

NUMERICAL INVESTIGATION OF CARBON DIOXIDE SEQUESTRATION IN GEOLOGIC MEDIA USING THE MASSIVELY PARALLEL COMPUTER CODE PFLOTRAN

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ABSTRACT

CO₂ sequestration (capture, separation, and long term storage) in various geologic media (such as depleted oil reservoirs, saline aquifers, and oceanic sediments) is being considered as a possible solution to reduce green house gas emissions. In this study we utilize the PFLOTRAN simulator to investigate geologic sequestration of CO₂. PFLOTRAN is a massively parallel 3-D reservoir simulator for modeling subsurface multiphase (CO₂, H₂O), multicomponent reactive flow and transport based on continuum scale mass and energy conservation equations. The mass and energy equations are sequentially coupled to reactive transport equations describing multi-component chemical reactions within the formation including aqueous speciation, and precipitation and dissolution of minerals including CO₂-bearing phases to describe aqueous and mineral CO₂ sequestration. The effect of the injected CO₂ on pH, CO₂ concentration within the aqueous phase, mineral stability, and other factors can be evaluated with this model. Parallelization is carried out using the PETSc parallel library package based on MPI providing a high parallel efficiency and allowing simulations with several tens of millions of degrees of freedom to be carried out ideal for large-scale field applications involving multi-component chemistry. In this work, our main focus is on the investigation of long term storage and possible leakage processes of CO₂, their sensitivity to reservoir and fluid properties, such as permeability and capillary pressure, diffusion coefficients, component solubility, etc. Important issues include mobility of a supercritical CO₂ plume in a heterogeneous porous medium, gravity induced instabilities during CO₂ plume buoyancy, mineral reaction induced permeability change and consumption or production of CO₂. These investigations will help provide preliminary criteria for site selection and develop methods for prevention of leakage.

1. INTRODUCTION

To mitigate the continuous increase in the atmospheric concentration of CO₂, geologic disposal of CO₂ has been suggested as an attractive alternative. Three storage mechanisms can be identified for subsurface geologic sequestration of CO₂: (*i*) as a separate gas phase or supercritical fluid (phase trapping); (*ii*) dissolved in groundwater (solubility trapping); and (*iii*) precipitated as secondary minerals such as calcite, magnesite, dawsonite, etc. (mineral trapping). To investigate the effectiveness of these different sequestration mechanisms, numerical modeling is essential for gaining an understanding of the fate of CO₂ injected in subsurface geologic formations over time spans of tens of thousands of years. To capture these processes the parallel computer model PFLOTRAN is introduced which couples multiphase, multicomponent reactive flow and transport.

The computational effort necessary to carry out such an investigation for a realistic 3D field site is enormous. Length scales involved range from the size of the geologic formation itself, on the order of kilometers, to much smaller length scales characteristic of fingering phenomena on the order of meters or less to chemical interactions that may be smaller than centimeters. For example, to discretize a domain $1 \text{ km} \times 1 \text{ km} \times 500 \text{ m}$ with $100 \times 100 \times 100 = 10^6$ nodes leads to a typical grid block size of $10 \text{ m} \times 10 \text{ m} \times 5 \text{ m}$, or roughly the size of a small conference room. For a grid block of this size, features that require smaller scales for their resolution such as fingering, and chemical interactions may be lost. Not accounting for these processes may give erroneous predictions for the rate of sequestration of the CO_2 plume over time. Incorporating chemical processes may require anywhere from 5–15 additional degrees of freedom per node, depending on the sophistication of the simulation and what processes are deemed important.

Obtaining solutions to these large systems of equations calls for a massively parallel implementation to reduce both computation time and memory requirements. For example, assuming ideal speedup running a problem with ten million nodes on 500 processors is roughly equivalent to running a problem with 20,000 nodes on a single processor workstation—a relatively small sized problem. With present day computational facilities, a single processor may have 4GB or more of RAM, which is more than adequate to solve millions of equations using fully implicit Newton-Krylov techniques employing domain decomposition. This approach is described in more detail in what follows for the computer code PFLOTRAN (Lu and Lichtner, 2005; Lu et al., 2005, Mills et al., 2005). This code solves equations for multiphase-multicomponent reactive flow and transport for nonisothermal, variably saturated porous media for implementation either on a single workstation or massively parallel computing architectures.

It is essential to incorporate accurate estimates of the density of CO_2 - H_2O mixtures for an accurate simulation of the behavior of the dissolved CO_2 plume. Model calculations are sensitive to constitutive relations including mixture properties, relative permeability, and Henry coefficients for which data is still lacking. A key issue in evaluating geologic sequestration of CO_2 is the potential for leakage through, for example, abandoned oil wells and faults. Recently, Pruess (2004) carried out three phase simulations involving liquid and gaseous CO_2 and an aqueous phase to evaluate the escape of CO_2 to the ground surface. CO_2 sequestration in abandoned oil fields will also require including oil as a separate fluid phase.

1.1. Mass and Energy Conservation Equations: PFLOW & PTRAN. PFLOTRAN solves a coupled system of mass and energy conservation equations for the two-phase system consisting of supercritical CO_2 and H_2O . The code consists of two sequentially coupled routines PFLOW and PTRAN, which may also be run separately in standalone mode. Briefly the equations solved by PFLOW for mass and energy conservation can be summarized as:

$$\frac{\partial}{\partial t} [\phi(s_l \rho_l X_w^l + s_g \rho_g X_w^g)] + \nabla \cdot [\mathbf{q}_l \rho_l X_w^l + \mathbf{q}_g \rho_g X_w^g - \phi(s_l D_l \rho_l \nabla X_w^l + s_g D_g \rho_g \nabla X_w^g)] = Q_w, \quad (1a)$$

$$\frac{\partial}{\partial t} [\phi(s_l \rho_l X_c^l + s_g \rho_g X_c^g)] + \nabla \cdot [\mathbf{q}_l \rho_l X_c^l + \mathbf{q}_g \rho_g X_c^g - \phi(s_l D_l \rho_l \nabla X_c^l + s_g D_g \rho_g \nabla X_c^g)] = Q_c, \quad (1b)$$

$$\frac{\partial}{\partial t} [\phi(s_l \rho_l U_l + s_g \rho_g U_g) + (1 - \phi) \rho_r c_r T] + \nabla \cdot (\mathbf{q}_l \rho_l H_l + \mathbf{q}_g \rho_g H_g - \kappa \nabla T) = Q_e. \quad (1c)$$

In these equations, phases l and g refer to liquid water and supercritical CO₂, respectively, species are designated by $w = \text{H}_2\text{O}$, $c = \text{CO}_2$, ϕ denotes porosity of the geologic formation, $s_l = 1 - s_g$ refer to liquid and gas saturation; X_i^π , ($\pi = l, g$), denotes the mole fraction of species $i = \text{CO}_2, \text{H}_2\text{O}$; ρ_π, H_π, U_π refer to the molar density, enthalpy, and internal energy of each fluid phase, respectively; \mathbf{q}_π denotes the Darcy flow rate defined by

$$\mathbf{q}_\pi = -\frac{k k_\pi}{\mu_\pi} \nabla (p_\pi - W_\pi \rho_\pi g z), \quad (2)$$

where k refers to the water saturated permeability, k_π denotes the relative permeability, μ_π denotes the fluid viscosity, W_π denotes the formula weight, and g denotes the acceleration of gravity. The source/sink terms Q_w, Q_c and Q_e , describe injection and extraction at wells and provide coupling terms to the multi-species transport equations resulting from reaction with solids. This latter aspect is discussed in more detail below.

Chemical reactions included in PTRAN involve aqueous species and minerals which can be written in the general form

$$\sum_j \nu_{ji} \mathcal{A}_j \rightleftharpoons \mathcal{A}_i, \quad (3)$$

and

$$\sum_j \nu_{jm} \mathcal{A}_j \rightleftharpoons \mathcal{M}_m, \quad (4)$$

respectively, where the set of species $\{\mathcal{A}_j\}$ refer to a set of primary or basis species, species \mathcal{A}_i denotes an aqueous complex referred to as a secondary species, and \mathcal{M}_m refers to a mineral. The corresponding thermodynamic equilibrium constants K_i, K_m , and reaction stoichiometric coefficients ν_{ji}, ν_{jm} are derived from an extensive database for aqueous species, gases, and minerals. Partitioning CO₂ between H₂O and supercritical CO₂ is accomplished with the reaction



where the subscript (g) refers to the supercritical CO₂ phase and (aq) to the aqueous phase.

The multiphase, multicomponent reactive transport equations solved by PTRAN have the form

$$\frac{\partial}{\partial t} [\phi (s_l \Psi_j^l + s_g \Psi_j^g)] + \nabla \cdot (\Omega_j^l + \Omega_j^g) = -\sum_m \nu_{jm} I_m, \quad (6)$$

for the j th primary species, and

$$\frac{\partial \phi_m}{\partial t} = \bar{V}_m I_m, \quad (7)$$

for the m th mineral, where $\Psi_j^{l,g}, \Omega_j^{l,g}$ denote the total concentration and flux, defined by the expressions ($\pi = l, g$),

$$\Psi_j^\pi = \delta_{\pi l} C_j^\pi + \sum_i \nu_{ji} C_i^\pi, \quad (8)$$

and

$$\Omega_j^\pi = (-\tau \phi s_\pi D_\pi \nabla + \mathbf{q}_\pi) \Psi_j^\pi, \quad (9)$$

where C_j^π denotes the solute concentration in phase π , C_i^π denotes the concentration of the i th secondary species related to the concentration of primary species through the mass action equations

$$C_i^\pi = (\gamma_i^\pi)^{-1} K_i^\pi \prod_j (\gamma_j^\pi C_j^\pi)^{\nu_{ji}^\pi}, \quad (10)$$

where γ_j^π denotes the activity coefficient, K_i^π the equilibrium constant for reaction (3). The mineral concentration is represented by the volume fraction ϕ_m with molar volume \bar{V}_m . The kinetic reaction rate I_m for the m th mineral is assumed to have the form

$$I_m = -k_m A_m (1 - K_m Q_m) \Phi(\phi_m), \quad (11)$$

based on transition state theory, where k_m denotes the kinetic rate constant, K_m the equilibrium constant for reaction (4), A_m the mineral specific surface area, and Q_m the ion activity product defined by

$$Q_m = \prod_j (\gamma_j^\pi C_j^\pi)^{\nu_{jm}^\pi}. \quad (12)$$

The factor $\Phi(\phi_m)$ is unity if $\phi_m > 0$ or $K_m Q_m > 1$, and zero otherwise, where ϕ_m denotes the mineral volume fraction. The sign of the rate is positive for precipitation and negative for dissolution and vanishes at equilibrium when $K_m Q_m = 1$.

1.2. Structure of PFLOTRAN. PFLOTRAN consists of two separate modules PFLOW and PTRAN that can be run either in standalone or coupled modes. PFLOW solves multiphase flow equations and PTRAN solves multicomponent reactive transport equations. In coupled mode, flow velocities, saturation, pressure and temperature fields computed from PFLOW are fed into PTRAN. For transient problems, sequential coupling allows changes in porosity and permeability due to chemical reactions to alter the flow field.

Both codes employ a modular design and use Fortran 90 features to provide some degree of object orientation. Fortran 90 modules reduce unnecessary sharing of program variables and procedures. PFLOW uses modules and derived types to encapsulate data and the methods that operate on them. A PFLOW driver program loads `pflow_grid_module`, which provides a constructor function `pflowGrid_new` that returns a `pflowGrid` object. That object contains all data about the state of the variables on the flow grid, but the driver does not access those directly. Instead, method subroutines provided by `pflow_grid_module` are used, for example `pflowGrid_step` which advances the flow simulation one time step.

The Jacobin matrix is evaluated numerically using a finite difference method. This approach gives PFLOTRAN great flexibility in applications to various systems, with only changes to the EoS (equation of state) module needed. The residual and Jacobian for PFLOW and PTRAN are calculated in terms of primary and secondary variables, as shown in Figure 1. At phase changes the choice of primary variables used is listed in Table 1.

TABLE 1. Primary variable assignment used in PFLOTRAN for the system $\text{H}_2\text{O}-\text{CO}_2$.

| Phase Condition | Primary Variables | | |
|-----------------------------|-------------------|-----|------------------------|
| Supercritical CO_2 | p | T | $X_{sc}^{\text{CO}_2}$ |
| Aqueous | p | T | $X_w^{\text{CO}_2}$ |
| Two Phase | p | T | S_{CO_2} |

Parallelism is achieved using a domain-decomposition approach. Each processor is assigned a subdomain of the system and a parallel solve of the system is implemented over all processors. Message passing is required at the boundary nodes to adjacent processors to compute flux terms.

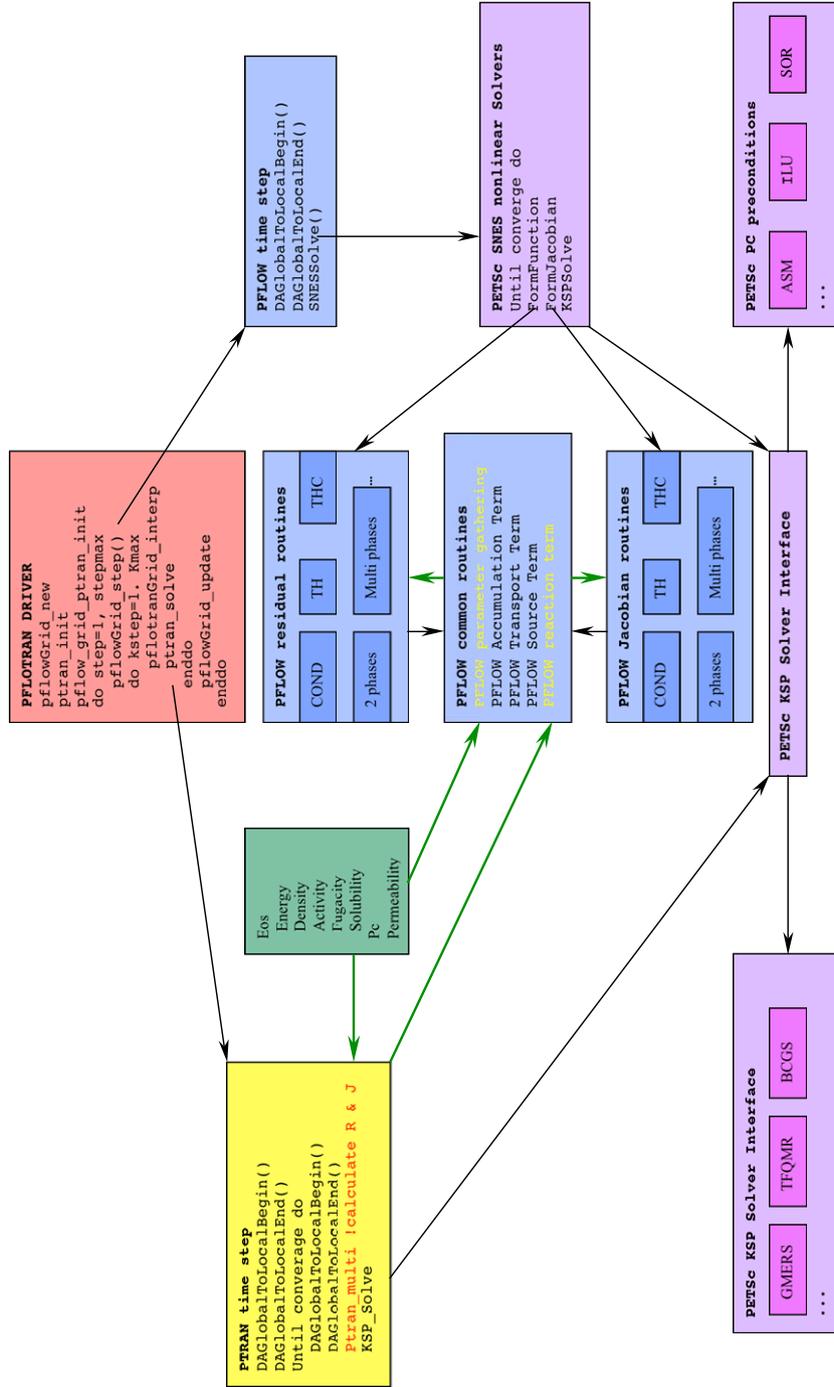


FIGURE 1. Structure of PFLOTRAN.

1.3. Performance and Scalability. PFLOWTRAN been designed from scratch with parallel scalability in mind, and it displays excellent scaling characteristics on modern supercomputers. The figure at right shows the performance of PFLOW running a single phase thermohydrologic bench mark problem on a $256 \times 64 \times 256$ grid with three degrees of freedom per node (approximately 12.6 million degrees of freedom total). The bench mark was run on both the MPP2 cluster at PNNL/EMSL, a cluster of 1960 1.5 GHz Itanium 2 processors with Quadrics QsNe tII interconnect, and Jaguar, the 5200 Opteron processor Cray XT3 at ORNL/NCCS. PFLOW scales quite well on both machines, bottoming out at around 1024 processors on MPP2, and scaling exceptionally well on Jaguar, displaying linear speedup all the way up to 2048 processors, and still displaying modest speedup when going from there to 4096 processors.

PTRAN scales similarly, which is not surprising because its computational structure is nearly identical to that of PFLOW. The figure shows the performance of PTRAN on MPP2 running a bench mark problem on $256 \times 64 \times 256$ grid with four degrees of freedom per node.

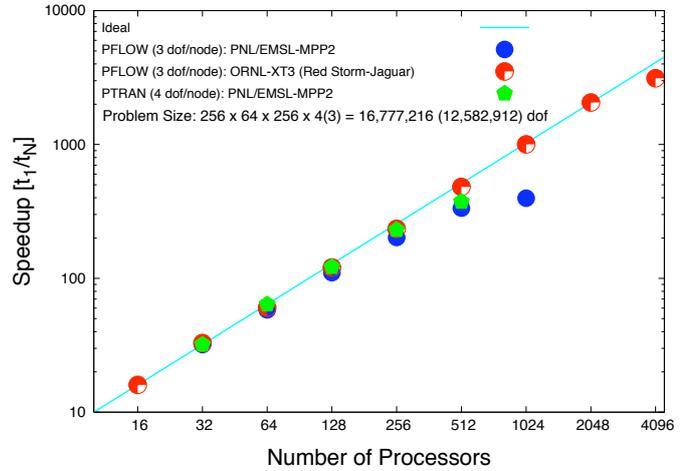


FIGURE 2. Speedup curves for PFLOW and PTRAN.

2. APPLICATION

Density-driven convection can cause quite complex flow and concentration patterns. Supercritical CO_2 is injected for 10 years at a rate of 10^{-4} kg/s and at a depth of 35 meters from the top of the domain. The simulation is carried out for 8,000 years. A cap rock 10 m thick with low permeability (10^{-18} m²) and porosity (0.05) was emplaced at depth of 10–20 m. The reservoir permeability used is 10^{-15} m² and porosity 0.15. A snapshot of the dissolved CO_2 concentration calculated at 2750 years is shown in Figure 3. The corresponding supercritical CO_2 saturation profile is shown in Figure 4. The supercritical CO_2 ponds at the base of the cap rock. A residual supercritical CO_2 phase remains below the cap rock left behind during upward migration. Included in the calculation is diffusion which leads to damping of induced instabilities. The dominant plume in the center of the figure is formed by downward gravity flow due to the increase in density caused by CO_2 dissolving into the aqueous solution. Convection cells form symmetrically around central plume bringing in CO_2 at the top. The distribution of CO_2 is shown in Figure 5 as a function of time. The supercritical phase disappears after approximately 7,000 years. As time increases the dissolved CO_2 plume retreats towards the center of the plume. In this simulation the dissolved CO_2 plume remains connected.

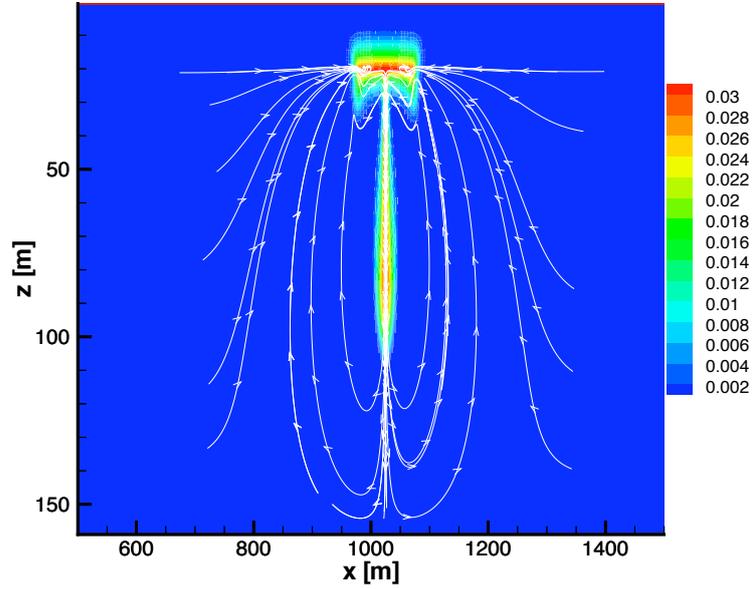


FIGURE 3. Dissolved CO₂ distribution showing streamlines in a 2D domain at 2750 years.

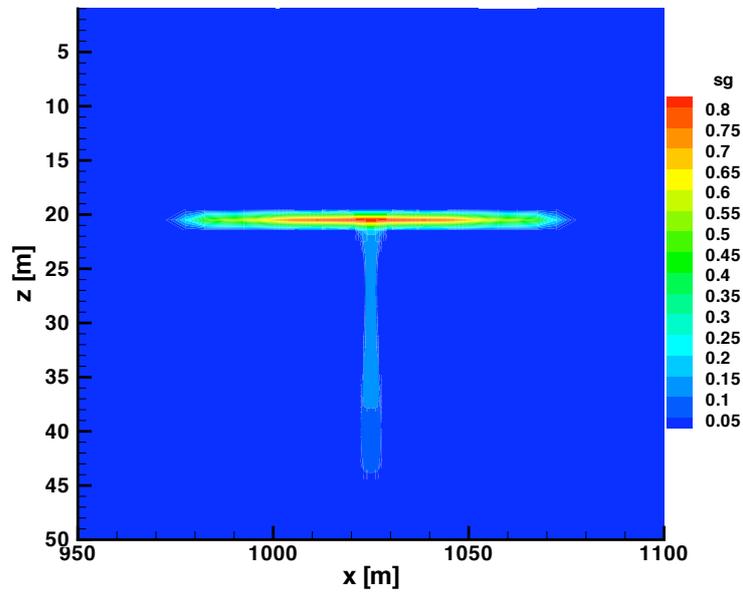


FIGURE 4. Supercritical CO₂ profile at 2750 years.

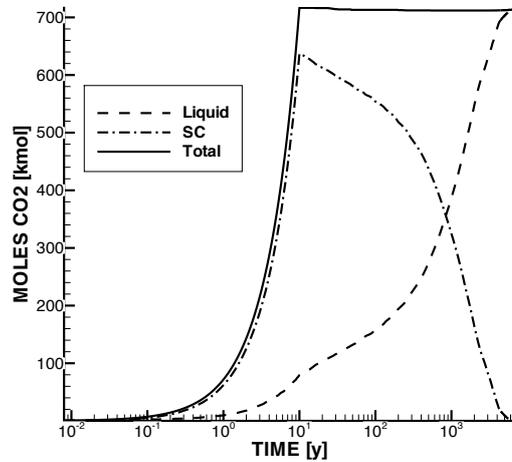


FIGURE 5. Distribution of CO_2 in supercritical and liquid phases plotted as a function of time.

3. CONCLUSION

The PETSc library for parallel computing was successfully implemented in PFLOTRAN, providing speedups of over 3000 times for 4096 processors (Jaguar at ORNL) for a 3D problem with $256 \times 64 \times 256$ nodes, exhibiting excellent scalability. The code is easily extended to include additional phases and components such as oil.

According to the simulation presented, there is limited escape of CO_2 through the cap rock with most of the CO_2 sinking to the bottom of the domain. Limited lateral spreading occurred due to the small amount of injected CO_2 .

These calculations can be easily extended to 3D on massively parallel computing architectures and include sequentially coupled reactive flow and transport processes using the existing code.

ACKNOWLEDGMENTS

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