High Performance Computations of Subsurface Reactive Transport Processes at the Pore Scale

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Abstract. Field applications such as carbon sequestration drive the geochemistry of porous media far from equilibrium in relatively short time scales. In these short time frames, feedback processes between flow and geochemical reactions (e.g., mineral dissolution-precipitation) that take place at the pore scale are key to understanding the discrepancy between lab-derived reaction rates and the continuum scale reaction rates that are typically used in reservoir scale models. In the DOE Energy Frontier Research Center for Nanoscale Control of Geologic Carbon (NCGC), pore scale modeling is being used to gain insight into the scale dependence of parameters such as reactive surface area or reaction rates as they affect CO_2 sequestration, with an objective of upscaling these parameters to continuum scale models. Under the SciDAC-e program we have partnered with the NCGC EFRC to develop a new capability for direct numerical simulation of reactive transport processes associated with CO_2 sequestration at the pore scale. Building on high performance computations of microscale flows in complex geometries developed in the Chombo framework at LBL as part of the SciDAC APDEC project, we use operator splitting to couple a new flow and scalar transport solver in Chombo with the geochemical code CrunchFlow. The framework makes use of higher-order algorithms based on adaptive mesh refinement and finite volume methods. In current work we are focusing on experimental validation of flow and reactive transport in 3D packed bed systems. Here we discuss performance optimizations that enable high resolution calculations of flow and reactive transport in tightly packed capillary tubes using the new Chombo-CrunchFlow framework. We demonstrate resolution of less than 4 microns for problems involving calcite dissolution and precipitation.

1. Introduction

Geologic sequestration of CO_2 is considered one of the viable approaches to mitigating the climatic impact of greenhouse gas emissions [12, 6]. However, knowledge of the fate of CO_2 injected into deep subsurface aquifers, especially after long time (thousands of years), is still inadequate [2]. Geochemical transport modeling has served as a valuable predictive tool in evaluating these scenarios [7]. Traditionally, the consideration of flow and reactive transport in subsurface porous media has focused on treating the media as continuous domains with macroscopic parameters such as hydraulic conductivity, porosity, reactive area, dispersion coefficient and reaction rates. Flow is usually assumed to obey phenomenological laws, e.g., Darcy's law [13]. It has been long realized that these parameters are scale-dependent and mass transport limitations can introduce large deviations from volume-averaged processes [4, 5]. The pore-scale variation of species concentrations is also suspected to contribute to the "field-lab discrepancy" commonly observed between laboratory and field measurements [4]. Indeed, there has been growing interest in modeling reactive transport in the subsurface at the pore scale.

Pore scale modeling can be used to gain insight into the scale dependence of continuum macroscale parameters by first resolving physico-chemical processes that would otherwise not be modeled in an effective medium Darcy approach and then upscaling these results to the continuum scale. Popular approaches to pore scale modeling include pore network models (e.g., [4]) and the Lattice-Boltzmann method (e.g., [3]). Due to high performance computing, well-established numerical methods in computational fluid dynamics such as finite volume and finite difference methods have also become practical for direct numerical simulation of flow and

transport in the complex geometry of heterogeneous pore space. In this work, we present results of such a CFD method. We have developed a methodology to simulate subsurface flow and reactive transport at the pore scale by direct numerical simulation techniques based on advanced finite volume methods and adaptive mesh refinement. Specifically, we have combined the high performance simulation tools and algorithms for incompressible flow and conservative transport in the software framework, Chombo [11, 10], with the geochemical package, CrunchFlow [8].

2. Chombo-CrunchFlow Model

For governing equations we consider the 3D incompressible Navier-Stokes equations for incompressible flow plus the advection-diffusion-reaction equations for scalar species concentration

$$
\begin{aligned}
\mathbf{u}_t + (\mathbf{u} \cdot \nabla)\,\mathbf{u} + \nabla p &= \nu \Delta \mathbf{u} \\
\nabla \mathbf{u} &= 0 \\
\frac{\partial c_k}{\partial t} + \nabla \cdot \mathbf{u} c_k &= \nabla \cdot D_k \nabla c_k + \dot{\omega}_k
\end{aligned}
\tag{1}
$$

where $\mathbf{u}$ is the fluid velocity, ∇p is the pressure gradient, c_k is the concentration of species k, ν is the kinematic viscosity, D_k is the diffusivity of species k in the fluid and $\dot{\omega}_k$ is the reaction rate of species k. The equations are solved by a predictor-corrector method based on a projection method [9, 1]. In our approach fluid-solid interfaces are represented as an embedded boundary on a Cartesian grid and discretized by a finite volume method. Details of the flow and conservative transport algorithm will appear in [10].

In order to incorporate the reaction rate term $\dot{\omega}_k$ in the equations, and, specifically, model reactive transport due to geochemistry, we couple the flow and conservative transport (advection-diffusion) solver in Chombo to the complex geochemical reaction network module of CrunchFlow using operator splitting. The conservative transport step advances the total component concentrations, c_k, subject only to the fluid CFL condition. These quantities are the sum of one component species concentration and several secondary species multiplied by the corresponding stoichiometric coefficient. They do not change due to equilibrium reactions. In the geochemical reactive transport step, the aqueous reactions are assumed to take place instantaneously, while mineral dissolution-precipitation are described kinetically. The reaction pathways are defined as inputs to CrunchFlow. The resulting geochemical reaction network is solved by Newton iteration. In the combined approach, the reaction is a "point-by-point" calculation that scales with the Chombo computations. Compared to a fully implicit approach, which solves the reaction network together with the conservative transport, operator splitting greatly reduces the size of the problem, making it much more efficient computationally.

3. Performance Optimizations

The Chombo CFD solver for complex geometry has been previously optimized for high performance computations in terms of both speed and memory footprint [11]. Those enhancements mainly included fast stencil operations using data pointers and integer offsets, as well as efficient relaxation schemes for elliptic and caching techniques for updating in place. For the current work we build off of the previous optimizations and discuss additional issues and optimization techniques in the Chombo framework pertaining to simulation in very complex geometries, especially packed bed systems with long aspect ratios.

We identified a performance bottleneck for flows in long, thin computational domains (cylinder aspect ratio > 10) with tightly packed materials. The multigrid coarsening process creates many irregular, or partially occupied, cells which can become multi-valued at the coarsest levels. The bottom solver, BiCGStab (bi-conjugate gradient stabilized), which is preconditioned
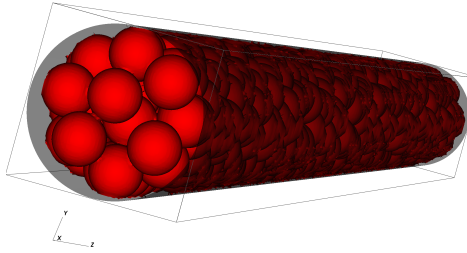
Figure 1. Capillary tube packed with spheres: a view of the geometry. The tube is 1 cm long, 250 μm in diameter and is packed with 900 spheres, radii $= 39.55$ μm, for porosity of 0.52488.

by multigrid and also calls the relaxation step, therefore constantly accesses multi-valued data stored in the irregular partition of the Chombo data holder, `EBCellFAB`. The large number of multi-valued cells along with the iterative nature of `BiCGStab` resulted in excessively large amounts of stack retrievals and high-order indirection access. A similar problem was first reported in [11] where integer offsets and pointers to the data were employed to enable fast stencil operations. We applied this stencilization to all remaining operations in the relaxation scheme which had not been previously optimized. We also re-configured the operations of `EBCellFAB` to take advantage of the vector storage format and to transform the high-order access to integer offsets. Profiling analysis revealed that the optimizations reduced approximately 90% of the time it took to compute without the optimizations.

4. Results

To demonstrate the ability of Chombo to handle very complex geometries, we simulate flow in a 1 cm long, 250 μm diameter capillary tube with a tight packing of 900 spheres, as shown in Figure 1. The spheres each have the same radius of 39.55 μm, and are randomly placed inside the capillary tube. The spheres are allowed to touch each other, resulting in a tight packing (porosity $= 0.52488$).

The test case is a calcite dissolution problem with 6 components and 10 species as in [5]. We model flow in a tube with a mean inlet velocity of 0.035 cm/sec. The solution pH is 5 and is undersaturated with respect to calcium. The packed spheres represent calcite grains. The kinetic calcite dissolution-precipitation reactions are (units of k in mol m^{-2}sec^{-1} at 25°C, reactive surface area is calculated from the geometry of the mineral-water interface):

$$
\begin{array}{rcll}
\mathrm{CaCO_3}(s) + \mathrm{H^+} & \rightleftharpoons & \mathrm{Ca^{2+}} + \mathrm{HCO_3^-} & k_1 = 0.89 \\
\mathrm{CaCO_3}(s) + \mathrm{H_2CO_3}* & \rightleftharpoons & \mathrm{Ca^{2+}} + 2\mathrm{HCO_3^-} & k_2 = 5.01 \times 10^{-4} \\
\mathrm{CaCO_3}(s) & \rightleftharpoons & \mathrm{Ca^{2+}} + \mathrm{CO_3^{2-}} & k_3 = 6.6 \times 10^{-7}
\end{array}
\tag{2}
$$
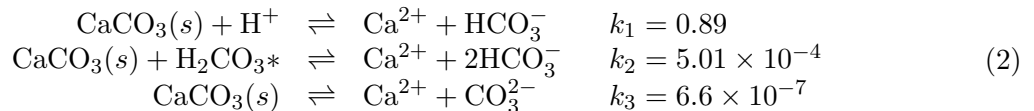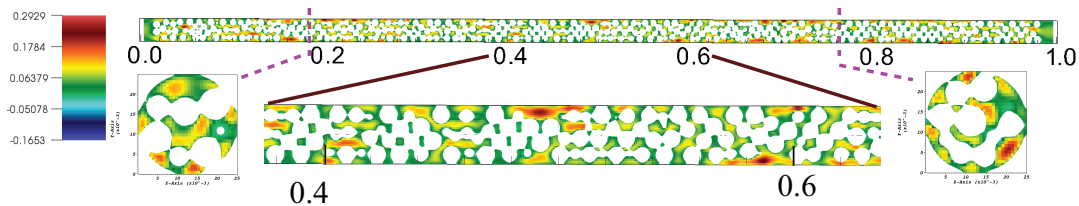
Figure 2 shows the x-z slice view of the x-velocity field. We observe higher velocities in the microchannels that form in relatively sparse regions. Velocities are slower near the spheres and in some areas may become negative immediately downwind of the spheres due to recirculation. The quick flow paths are frequently obstructed by downstream spheres due to the tight and random packing algorithm used. Figure 3 shows the total calcium concentration at steady-state. Inside the tube from the inlet at left, total calcium concentration increases as the calcite, which is dissolved upstream, is transported downstream. At about two-thirds the length of the tube, the total calcium concentration reaches equilibrium with the calcite spheres. We observe that the total calcium concentration is essentially an one-dimensional feature except for the short region near the inlet. Closer examination of the figure reveals that in the first one-third of the tube there are dissolution fingers that originate from the spheres. However, these

Figure 2. Calcite dissolution in a tightly packed capillary tube at steady-state: axial velocity (cm/sec). The upper figure shows the x-z slice of the tube at the center of the tube. The lower center figure shows a blow-up view of the segment from $x = 0.4$ to $x = 0.6$. Two slices (y-z plane) on the sides show a cross-sectional view of axial velocities at $x = 0.19$ and $x = 0.75$
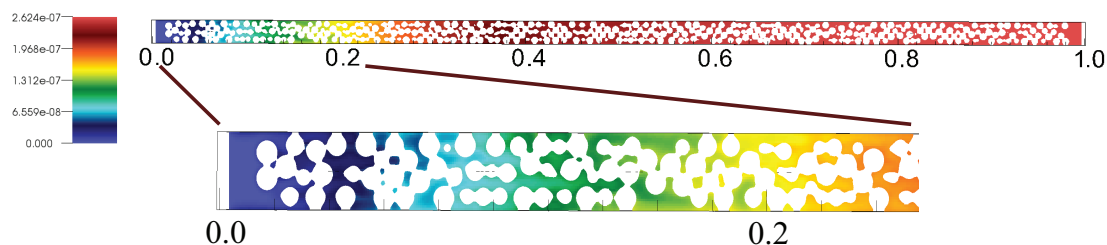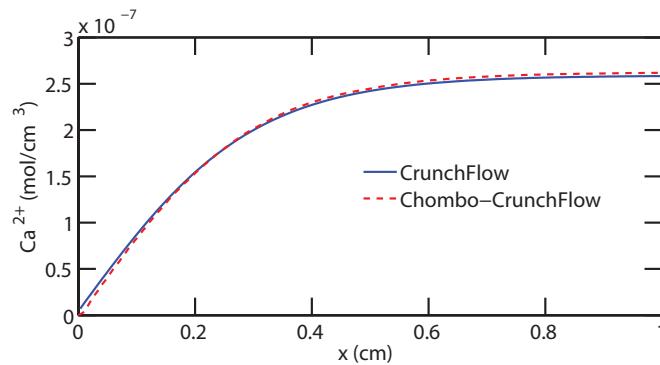

Figure 3. Calcite dissolution in a tightly packed capillary tube at steady-state: total calcium concentration (mol/cm^3). The upper figure is an x-z slice of the tube at the center of tube. The lower center figure is a blow-up view of the tube from $x = 0.0$ to $x = 0.2$. Concentration fingers are noticed in various locations in the tube.

fingers quickly disappear when they encounter downstream spheres, due to the enhanced mixing by the meandering flow paths, and possibly diffusion. In this scenario, the pore-scale model does not behave very differently from an one-dimensional macroscopic model. Figure 4 shows the close-agreement of the cross-sectionally averaged total calcium concentrations between the Chombo-CrunchFlow pore-scale model and CrunchFlow alone, which solves reactive transport on the contiuum-scale using the volume porosity and surface area calculated by the pore-scale model.

In regard to performance, the calcite dissolution problem is simulated on a Cartesian grid with 2560×64×64 cells using 512 processors on a Cray XT4. Mesh spacing is 3.9 μm. A fluid time step takes 20 seconds CPU time; a transport step (conservative + reactive) is 1/3 of fluid.

5. Conclusions

We have coupled the Chombo flow and scalar transport solver with the geochemical code CrunchFlow to simulate flow and reactive transport at the pore scale. This high performance simulation capability provides an alternative modeling methodology for very complex geometries, and therefore has the potential to offer new insight into emergent processes that occur at the pore scale in geologic carbon sequestration. The code has been optimized to run on massively parallel machines. We used the coupled model to simulate calcium carbonate dissolution in tightly packed capillary tubes with 4 μm resolution. We demonstrated that the model agrees well with the macroscopic model for this particular test case. The need of simulation of calcite dissolution in a high aspect ratio capillary tube is driven by the requirements of experiments

Figure 4. Calcite dissolution in a tightly packed capillary tube at steady-state. Comparison of cross-sectionally averaged calcium concentration between the pore-scale and macroscopic models.

designed to validate the pore scale model. The optimizations and the 4 micron resolution we achieved are significant because they will allow us to perform direct simulation from image data obtained at this resolution by computed x-ray tomography from validation experiments.

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