A PARALLEL SECOND-ORDER ADAPTIVE MESH ALGORITHM FOR REACTIVE FLOW IN GEOCHEMICAL SYSTEMS

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ABSTRACT

We present a second-order accurate adaptive algorithm for solving reactive transport flow in geochemical systems. A Strang-splitting approach is used to numerically decouple the transport component and the reaction component of the problem. The transport component is solved using a second-order accurate IMPES-like algorithm that exhibits excellent control of numerical dispersion. The numerical scheme for the reaction component uses reaction network details from the chemistry module of TOUGHREACT, COREREACT, and VODE, a high-order ODE integrator, to maintain second-order accuracy of the algorithm. The algorithm is implemented within an adaptive refinement framework that uses a nested hierarchy of logically rectangular grids with simultaneous refinement of the grids in both space and time. The integration algorithm on the grid hierarchy is a recursive procedure in which coarse grids are advanced in time, fine grids are advanced multiple steps to reach the same time as the coarse grids, and the data at different levels are then synchronized. Numerical examples are presented to demonstrate the algorithm's accuracy and convergence properties. We conclude with a simulation of a reactive salt dome problem.

INTRODUCTION

Accurate modeling of a reacting flow has many important ramifications in geologically important problems such as carbon sequestration and environmental remediation. The increasing role of simulation in the analysis and decision-making process places significant demands on the fidelity of the simulation codes. However, coupling between transport and reaction can be complex due to scale differences in both space and time, placing severe demands on computational methodology.

One of the challenges in simulation of reactive flow lies in the large number of chemical species in a geochemical system. In addition, the reaction rates can be disproportionably high compared to the flow rate, posing significant difficulties in devising an efficient numerical algorithm. In Steefel and MacQuarrie (1996), the number of species that needs to be tracked during transport is significantly reduced by assuming local equilibrium between aqueous species. Precipitation and dissolution are the only reactions with finite rates, which are usually slower than reaction rates between aqueous species. Even with this simplification however, small time steps may still be needed to integrate the reaction equations accurately, especially if the reaction rates are strongly nonlinear function of species' concentrations. Grid resolution requirements can also be steep since reactions occur at the pore scale. A fully implicit approach to simulating geochemical system can thus be computationally very demanding.

In this work, we develop a second-order accurate adaptive scheme for the accurate simulation of reactive flow. We describe the details of our method and how we make use of a reaction module of TOUGHREACT, COREREACT, in the next section. We then solve several geochemical systems based on our method to demonstrate its convergence properties and accuracy. We also compare our results to TOUGHREACT.

NUMERICAL SCHEME

The formulation of the chemical system we use follows Steefel and MacQuarrie (1996). Aqueous species are assumed to be in local equilibrium and only precipitation and dissolution reactions are finite-rate reactions. The species in a chemical system can be divided into primary and secondary species. This formulation allows the mass conservation equations to be written down in terms of the concentration of aggregated species c_i^t, defined as

$$c_i^t = c_i^p + \sum_{j=1}^{N_s} v_{ji} c_j^s, \quad i = 1, \dots, N_p \qquad (1.1)$$

where c_i^p and c_j^s are the concentration of the primary and secondary species, N_p and N_s are the number of primary and secondary species, and v_{ij} are the stoichiometric coefficients. We utilize databases in COREREACT in our code development efforts.

The operator-split formalism (Day and Bell, 2000) is used to computationally decouple the problem into two independent operators that represent the transport and reaction components. The transport operator is based on the total velocity formulation that decomposes the mass conservation equations and Darcy's law into an elliptic pressure equation and a system of parabolic equations. This allows us to employ the second-order IMPES-like discretization approach described in Pau et al. (2009). The reaction component is described by a coupled system of pointwise nonlinear ordinary differential equations (ODEs). These ODEs can be very efficiently and accurately solved by the VODE solver, a high-order adaptive ODE integrator developed by Brown et al. (1989). Reaction rates are computed based on COREREACT. The flow and reactions operators are then coupled using the Strang-splitting approach, which consists of the following sequential steps within a time step Δt:

1. We advance the reaction operator for $\Delta t/2$ to obtain solution at $t + \Delta t/2$ using VODE;

2. We integrate the flow operator for an interval of Δt based on the discretization described earlier; and finally

3. We advance the reaction operator for another $\Delta t/2$ to obtain solution at $t + \Delta t$ using VODE.

The operator-splitting approach we have adopted here is somewhat similar to the sequential noniterative algorithm option of TOUGHREACT. However, there are significant differences between our method and TOUGHREACT in how the individual operators are handled, as well as in the coupling scheme itself. The TOUGHREACT flow module uses a fully implicit temporal discretization coupled with a first-order upstream weighting to compute spatial derivatives. This approach provides a robust discretization, but requires the solution of a large nonlinear system of algebraic equations. In our sequential approach, we first solve the pressure equation to determine a total velocity and then solve the component conservation equations in total velocity form. Discretization of each component is tailored to reflect its underlying mathematical character. The pressure equation is solved implicitly using a finite difference method. The mass conservation equations are solved semi-explicitly using an explicit second-order Godunov method for advection and an implicit Crank-Nicolson discretization of diffusion, resulting in excellent control of numerical dispersion.

The reaction module of TOUGHREACT uses fixed time steps and Newton's method to solve the resulting systems of nonlinear ODEs. In contrast, the VODE solver applied here utilizes an automatic adaptive time subcycling procedure to numerically integrate the ODEs to the desired level of accuracy. Also, the Strang-splitting approach is formally second-order accurate, while the sequential noniterative approach is only first-order accurate. These enhancements allow our method to work in many cases where TOUGHREACT fails with the sequential noniterative algorithm option.

The extension of the aforementioned single-grid algorithm to an adaptive hierarchy of nested rectangular grids follows the algorithmic details outlined in Pau et al. (2009). The structured-grid adaptive mesh refinement approach, introduced for gas dynamics by Berger and Colella (1989), was first applied to porous media flow by Hornung and Trangenstein (1997) and by Propp (1998). We note that the use of adaptive mesh refinement strategies in reactive flow is particularly advantageous, because it allows the simulation to efficiently capture localized phenomena, such as localized reactions, steep concentration gradients, and saturation fronts. As we will show later, grid resolution strongly influences the solutions of reactive flow. Dynamic gridding capability then allows efficient amortization of computing resources. Figure 1 shows a snapshot of the grid for a problem where the specie AB is formed along the center of the domain where aqueous solutions of A and B mix. Two successive levels of fine grids are placed where gradients of the species' concentrations are steep.

The adaptive mesh refinement (AMR) framework used here can be efficiently parallelized (Rendleman et al., 2000). The reaction component of the procedure is a pointwise operation and thus trivially parallelizable. The parallelization of the flow operator, which involves solving an elliptic equation, is less efficient, but the code is scalable up to several thousands CPUs. In most cases, since the computational cost of the reaction operator dominates the total computational cost, good scaling behavior is usually achieved.
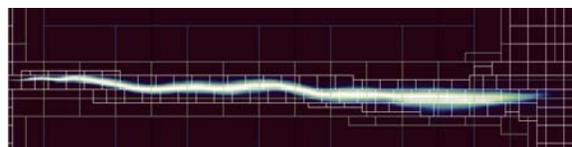
Figure 1. AMR grid with two levels of refinement. Refinement criterion is based on sum of concentration gradients of all components. Shown is the component $AB_{(aq)}$ of a simple reaction $A_{(aq)} + B_{(aq)} \Leftrightarrow AB_{(aq)}$.

RESULTS

We first look at the convergence properties of the method based on a simple kinetic reaction with a finite rate. This is followed by a more realistic geochemical system that utilizes the TOUGHREACT framework. We conclude the section with a simulation of a reactive salt dome problem. Comparisons are made to results using TOUGHREACT and its sequential iterative algorithm option.

Convergence Properties

As a first test, we consider a simple reaction where $A_{(aq)} + B_{(aq)} \Leftrightarrow AB_{(aq)}$, with a finite reaction rate. The problem setup for this test is shown in Figure 2. The 2D rectangular domain is of width $W = 4$ m and height $H = 1$ m. The top and bottom boundaries are impermeable. Fluid flows into the domain from the left boundary and flows out of the domain at the right boundary. The domain is initially filled with aqueous solution of A. Aqueous solution of B is then injected into the domain from the left boundary with a smoothly increasing injection rate to prevent the initial discontinuity in the rate from affecting the determination of the theoretical convergence rate. For the same reason, the permeability function varies vertically from 200 mD at the center of the domain to 100 mD at the top and bottom boundaries. The time step is determined based on a fixed Courant-Friedrichs-Levy (CFL) number of 0.5.
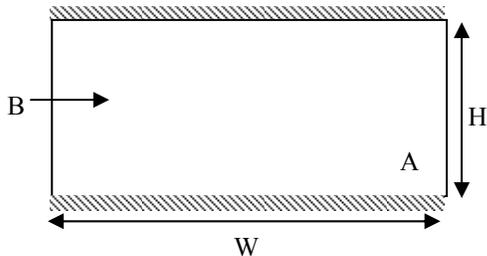
Figure 2.   Configuration for the test problem. The domain is initially filled with Solution A. Solution B is then injected into the domain from the left boundary.

Table 1 shows the discrete L_1 and L_2 norms of the difference between the concentration of A obtained on each grid and that obtained on the next finer grid, and the resulting convergence rates. The rate between the two columns of error norms is defined as $\log_2 (\varepsilon_l/\varepsilon_r)$ where ε_l and ε_r are the errors shown in the columns to the left and right of the rate columns. It clearly demonstrates the second-order convergence property of the algorithm.

Table 1. Convergence rate of algorithm

Δx	$1/2^4$	rate	$1/2^5$	rate	$1/2^6$
L_1	1.68e-2	2.00	4.21e-3	2.00	1.05e-3
L_2	2.82e-2	1.99	7.12e-3	1.99	1.79e-3

In addition to maintaining the second-order accuracy of our method, the use of VODE has the added advantage of having an adaptive time-stepping procedure that automatically subcycles the reactions in time to achieve the desired level of accuracy. As a second test, we compare our approach to TOUGHREACT based on a simple chemical system that examines the precipitation of calcite, using the same physical setup shown in Figure 2. The system involves seven primary species (H_2O, H^+, Ca^2, Na^+, HCO_3^-, Cl^- and $CaCO_{3(s)}$) and 11 secondary species. The domain's size is given by $H = 0.01$m and $W = 0.1$ m. It is initially saturated with $CaCl_{2(aq)}$ (0.4 mol/kg water). $NaHCO_{3(aq)}$ in concentration of 0.8 mol/kg water is then injected from the left boundary at a speed of 1.12354×10^{-6} m/s. Under these conditions, calcite will precipitate, with the precipitation front moving from one end to the other. We will compare the concentration of calcite we obtained along the length of the simulation domain with results from TOUGHREACT.

As shown in Figure 3, results based on our method for $\Delta t = 10$ s and 1 s are identical. On the other hand, solutions obtained from TOUGHREACT for $\Delta t = 5$ s and 0.1 s deviate significantly, suggesting that even at $\Delta t = 0.1$ s, the solution from TOUGHREACT has not converged to an accurate solution. Furthermore, the peak decreases as Δt is decreased, suggesting that solutions from our method are closer to the converged value. The discrepancy can be attributed to the fact that the precipitation rate is a discontinuous function of the species' concentrations for this particular problem (i.e., the rate equation is not a continuously differentiable function through the equilibrium point). A very small time step is needed to resolve this discontinuity. VODE's adaptive time integration scheme is able to automatically resolve this discontinuity to the desired accuracy efficiently without using a fixed small time step. We finally note that if the sequential noniterative algorithm option is used in TOUGHREACT, an incorrect solution is obtained. The above observations thus suggest that when reactions are not too stiff, our method is able to treat nonlinearity in the reaction rate accurately.
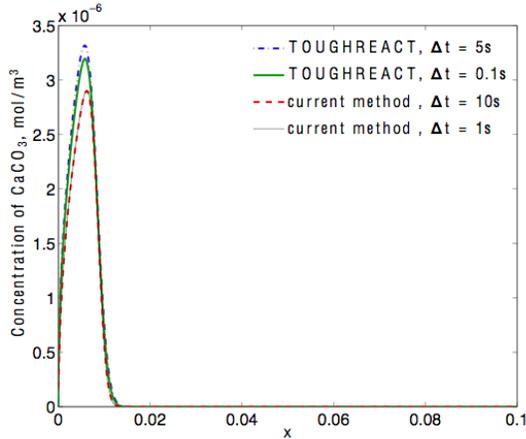
Figure 3. *Comparison of the concentration of $CaCO_{3(s)}$ determined by TOUGHREACT and current method for different time steps.*

Resolution effect in reactive flow

We now consider the simulation of an experimental setting reported in Redden et al. (2007) and shown in Figure 4. We again consider a chemical system involving the precipitation of $CaCO_3$. The simulation domain of size 0.075 m × 0.6 m is initially filled with aqueous species in low concentration, and these species are in equilibrium. High concentrations of aqueous $CaCl_2$ (0.4 mol/kg water) and aqueous $NaHCO_3$ (0.8 mol/kg water) are respectively injected from the left and right half of the lower boundary of the domain with a Darcy velocity of 1.67×10^{-4} m/s.
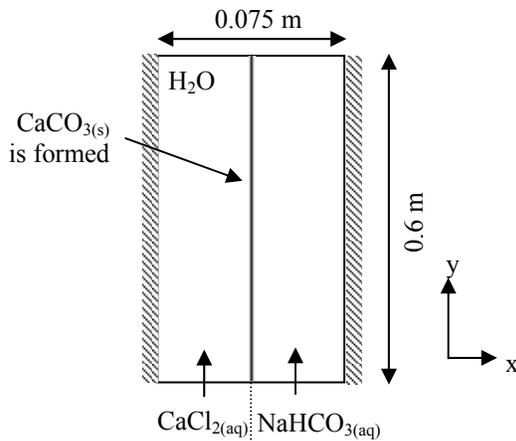
Figure 4. *Configuration for problem in Redden et al. (2007). The domain is initially filled with H_2O. $CaCl_{2(aq)}$ and $NaHCO_{3(aq)}$ are respectively injected from the left and right half of the lower boundary of the domain.*

Upon mixing, $CaCO_3$ will form along y, the vertical axis, and at center of the domain where the two aqueous solutions mix with each other through diffusion. Experimental results in Redden et al. (2007) show that precipitate will form along the entire y-axis.

Figure 5 shows how the precipitate varies along y at different resolutions; the grid resolutions are increased by placing levels of successively finer grids using our AMR scheme. The higher-resolution result captures the mixing, and thus reactions that occur close to the inlet. It thus qualitatively matches the experimental result shown in Redden et al. (2007). At coarser resolutions, precipitate only begins to form at some distance away from the inlet. It is clear from Figure 5 that resolution plays an important role in the simulation of reactive flow.
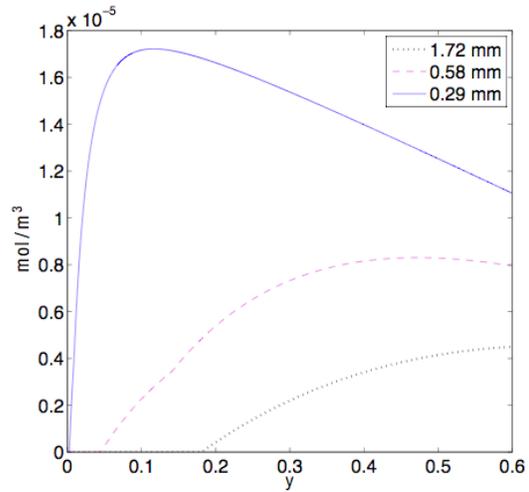
Figure 5. *Concentration of the precipitate determined from grids at different resolutions*

Interaction between complex flow dynamics and reaction

Here, we consider a salt dome problem coupled with the geochemical system described in the previous section. We consider a small rectangular domain of size 3 m × 9 m as shown in Figure 6, and two solutions A and B (Table 2). An aqueous solution of $CaCl_2$ is allowed to diffuse into the domain at 3 m < x < 6 m along the bottom boundary. The bottom, left and right boundaries are otherwise impermeable. The top boundary is an inflow/outflow boundary where a pressure gradient 0.01 atm/m is applied. We will examine four different cases to demonstrate the interaction between flow and reaction by varying the species and densities of solutions A and B. These four cases are described in Table 2. The density of the $CaCl_2$ solution is 1007 kg/m³. Concentrations of the species are as given in the previous section.
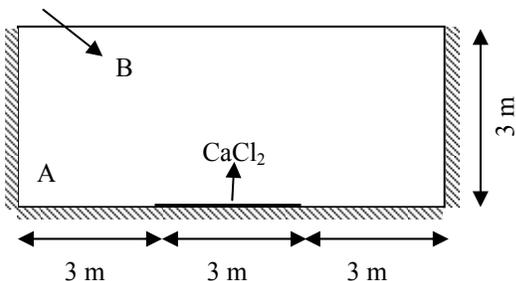
Figure 6.   *Configuration for the salt dome problem with reaction.   CaCl₂ diffuses into the domain, which is initially filled with solution A, from the center of the bottom boundary. Solution B flows into the domain from the top boundary due to the pressure gradient applied at the top boundary.*

Table 2. *Cases considered. The density is the density of aqueous solutions A or B.*

Case	Solution A		Solution B	
	Species	Density, kg/m^3	Species	Density, kg/m^3
1	$NaHCO_3$	997.16	$NaHCO_3$	997.16
2	$NaHCO_3$	1018	H_2O	997.16
3	H_2O	997.16	$NaHCO_3$	997.16
4	H_2O	997.16	$NaHCO_3$	1018

As previously, the reaction of $NaHCO_{3(aq)}$ with $CaCl_{2(aq)}$ causes the precipitation of $CaCO_{3(s)}$. The concentrations of the $CaCO_{3(s)}$ after 3×10^7 s for all the case 1-4 are shown in Figure 7. In Case 1, we see that the continual replenishment of $NaHCO_3$ leads to large amounts of $CaCO_{3(s)}$ precipitation. In Case 2, as H_2O squeezes out $NaHCO_{3(aq)}$, the buildup of $CaCO_{3(s)}$ is less. In Cases 3 and 4, there is no reaction until $NaHCO_{3(aq)}$ has advanced to a point where it mixes with $CaCl_{2(aq)}$. This results in lower concentrations of $CaCO_{3(s)}$ compared to Cases 1 and 2. The concentration of $CaCO_{3(s)}$ in Case 4 is also lower than that in Case 3 because the heavier $NaHCO_{3(aq)}$ in Case 4 leads to less mixing. We note that there is no precipitate in the right lower corner, indicating that the flow dynamics is such that there is a region where $NaHCO_{3(aq)}$ does not mix with $CaCl_{2(aq)}$.
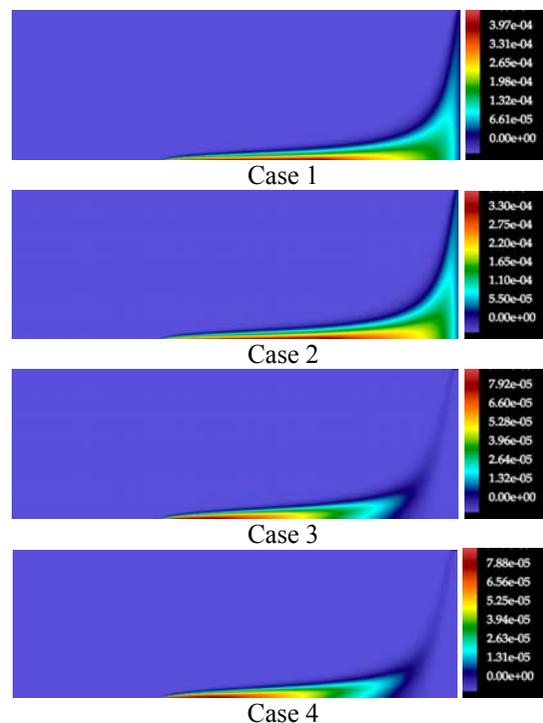
Figure 7.   *Calcite distribution in mol/dm³ for cases described in Table 2 at time 3×10^7 s*

CONCLUSION

This paper describes a second-order accurate algorithm for reactive flow that utilizes the reaction module of TOUGHREACT. Distinctions are made between the current code and TOUGHREACT. We demonstrated the second-order accurate convergence property of our method. We also showed that the use of AMR allows efficient resolution of localized reactions and flow features, resulting in accurate determination of the solution. Finally, we looked at a reactive salt dome problem, in which we captured the complex interaction between transport and reaction.

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REFERENCES

Bell, J., M. Berger, J. Saltzman, and M. Welcome, A Three-dimensional Adaptive Mesh Refinement for Hyperbolic Conservation Laws, *SIAM J. Sci. Statist. Comput.*, 15(1), 127-138, 1994.

Berger, M. J. and P. Colella, Local Adaptive Mesh Refinement for Shock Hydrodynamics, *J. Comp. Phys.*, 82 (1), 64-84, 1989.

Brown P. N., G. D. Byrne, and A. C. Hindmarsh, VODE: A Variable Coefficient ODE solver, *SIAM J. Sci. Stat. Comput.*, 10, 1038-1051, 1989.

Day, M. S. and J. B. Bell, Numerical Simulation of Laminar Reacting Flow with Complex Chemistry, *Combust. Theory Modeling*, 4(4), 535-556, 2000.

Hornung, R. D. and J. A. Trangenstein, Adaptive Mesh Refinement and Multilevel Iterations for Flow in a Porous Media, *J. Comp. Phys.*, 136, 522-545, 1997.

Pau, G. S. H., A. S., Almgren, J. B. Bell, and M. J. Lijewski, A Parallel Second-Order Adaptive Mesh Algorithm for Incompressible Flow in Porous Media, *Phil. Trans. R. Soc. A*, 2009.

Propp, R. M., *Numerical Modeling of a Trickle Bed Reactor*, Ph.D. Thesis, Dept. of Mechanical Engineering, Univ. of California, Berkeley, 1998.

Redden G. D., D. Fox, Y. Fujita, Y. Fang, T. Scheibe, and A. Tartakovsky, Fluid Flow, Solute Mixing and Precipitation in Porous Media, in *Proceedings of the 2nd International Conference on Porous Media and its Applications in Science and Engineering,* Kauai, Hawaii, June 17-21, 2007.

Rendleman, C. A., V. E. Beckner, M. J. Lijewski, W. Y. Crutchfield, and J. B. Bell, Parallelization of Structured, Hierarchical Adaptive Mesh Refinement Algorithms, *Computing and Visualization in Science*, 3 (3), 147-157, 2000.

Steefel, C. I. and K. T. B. MacQuarrie, Approaches to Modeling of Reactive Transport in Porous Media, *Reviews in Mineralogy and Geochemistry*, 34(1), 85-129, 1996.

Xu, T., E. Sonnenthal, N. Spycher, and K. Pruess. *TOUGHREACT User's Guide: A Simulation Program for Non-isothermal Multiphase Reactive Geochemical Transport in Variable Saturated Geologic Media*, Report LBNL-55460, Lawrence Berkeley National Laboratory, Berkeley, Calif., 2004.