High resolution numerical investigation on the effect of convective instability on long term CO$_2$ storage in saline aquifers

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Abstract. CO$_2$ sequestration (capture, separation, and long term storage) in various geologic media including depleted oil reservoirs, saline aquifers, and oceanic sediments is being considered as a possible solution to reduce green house gas emissions. Dissolution of supercritical CO$_2$ in formation brines is considered an important storage mechanism to prevent possible leakage. Accurate prediction of the plume dissolution rate and migration is essential. Analytical analysis and numerical experiments have demonstrated that convective instability (Rayleigh instability) has a crucial effect on the dissolution behavior and subsequent mineralization reactions. Global stability analysis indicates that a certain grid resolution is needed to capture the features of density-driven fingering phenomena. For 3-D field scale simulations, high resolution leads to large numbers of grid nodes, unfeasible for a single workstation. In this study, we investigate the effects of convective instability on geologic sequestration of CO$_2$ by taking advantage of parallel computing using the code PFLOTRAN, a massively parallel 3-D reservoir simulator for modeling subsurface multiphase, multicomponent reactive flow and transport based on continuum scale mass and energy conservation equations. The onset, development and long-term fate of a supercritical CO$_2$ plume will be resolved with high resolution numerical simulations to investigate the rate of plume dissolution caused by fingering phenomena.
1. Introduction

Sequestration of CO$_2$ in subsurface geologic formations containing saline aquifers could provide permanent storage for a major greenhouse gas and thereby help to mitigate global climate change. Saline aquifers have an estimated world-wide storage capacity for CO$_2$ of 320-10,000 Gt CO$_2$ [1]. A typical scenario is injection into a relatively deep saline aquifer above the critical point where CO$_2$ exists as a supercritical fluid ($T_{\text{crit}} = 31.04^\circ\text{C}$, $p_{\text{crit}} = 73.82$ bar). As supercritical CO$_2$ is injected into the aquifer it becomes buoyant because of its lower density compared to the brine and begins to rise. Eventually it may become trapped by a low permeability zone or caprock and spread laterally as it gradually dissolves into the surrounding brine. As the CO$_2$ dissolves into the brine, however, the brine becomes heavier and begins to sink resulting in density-driven convection which can lead to instabilities resulting in the formation of CO$_2$-concentrated brine fingers protruding downward. This convective mixing can result in much more rapid dissipation of the supercritical CO$_2$ plume compared to diffusive processes alone. Important to this scenario is the areal extent of the plume as this can lead to accidental release of CO$_2$ to the surface through abandoned bore holes and faults. The areal extent is controlled by competition between the rate of spreading of the plume and the rate at which it dissolves into the brine. Thus it is important to understand the properties of the aquifer which determine the size and onset of fingering during the convective mixing process.

Recently, Ennis-King and Paterson [3] and Xu et al. [7] have presented stability analyses of convective mixing of CO$_2$ in deep saline aquifers. The study by Xu et al. [7] applies both linear stability analysis and nonlinear global stability analysis to investigate the onset of convective mixing during CO$_2$ sequestration in isotropic and anisotropic porous media. The two analyses provide complementary approaches: linear stability analysis is based on infinitesimal perturbations giving sufficient conditions for the threshold for instability; whereas global stability analysis based on finite perturbations provides a sufficient condition for stability of the CO$_2$ plume. While stability analysis can provide rough guidance for determining the conditions of instability and an estimate of the grid size needed to resolve fingering, it leaves a number of issues unanswered. For example, a wide gap exists between the prediction of the onset of instability and stability as determined by linear and nonlinear analysis. The analysis applies only to homogeneous media and not to heterogeneous media which is essential for representing natural geologic systems. And finally a discrepancy was noted by Xu et al. [7] between their study and an earlier study by Epherre [4] on the effect of increasing horizontal permeability for fixed vertical permeability. Xu et al. found that the critical time and wavelength decrease resulting in more unstable conditions, just opposite to the results found by Epherre. One approach to resolve these issues is to perform numerical experiments employing high-resolution grids. The purpose of this work is to provide preliminary results obtained from high-resolution simulations carried out on massively parallel computers and compare these results with the predictions of stability analysis.

As a caveat, it should be noted that for media with sufficiently high permeability, even parallel computing with present day architectures will be insufficient to resolve finger widths on orders of centimeters or less as predicted by stability analysis in large-scale domains of kilometers. Although beyond the scope of this contribution, it is clear that for such cases upscaling methods will be needed to properly account for the role of convective mixing on dissipation of a supercritical CO$_2$ plume.

2. Massively parallel multiphase code PFLOTRAN

To investigate the role of convective mixing numerically, the massively parallel computer code PFLOTRAN is used. In this study, the multicomponent reactive transport module PTRAN
is sequentially coupled to the flow module PFLOW to describe injection of supercritical CO$_2$ into an arkosic sandstone containing calcite cement involving coupled reactive flow and transport. PFLOTRAN provides for phases CO$_2$ and brine for nonisothermal conditions. Phase transformations are described using a variable switching approach as the thermodynamic state of a grid block changes from brine, to two phases CO$_2$–brine, to pure CO$_2$. The chemical system involves 10 primary species \{Al$^{3+}$, Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$, H$^+$, Cl$^-$, SiO$_2$(aq), CO$_2$(aq), H$_2$O\}, and primary minerals quartz (55%), K-feldspar (20%), and calcite (10%), where quantities in parentheses denote volume fractions. Secondary precipitates include dawsonite, calcite, and dolomite.

In this work the correlation developed by Garcia [5] is used which gives a greater mixture density in agreement with experiment [5]. Finally, a Henry’s law relation from [2] is used to compute the equilibrium concentration of CO$_2$ dissolved in H$_2$O of the form

$$X_i^\beta = K_{i,\beta\alpha}X_i^{\alpha},$$

with Henry constant $K_{i,\beta\alpha}$, with $i = \text{CO}_2$, $\alpha = \text{CO}_2$(aq), and $\beta = \text{H}_2\text{O}$. 

The mass and energy conservation equations solved by the massively parallel, multiphase, code PFLOTRAN can be written in the form

$$\frac{\partial}{\partial t} \left[ \varphi \sum_\alpha (\rho_\alpha s_\alpha X_i^\alpha) \right] + \nabla \cdot \sum_\alpha \left( \rho_\alpha X_i^\alpha q_\alpha - \varphi s_\alpha \tau_\alpha D_\alpha \rho_\alpha \nabla X_i^\alpha \right) = S_i, \quad (1)$$

and

$$\frac{\partial}{\partial t} \left[ \varphi \sum_\alpha (\rho_\alpha s_\alpha U_\alpha) + (1 - \varphi) \rho_c C_{p,r} T \right] + \nabla \cdot \left[ \sum_\alpha (q_\alpha \rho_\alpha H_\alpha) - \lambda \nabla T \right] = Q, \quad (2)$$

where $\varphi$ denotes porosity, and $\rho_\alpha$, $s_\alpha$, $D_\alpha$, $\tau_\alpha$, $U_\alpha$, $H_\alpha$ refer to the density, saturation, diffusion coefficient, tortuosity, internal energy, and enthalpy of fluid phase $\alpha$, respectively. The quantities $X_i^\alpha$ denote the mole fraction of component $i$ in phase $\alpha$. The quantities $C_{p,r}$ and $\lambda$ denote the rock heat capacity and conductivity, respectively. The summation is carried out over all fluid phases $\alpha$ present in the system. The system is assumed locally to be in thermodynamic equilibrium with temperature $T(r, t)$ at position $r$ and time $t$. The quantity $S_i$ denotes a source/sink term for the $i$th primary species describing reaction with minerals given by

$$S_i = - \sum_m \nu_{im} I_m, \quad (3)$$

with stoichiometric reaction coefficients $\nu_{im}$ and kinetic rate $I_m$ for the $m$th mineral with the form adopted from transition state theory [6], taken as positive for precipitation and negative for dissolution. The quantity $Q$ denotes an energy source/sink term. The flow rate $q_\alpha$ of fluid phase $\alpha$ is given by the extended Darcy’s law

$$q_\alpha = - \frac{kk_\alpha}{\mu_\alpha} (\nabla p_\alpha - \rho_\alpha g z), \quad (4)$$

with saturated permeability $k$, relative permeability $k_\alpha$, fluid viscosity $\mu_\alpha$ and pressure $p_\alpha$ of phase $\alpha$. The difference of pressure between two phases $p_\alpha$ and $p_\beta$ satisfies the relation

$$p_\alpha = p_\beta - p_{c,\alpha\beta}, \quad (5)$$

where $p_{c,\alpha\beta}$ refers to the capillary pressure. Both $p_c$ and $k_\alpha$ are functions of saturation $s_\alpha$ evaluated through capillary correlation formulas such as the van Genuchten or Brooks-Corey relations.

The density $\rho_\alpha$ of fluid phase $\alpha$ appearing in Eqs. (1) and (2) refers to the density of the fluid mixture. Use of ideal mixing for the system H$_2$O–CO$_2$ leads to a lower density for the mixture. In this work the correlation developed by Garcia [5] is used which gives a greater mixture density in agreement with experiment [5]. Finally, a Henry’s law relation from [2] is used to compute the equilibrium concentration of CO$_2$ dissolved in H$_2$O of the form

$$X_i^\beta = K_{i,\beta\alpha}X_i^{\alpha},$$

with Henry constant $K_{i,\beta\alpha}$, with $i = \text{CO}_2$, $\alpha = \text{CO}_2$(aq), and $\beta = \text{H}_2\text{O}$. 

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3. Convective Mixing

3.1. Stability Analysis

Theoretical linear stability analysis predicts the critical wavelength and time for instability ranging from millimeters to meters and seconds to hundreds of years depending on a number of factors. These include the permeability and porosity of the rock formation $k$ and $\phi$, the fluid viscosity $\mu$, effective diffusivity $D$, the acceleration of gravity $g$, and the difference in fluid densities $\Delta \rho$ between the CO$_2$-rich solution and the formation water according to the relation [7]

$$\lambda_c = C_{\lambda} \frac{\mu \phi D}{kg \Delta \rho},$$

for the critical wavelength $\lambda_c$, where $C_{\lambda}$ is a constant approximately equal to 96.23. The critical time $\tau_c$ for the onset of instability is found to be

$$\tau_c = C_{\tau} \left( \frac{\mu \phi}{kg \Delta \rho} \right)^2 D,$$

with $C_{\tau} = 75.19$. The critical wavelength and time are related by

$$\lambda_c = \frac{C_{\lambda}}{\sqrt{C_{\tau}}} \sqrt{D \tau_c}.$$  \hspace{1cm} (9)

Noteworthy, is that the critical wavelength is independent of the aquifer thickness. A plot of Eqns.(7) and (8) is shown in Figure 1 as a function of permeability with fixed values for porosity $\phi = 0.2$, viscosity $\mu = 5 \times 10^{-4}$ Pa·s, effective diffusivity $D = 10^{-9}$ m$^2$/s, acceleration of gravity $g = 9.8$ m/s$^2$, and density difference $\Delta \rho = 10$ kg/m$^3$.

3.2. PFLOTRAN Simulations

Two 3D simulations are presented involving a coarse and fine grid. In both simulations a isotropic permeability of $2 \times 10^{-12}$ m$^2$ is used with a porosity of 15%. The nominal temperature and pressure is 50°C and 200 bars. The computational domain is 250 m thick and $7 \times 7$ km in lateral extent. CO$_2$ is injected at a depth of 50 m below the top of the domain. No flow boundary conditions
are imposed at the top and bottom and front and back of the domain with constant pressure at the left and right sides. An injection rate of 1 Mt/y for 20 years was used in the simulations. This corresponds to roughly 75% of the CO$_2$ produced by a 1000 MW gas-fired power plant in 20 years. The presentation of results for chemical interaction is beyond the scope of this contribution and will be presented elsewhere. Shown in Figure 2 is the dissolved CO$_2$ mole fraction corresponding to an elapsed time of 300 years calculated on a coarse-grid with $40 \times 40 \times 25$ nodes. The grid spacing is 175 m horizontally and 10 m vertically. In Figure 3 the grid is refined in the $x$ and $y$ directions by a factor 4 with the same grid spacing in the $z$ direction. For both simulations the finger width is equal to the horizontal grid spacing indicating that convergence is not obtained. Indeed, for the parameters used in the simulations, according to stability analysis the finger width should be on the order of $\lambda_c = 0.05$ m and $\tau_c = 6.2 \times 10^{-4}$ y. This is much too small to resolve even with the fastest computers using a uniform grid. In Figure 4 the total mols of CO$_2$ is plotted as a function of time for both the coarse and fine grids showing the amount of CO$_2$ dissolved in the brine and as supercritical CO$_2$. The supercritical phase disappears at approximately 400 years for the fine grid compared to 800 years for the coarse grid. A slight increase in total CO$_2$ occurs due to the dissolution of calcite cement resulting from acid produced by injection of supercritical CO$_2$.

4. Conclusion

The rate of dissolution of CO$_2$ into the formation brine of a saline aquifer in which supercritical CO$_2$ is injected was found to be highly dependent on grid resolution because of density-driven instabilities resulting in fingering of the dissolved CO$_2$. According to stability analysis, finger width can range over many orders of magnitude and for highly permeable regions may be too small to resolve even with massively parallel computing architectures. To some extent the use of adaptive grid refinement can reduce the number of nodes required, but under extreme conditions upscaling will required to reformulate the problem. Numerical experiments utilizing massive parallel computing can provide the basis for formulating such upscaling relations. Future work will focus on incorporating salinity effects which are expected to reduce the solubility of CO$_2$ in the formation brine and thereby increase the critical wavelength for instability and prolong the existence of the supercritical CO$_2$ phase.

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