions and 120 m vertically. The ore itself spans the domain laterally and 80 m vertically. It is situated between two impermeable sealing layers. The injection well extends down to the bottom of the ore deposit, where it then kicks off to horizontal for 400 m. The last 300 m of the lateral length of the well are screened; the rest of the well is cased. The
870 initial mineral composition of the deposit is based on Hammond et al. (2014) and Lichtner (1998) and is shown in Table 9. The reservoir conditions are such that CO₂ is a supercritical fluid: formation temperature is 40°C at the top of the domain and increases by 28°C/km with depth. Liquid pressure at the top of the domain is 8.3 MPa, and the formation brine has an initial salt mass fraction of 0.01 kg/kg. The well injects CO₂ and extracts formation fluids over three cycles for a total copper production period of 20 years. The well first injects 1 kg/s of CO₂ for one year, then shuts off for 3 months to allow CO₂ to
875 migrate and react with water to dissolve the rock minerals; the well then extracts formation fluids for one year at a rate of 1 kg/s. The process is repeated twice more, and then the production rate is held constant until Year 20.



Table 9. Minerals Considered in the Copper Leaching Problem

Mineral	Initial Volume Fraction	Rate Constant (mol/cm ² -sec)	Activation Energy (kJ/mol)	H ⁺ Prefactor
Chrysocolla	5.0E-3	1.0E-10	-	0.39
Goethite	2.5E-2	1.0E-11	-	-
Kaolinite	5.0E-2	1.0E-13	-	-
Muscovite	5.0E-2	1.0E-13	-	-
Quartz	8.7E-1	1.0E-14	-	-
Alunite	0.0	1.0E-11	-	-
Aragonite	0.0	5.01E-9	14.1	0.9
Azurite	0.0	1.55E-10	14.1	0.9
Calcite	0.0	1.55E-10	14.1	0.9
Dawsonite	0.0	1.55E-10	14.1	0.9
Gypsum	0.0	1.0E-10	-	-
Jarosite	0.0	1.0E-11	-	-
Jurbanite	0.0	1.0E-11	-	-
Malachite	0.0	1.55E-10	14.1	0.9
SiO ₂ (am)	0.0	1.0E-11	-	-

After 5.5 years, three cycles of CO₂ injections have injected a total of 9.46x10⁵ MT of CO₂ through the well. A buoyant free-phase CO₂ plume migrates upward through the reservoir above the well; since the CO₂ is also dissolved in the pore water, the associated change in pH of the pore water extends beyond the free-phase CO₂ plume, which results in a zone of enhanced copper dissolution (Figure 11). In this model, the minimum pH induced by CO₂ injection is 4.3. The original formulation of the copper leaching problem from Hammond et al. (2014) injects an aqueous solution with a strong acid of pH 1 into an ore deposit to induce copper leaching. For comparison, we modified our example problem to inject an aqueous solution with the acid used in Hammond et al. (2014) instead of CO₂. As expected, a very strong acid initially results in greater amounts of copper extracted from the deposit (Figure 12). But, interestingly, at later time copper extraction rates decay slower with CO₂ injection than with acid injection. This could be due to the differences in mobility between CO₂ and water and suggests that an optimal CO₂ injection strategy could be achieved that balances the timing of injection and production with the rates of free-phase CO₂ migration, copper leaching, and copper carbonate mineralization.

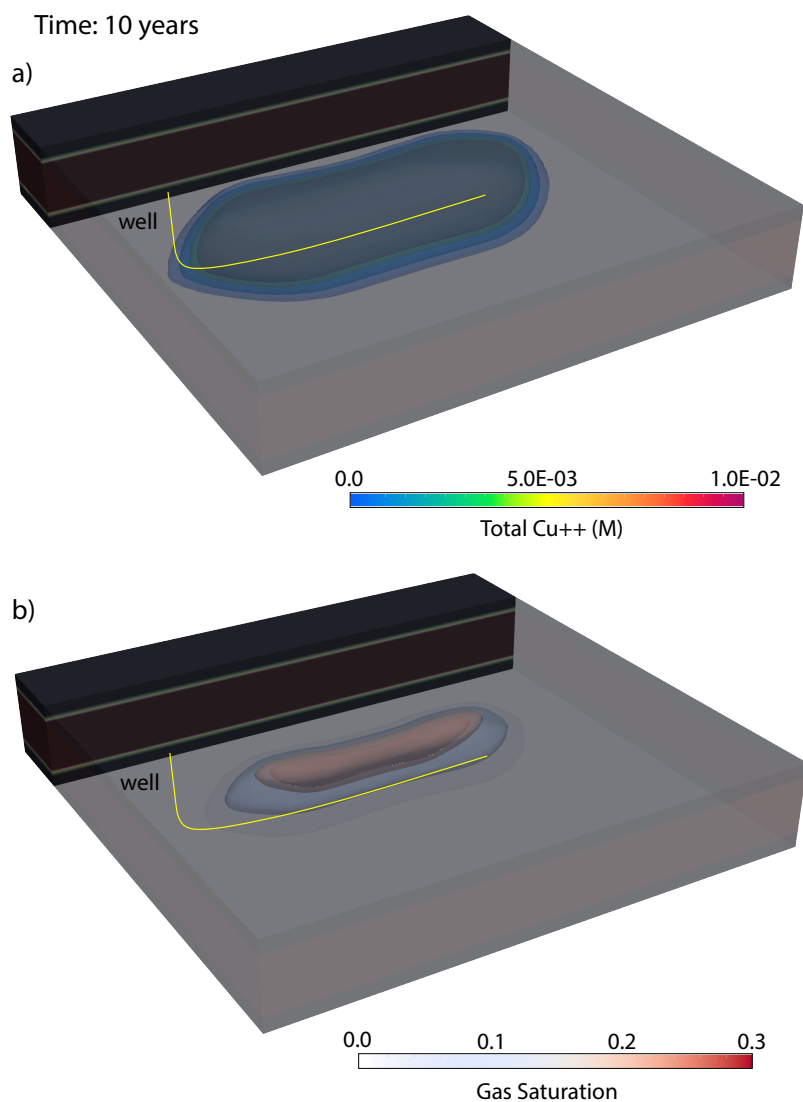


Figure 11. A snapshot of a) dissolved copper and b) free-phase CO₂ after 10 years.

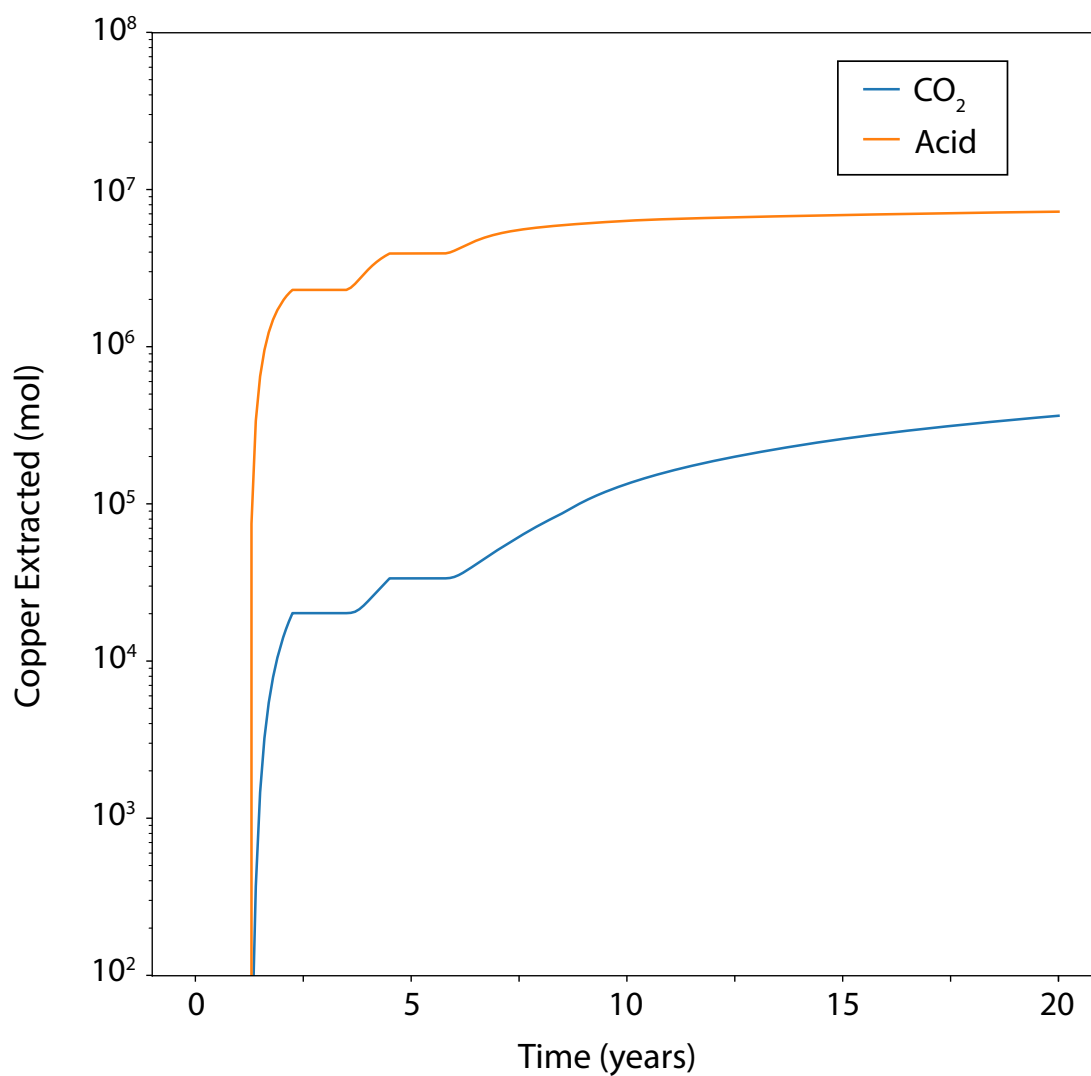


Figure 12. Total copper mass extracted from the well over 10 years, comparing CO_2 as the acidification agent to a strong acid (pH=1).

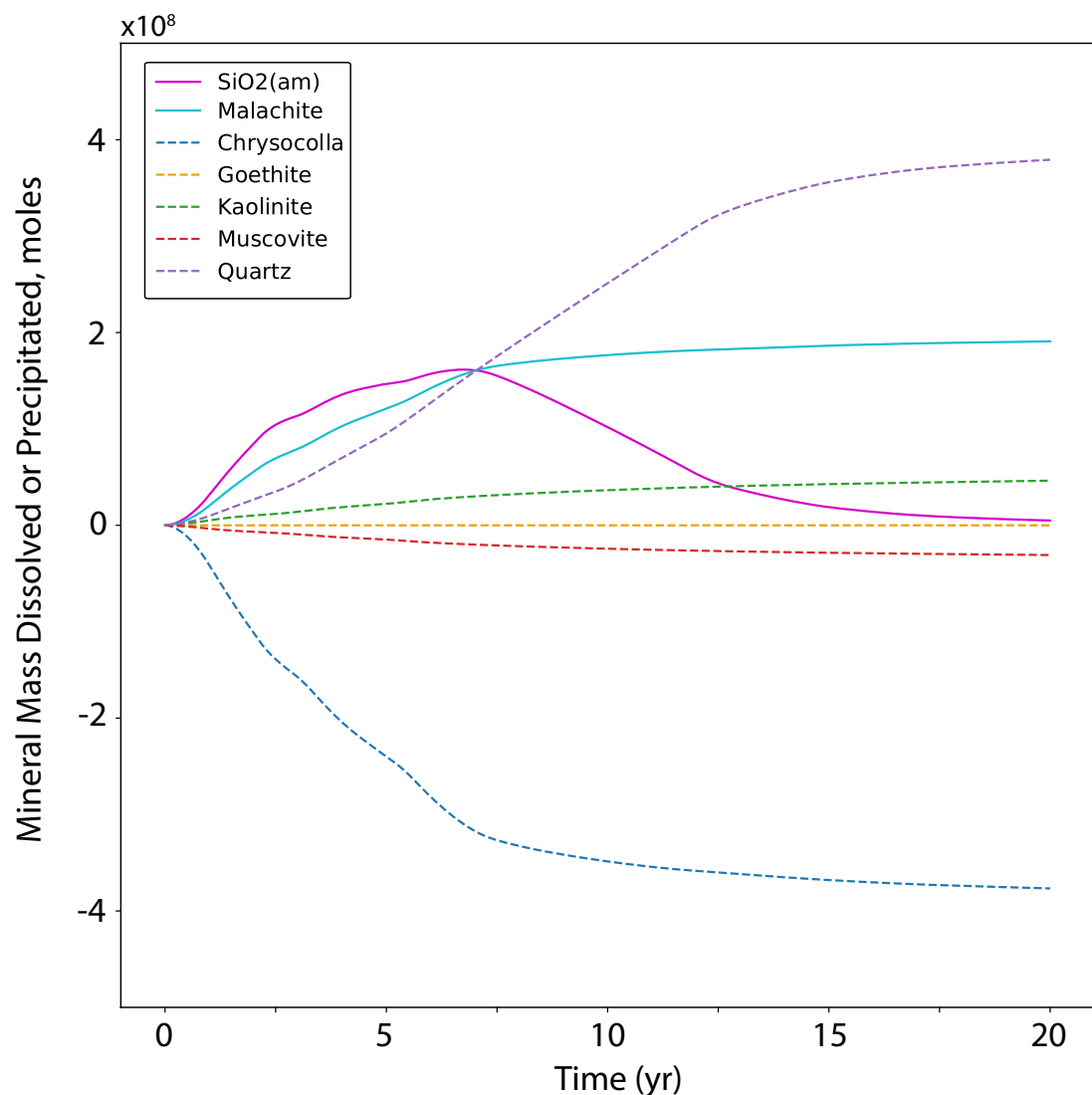


Figure 13. Total mineral mass precipitated (positive) or dissolved (negative). Dashed lines indicate primary minerals.

In addition to differences in system pH between a CO₂ injection and an acid injection, CO₂ can also react with copper cations in solution to form copper carbonates. In this model, the dominant copper carbonate mineral that forms is malachite, while the primary mineral that dissolves to release copper is chrysocolla (Figure 13). Interestingly, silica formation accounts for a significant fraction of the total mass of minerals formed, indicating that silica formation rates could be affecting overall mineral dissolution/precipitation and thus total copper extraction potential.



6 Conclusions

Recent developments in the open source multiphase flow and reactive transport simulator PFLOTTRAN now allow for modeling the flow of scCO₂ and brine with optional fully implicit coupling to a hydrostatic well model, fully implicit thermal coupling, and sequential coupling to PFLOTTRAN's well-established reactive transport capabilities. Many new features are now available, including flexible well trajectories, capillary pressure function extensions below residual saturation, and scanning path hysteresis for gas trapping. These new features are verified against the STOMP-CO₂ simulator for five benchmark test cases, which show excellent agreement between the two simulators. Finally, a new example problem involving critical mineral extraction is presented, demonstrating how CO₂ can be used as a working fluid for promoting copper leaching from an ore deposit. Critical mineral extraction using CO₂ as the working fluid would take advantage of CO₂-induced acidification to leach copper into the pore water, but the process should be optimized to avoid significant mineralization of secondary copper carbonate minerals. This example demonstrates how CO₂ could be used instead of strong acids to extract critical minerals using a potentially more environmentally friendly working fluid while simultaneously storing CO₂.

Code and data availability. The current version of PFLOTTRAN is available from the project website www.pflotran.org under the LGPL3 licence. The exact version of the model used to produce the results used in this paper is archived on Zenodo under DOI 10.5281/zenodo.14969296, as are all input data (Nole et al., 2025).



Appendix A: Verification Tests

910 A suite of verification tests were constructed to test individual functions, capabilities, or processes in isolation from larger, coupled, system-scale phenomena. These small, 0- and 1-dimensional test cases are designed to evaluate how well the new components developed in SCO2 Mode match their counterparts in STOMP-CO2.

A1 0D Test Cases

915 A set of single-cell tests cases was developed to confirm that SCO2 Mode represents the relevant CO₂ equations of state, constitutive relationships, initial/boundary conditions, phase behavior, and flow/reaction coupling in a manner that is consistent with STOMP-CO2.

A1.1 CO₂ Injection into a Brine Reservoir

920 In this test, a single grid cell is initialized at a brine pressure of 12 MPa, initial CO₂ mass fraction of 0.0 kg/kg, and initial salt mass fraction of 0.15 kg/kg. CO₂ is injected into the cell at a rate of 12.5 kg/s. Capillary pressure is described by a Van Genuchten function with a capillary entry head of 2 m, n equal to 1.84162, liquid residual saturation of 0.3, and gas residual saturation of 0.05. A liquid phase boundary condition on the east face of the cell is set to 12 MPa, a salt mass fraction of 0.22 kg/kg, and no dissolved CO₂. An isothermal temperature of 20 °C is set in the cell. PFLOTRAN and STOMP-CO2 report identical results, verifying the implementation of CO₂-brine phase partitioning, capillary pressure, salt precipitation models, and liquid phase boundary conditions in PFLOTRAN (Figure A1).

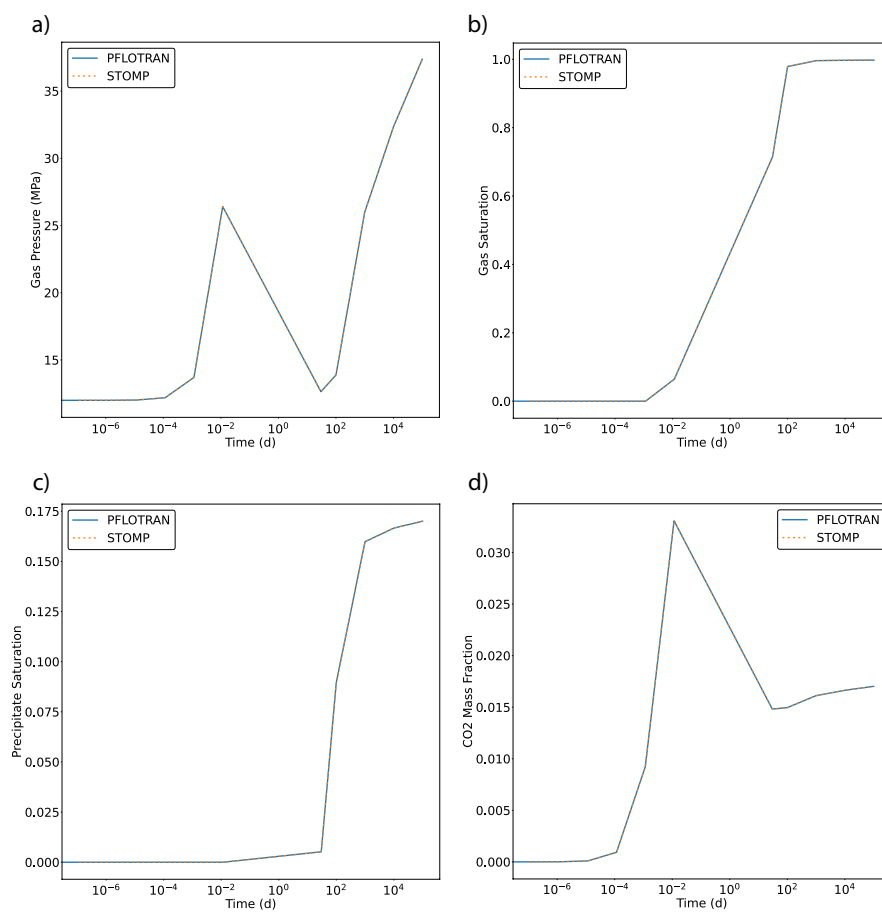


Figure A1. Single-cell CO₂ Injection: a) Gas Pressure, b) Gas Saturation, c) Precipitate Saturation, and d) Dissolved CO₂ Mass Fraction.

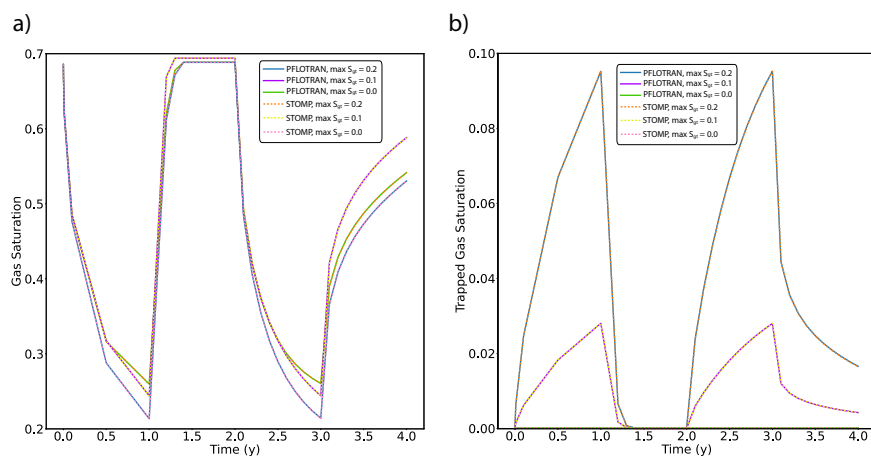


Figure A2. Trapped Gas Hysteresis: a) Gas Saturation, b) Trapped Gas Saturation

A1.2 Trapped Gas Hysteresis

925 This single-cell test was designed to verify PFLOTRAN's implementation of trapped gas hysteresis over several drainage and imbibition cycles. In this test, a single grid cell is initialized with a brine pressure of 12 MPa, a gas phase pressure of 14 MPa, and no dissolved salt. Using a Van Genuchten capillary pressure function with an entry head of 2 m, Van Genuchten n value of 1.84162, and liquid residual saturation of 0.3, a capillary pressure of 2 MPa is equivalent to an initial gas saturation of 0.6857. In this model, trapped gas hysteresis is enabled through the capillary pressure curve's optional input field for maximum trapped gas saturation. The model is isothermal at 20 °C, and boundary conditions are applied on the west and east faces of the cell. Both boundary conditions apply a liquid pressure of 12 MPa with no dissolved CO₂ or dissolved salt. Initially, the boundary conditions drive water to imbibe into the domain. After 1 year, CO₂ is injected into the cell at a rate of 1.0 kg/s, causing water to drain back out of the cell. After 2 years, the gas source is shut off, causing imbibition again. Finally, after 3 years CO₂ is injected at a slower rate of 0.1 kg/s until the end of the simulation at 4 years. Three simulations were run with different values for maximum trapped gas saturation. PFLOTRAN and STOMP-CO2 report identical results for all simulations, verifying PFLOTRAN's implementation of trapped gas hysteresis.

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A1.3 CO₂ Injection into a Reactive Brine Reservoir

This single-cell test contains a batch reactor in which a CO₂ injection drives dissolution of primary minerals and subsequent carbonate mineralization. Mineral chemistry is similar to the Mineral Trapping in Basalts benchmark problem chemistry.

940 The domain is initialized to a liquid pressure of 1 MPa, salt mass fraction of 0.01 kg/kg, and an isothermal temperature of 24°C. CO₂ is injected at a constant rate of 1.0×10^{-5} kg/s for 14 days; the simulation is run for a total of 10 years. pH initially drops in the cell to around a pH of 4; PFLOTRAN and STOMP-CO2 report nearly the same pH drop. The pH then rebounds to close to pH 5 by the end of the model. PFLOTRAN and STOMP-CO2 report nearly the same pH. Primary minerals clinopyroxene and plagioclase dissolve in this model; PFLOTRAN and STOMP-CO2 report very similar dissolution of these

945 primary minerals over the course of the 10 year simulation. PFLOTRAN and STOMP-CO2 report very similar secondary mineral mass precipitation; some differences at the point of mineral formation could be due to different timestepping in the reactive transport solve or slightly different treatment of mineral nucleation between the two reactive transport solvers. STOMP-CO2 reports nonzero masses of the least abundant secondary minerals (Dawsonite, Rhodochrosite, and Siderite), whereas PFLOTRAN reports those as zero. These mineral masses are 15 orders of magnitude smaller than the dominant secondary

950 minerals, so they are negligible. This test problem demonstrates an implementation of flow and reactive transport coupling in PFLOTRAN that is consistent with STOMP-CO2.

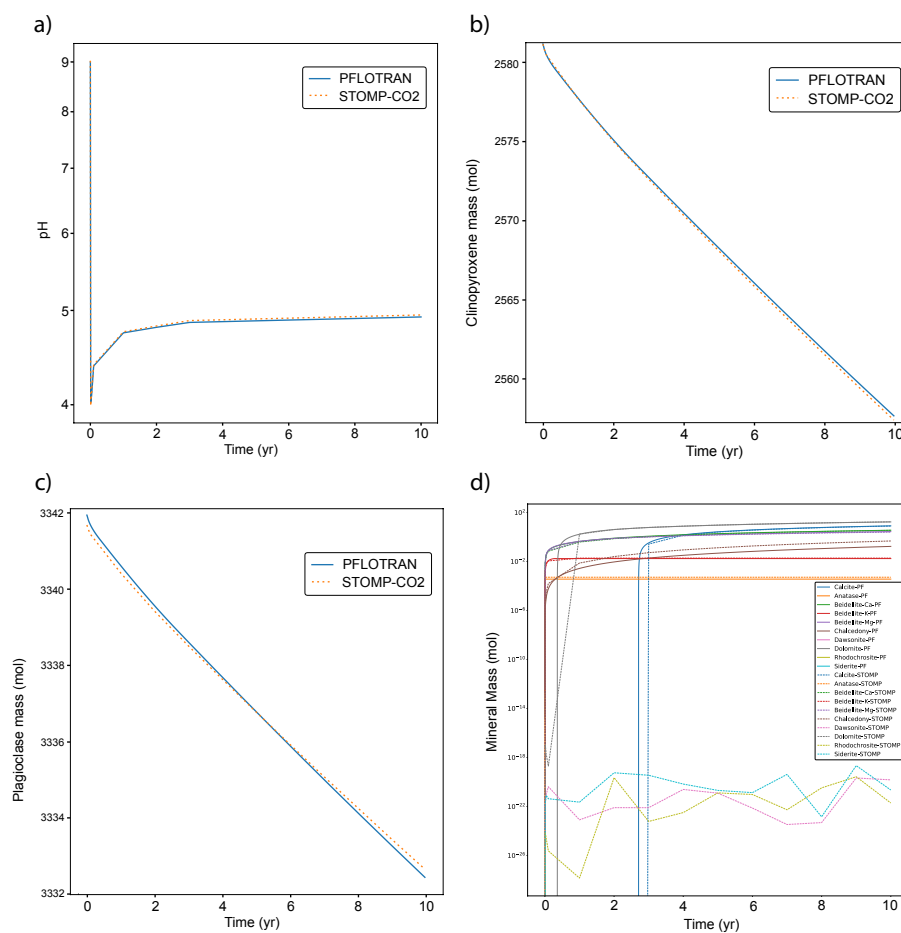


Figure A3. Single-cell Reactive CO₂ Injection: a) pH, b) Clinopyroxene, c) Plagioclase, and d) Secondary Minerals



A2 1D Test Cases

Several 1D test cases were built to evaluate SCO2 Mode's representation of boundary conditions, inter-block flux terms, gravity effects, and the fully coupled well model compare to those implemented in STOMP-CO2.

955 A2.1 Two-Cell CO₂ Injection into a Brine Reservoir

A 2-cell test problem was developed to verify the implementation of interior cell flux terms in SCO2 Mode. In this test, a 1D horizontal Cartesian model with two 15-m long grid cells is initialized to a constant liquid pressure of 12 MPa, zero dissolved CO₂ mass fraction, and dissolved salt mass fraction of 0.15 kg/kg. A source term in the left grid cell injects CO₂ at 12.5 kg/s, while a boundary condition on the right side of the model holds pressure at the initial pressure. The model is run for 1.0×10^5 days. PFLOTRAN and STOMP-CO2 results at several different output times are identical, verifying the implementation of inter-cell multiphase fluxes in SCO2 Mode.

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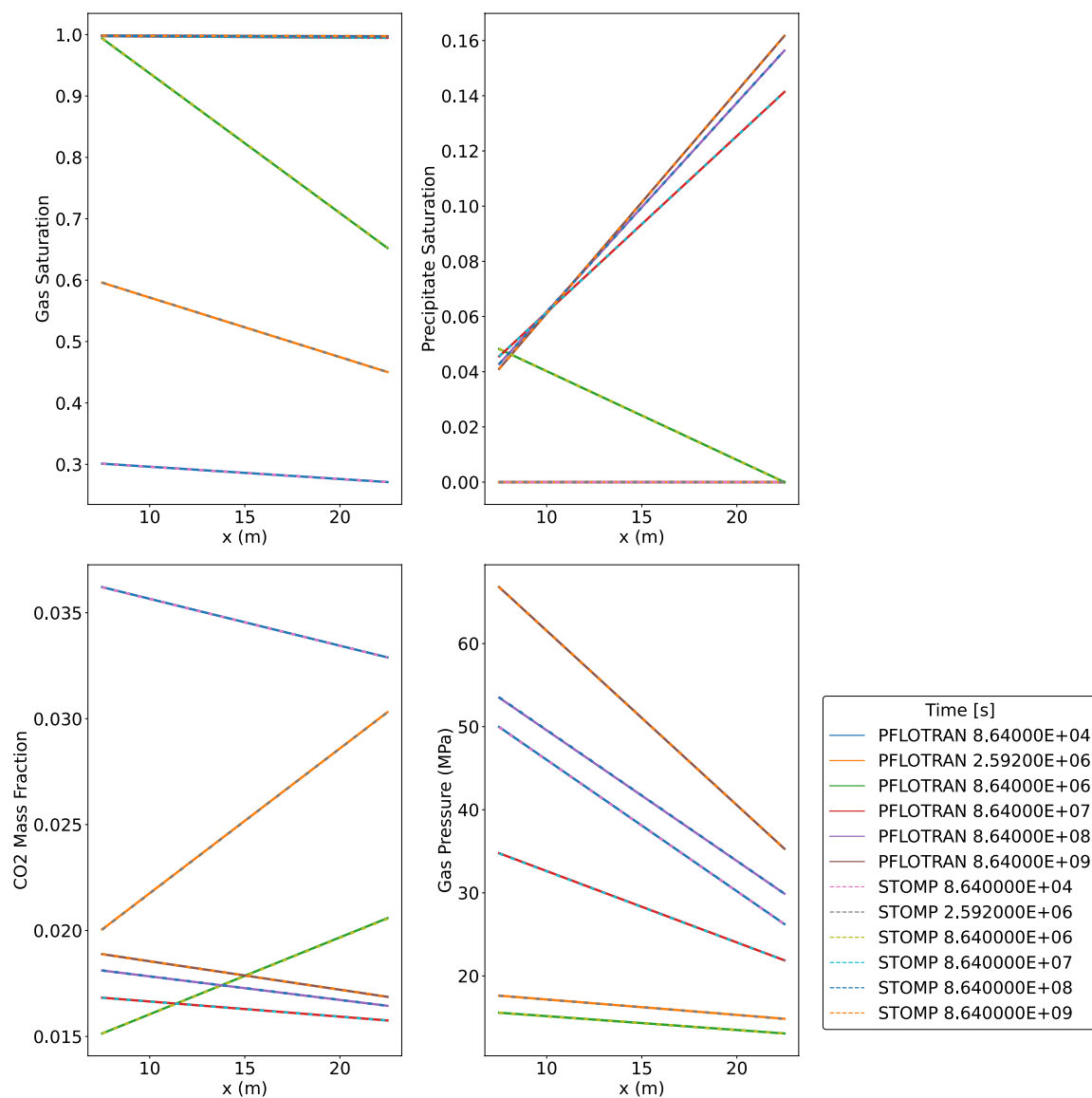


Figure A4. Two-Cell CO₂ Injection



A2.2 Two-Cell CO₂ Well Injection

In this test, a 2-cell Cartesian model is oriented vertically; each cell has a thickness of 100 m. A fully coupled well model injects CO₂ into the domain and is screened through both cells. The well injects CO₂ at a total rate of 1.0×10^6 kg/year. Since
965 the well is screened through both cells, mass rate of CO₂ injected into each cell therefore is distributed to each cell as a function of well pressure, cell pressure, and well index. The model is initialized to a constant liquid pressure of 12 MPa and a salt mass fraction of 0.0475 kg/kg. The top of the model is fixed at the initial liquid pressure and mass fractions; therefore, buoyancy drives upward flow of free-phase CO₂ throughout the simulation and the liquid phase sinks to achieve hydrostatic pressure. The model is run to 9×10^4 hours. Both the PFLOTRAN and STOMP-CO₂ simulations produce identical results at several output
970 times in the simulation, verifying the implementation of the coupled well model in SCO2 Mode.

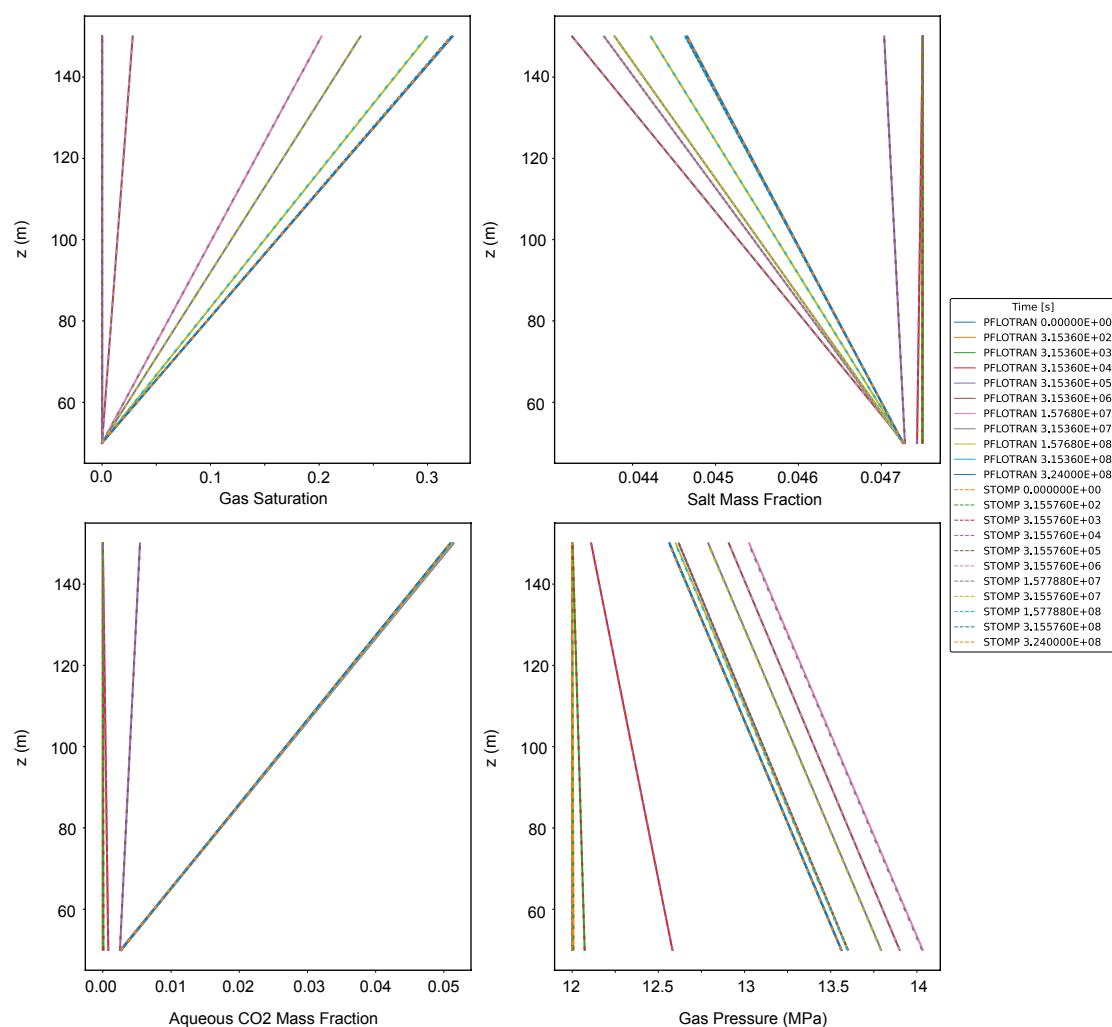


Figure A5. Two-Cell CO₂ Well Injection



A2.3 CO₂ Injection into a Vertical Brine Reservoir

This test case models a CO₂ injection into a 200-m vertical column using a fully coupled well model. Here, each cell is 1 m thick; the vertical well spans the entire domain and is screened throughout. Thus, the well model injects CO₂ into many more grid cells than in the previous problem. This problem tests the ability of the well model to inject into hundreds of reservoir grid cells adaptively depending on bottomhole pressure, reservoir pressure, and well index; additionally it tests the implementation of fluxes across hundreds of reservoir cells. The reservoir is initialized to a constant liquid pressure, zero CO₂ mass fraction, and a constant salinity of 0.0475 kg/kg, with a Dirichlet boundary condition at the top set at initial pressure and mass fractions. The model is isothermal at a constant temperature of 20 °C. The model is run for 9×10^4 hours. PFLOTTRAN and STOMP-CO2 produce nearly identical results at all output times. The one exception is in dissolved CO₂ mass fractions at late times in the deeper part of the model, where both simulators deviate very slightly. These results verify the implementation fully coupled wells in PFLOTTRAN where the wells are screened for hundreds of grid cells.

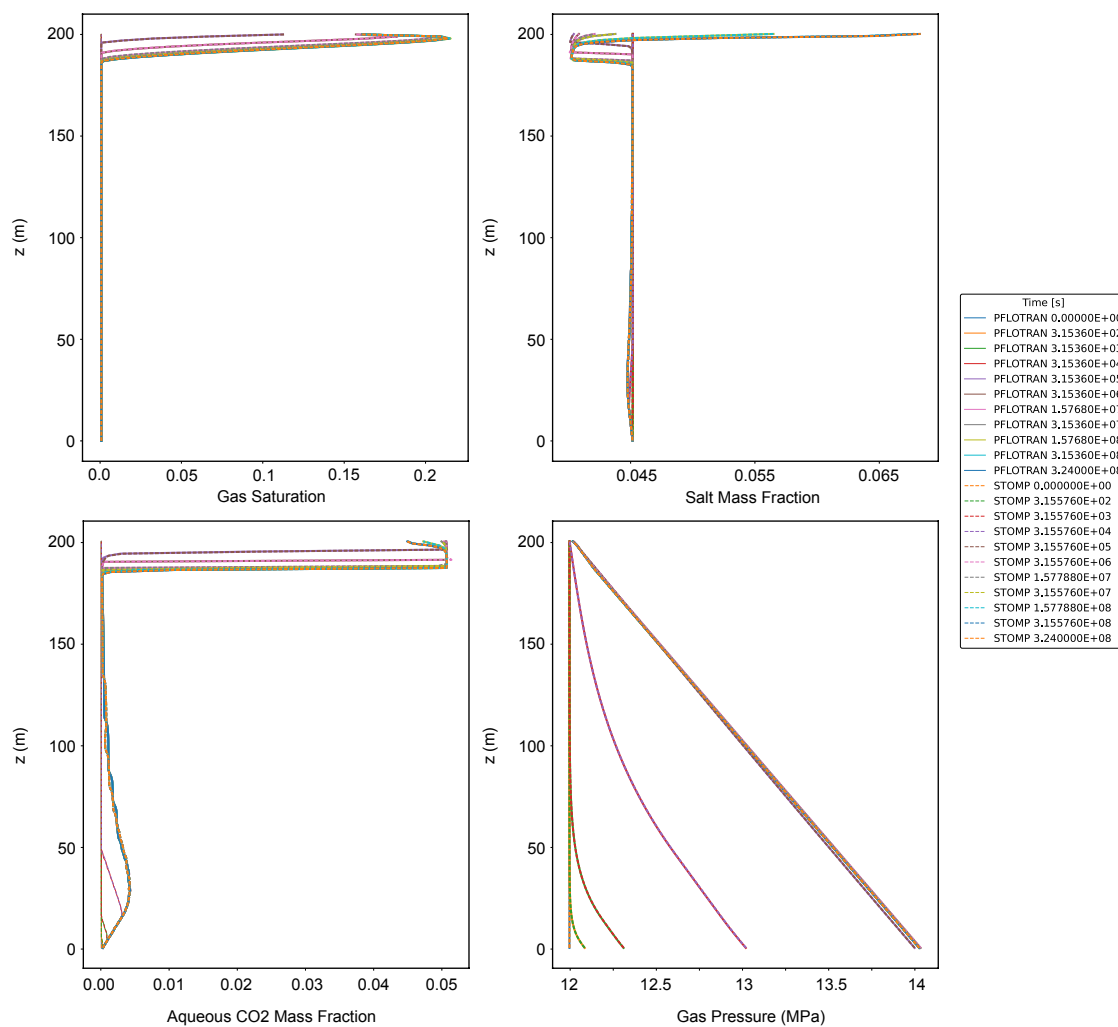


Figure A6. Column CO₂ Well Injection



Author contributions. MN: software development, model conceptualization, formal analysis, methodology, writing; KM: model conceptualization, writing; GH: software development, review, and editing; XH: model conceptualization, writing; PL: model conceptualization, development, and writing

985 *Competing interests.* The authors declare no competing interests.

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