

NEW COMPUTATIONAL APPROACHES FOR CHEMICALLY REACTIVE TRANSPORT IN POROUS MEDIA

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Abstract

Flow accompanied by chemical and nuclear reaction and mass transfer plays a central role in many environmental applications. The complexity of coupled flow, transport, and reaction phenomena imposes stringent performance criteria on numerical simulators. This article describes some recent developments that address these criteria. Particular emphasis is placed on robustness and parallel computation. Two practical examples illustrate briefly the role of numerical simulation in subsurface contaminant remediation and assessment.

1 Introduction

Groundwater contaminant transport typically involves flow of one or more phases through highly heterogeneous porous media, mass transfer between phases including the solid phases, advection with dispersion and reaction of chemical and biological species. These phenomena, augmented by others such as heat transfer, local injection and/or extraction of fluid, and imposed barriers to subsurface flow, play an important role in many site remediation techniques.

Flow, transport, and chemical reaction are complex phenomena individually, as the extensive literature on each subject attests. Chemical reactions common to groundwater/soil systems include complexation, oxidation-reduction, adsorption, ion exchange and precipitation-dissolution. These are ultimately limited by thermodynamic equilibrium, but on the time scale of many applications, they often proceed at finite rates by means of nonlinear reaction mechanisms occurring on widely disparate time scales. Add to this the movement of the species over meter to kilometer length scales and their phase changes, the biological, thermal and other processes, and it is necessary to resort to numerical solutions of the governing equations.

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A sophisticated simulator of the subsurface can be a powerful tool for assessing the current state of and possible sources of pollution at a contaminated site. Simulations can also predict the fate of contaminants under various scenarios, thereby giving aid in designing and monitoring the progress of site amelioration strategies.

A well designed simulator must accurately, efficiently, and robustly solve the governing equations. To design such a simulator requires an interdisciplinary mix of geological, physical, chemical, mathematical, and computational expertise.

On the discrete level, accuracy demands locally conservative schemes to maintain mass balances. Spurious oscillations must be suppressed so that negative concentrations do not appear. Relatively sharp concentration fronts must be captured. Subsurface heterogeneities and tensor permeabilities and dispersivities must be accurately handled. Grids must be able to follow geometrical features such as strata.

The computational complexity of these problems demands a highly efficient approach. In general, it is not possible to solve the entire system of governing equations on the scale of the fastest reactions. Efficient time-stepping is critical to the handling of phenomena that occur on widely disparate time scales. Linear and nonlinear solvers generally consume a large fraction of the overall computational time, so they deserve special attention. Grid spacing is often relatively coarse; it is desirable to use finer grids to obtain adequate resolution.

Without a robust algorithm the entire simulation can be jeopardized at any point in the simulation. It can be particularly difficult to solve the nonlinearities arising in the flow and chemistry subproblems.

The complexity of the physical and chemical phenomena is compounded by the difficulty of describing the boundary and initial conditions accurately. Geologic strata can be remarkably heterogeneous, and only limited sampling is possible in most situations. The nature of contamination events is often very poorly defined, e.g., leaks of unknown frequency, duration and volume from fuel storage tanks over many years. Thus the ability to handle multiple detailed realizations in a reasonable amount of time is a significant advantage in a simulator.

Parallel processing is one way to obtain increased computational power at relatively low cost. Parallel computation has, however, overhead associated with the communication of data between processors, their need to be synchronized before certain computations can proceed, and load imbalance. The best possible scenario is linear speed-up, in which runtime is inversely proportional to the number of processors used. Generally, the more that a calculation requires only local information (so that little or no parallel communication is required), the better the parallel efficiency.

In this article we describe briefly several computational techniques that address some of the difficulties of solving reactive flow and transport problems. First the equations for the flowing phases are set out, then for the transport of the chemical species, and finally for the chemical reaction subproblem. An overriding concern is to take maximum advantage of the increased computing power offered by parallel

processing. The paper closes with two practical applications of these computational techniques and some concluding remarks.

2 Solving for Flow

In this section, we present a model based on two flowing phases, an aqueous (water) phase and a gas (air) phase. The flow equations are similar to the well known black oil model from petroleum engineering as described by Peaceman [1] and to the formulation presented by Parker [2]. The coupled equations are:

$$\textit{Aqueous (Water) Phase:} \quad \frac{\partial(\phi\rho_w s_w)}{\partial t} + \nabla \cdot (\rho_w \mathbf{u}_w) = Q_w + \gamma_w. \quad (1)$$

$$\textit{Gas (Air) Phase:} \quad \frac{\partial(\phi\rho_a s_a)}{\partial t} + \nabla \cdot (\rho_a \mathbf{u}_a) = Q_a + \gamma_a. \quad (2)$$

$$\textit{Darcy's Law:} \quad \mathbf{u}_w = -\frac{K k_{rw}(s_w)}{\mu_w} (\nabla p_w - \rho_w g \nabla z), \quad (3)$$

$$\mathbf{u}_a = -\frac{K k_{ra}(s_w)}{\mu_a} (\nabla p_a - \rho_a g \nabla z). \quad (4)$$

$$\textit{Equations of State:} \quad \rho_w = \rho_w^0 e^{c_w p_w}, \quad \rho_a = \rho_a^0 e^{c_a p_a}. \quad (5)$$

$$\textit{Capillary Pressure:} \quad p_c(s_w) = p_a - p_w. \quad (6)$$

$$\textit{Volume Balance:} \quad s_w + s_a = 1. \quad (7)$$

Here ϕ is porosity, K absolute permeability tensor, g gravitational constant, z depth, and, for each phase, \mathbf{u} is the Darcy velocity, p pressure, p_c capillary pressure, ρ density, ρ^0 reference density, k_r relative permeability, μ viscosity, s saturation, c compressibility, Q an external source or sink, and the γ are source or sink terms due to mass transfer between phases (subscripts have been omitted). On these equations we impose appropriate initial and boundary conditions.

2.1 Single Phase

In the special case of saturated flow, the model is given by equations (1), (3), and the water phase part of the equation (5), with $s_w = 1$ and $\gamma_w = 0$. Time is discretized by using backward Euler, implicit time-stepping.

The spatial discretization of this system uses a locally conservative scheme so that mass balance is maintained cell-by-cell rather than merely over the entire domain. The scheme is based on an expanded mixed finite element method with the Raviart-Thomas lowest order approximating spaces [3] on rectangular grids; however, we are able to implement the method in a way that is able to handle non-rectangular domains easily and efficiently. We first map the true domain to a rectangular reference domain. A rectangular grid on the reference domain induces

a logically rectangular, curved grid on our true domain. Next, we apply the mixed method to the mapped equations on the rectangular reference grid. We approximate certain of the integrals in the mixed finite element method using the trapezoidal quadrature rule. The method then reduces to a locally conservative, cell-centered finite difference scheme that can handle tensor permeabilities [4, 5, 6]. Theoretical and computational convergence results show that the resulting scheme is highly accurate. If h denotes the maximal grid spacing, then the Darcy velocity is approximated spatially to order h globally, and to order h^2 at certain super-convergent points. Moreover, the finite difference stencil is compact, using only 19 points. This makes the scheme particularly well suited to parallel computation.

To solve the linear system that arises in the discretization, especially on a parallel computer, a substructuring or domain decomposition algorithm introduced by Glowinski and Wheeler [7] is employed. The domain is divided into a number of smaller subdomains (normally one per computer processor). The method requires solving only local flow problems on these smaller subdomains, and iterating until convergence is reached. The domain decomposition method introduces pressure unknowns (Lagrange multipliers) along the subdomain interface (this is equivalent to a partial hybridization of the original method [8, 9]). Convergence is reached when the pressures and mass fluxes match across the subdomain interfaces. To solve this interface problem efficiently on a distributed parallel system, a conjugate gradient iteration has been employed with the balancing preconditioner defined by Cowsar, Mandel, and Wheeler [10]. Unlike many other preconditioners, this one achieves almost linear speed-up on parallel machines.

2.2 Two Phases

The numerical scheme for two-phase flow uses implicit time-stepping with fully coupled wells. Capillary pressure and relative permeability are functions of water saturation that may vary with rock type. Functional forms can be defined by tables or by definition as piecewise C^2 splines. Equations (1)–(4) are discretized in a way similar to the single phase case. Constitutive laws (5)–(7) are used to close the system. The resulting nonlinear equations are treated by a Newtonian iteration. In the case of two full phases, Newton’s method converges much faster and more reliably than, say, a Picard iteration. We have used p_a and s_a as primary variables. Conjugate gradient iteration cannot be applied to solve the resulting linear system, since it is non-symmetric; thus, we have developed a preconditioned, domain decomposition, generalized minimum residual (GMRES) procedure [11].

3 Solving for Transport

We consider the transport and reaction of an arbitrary number N of chemical species which are present in an arbitrary number of phases including the solid phase. The

distribution of mass in the fluid phases is assumed to follow the linear Raoult's or Henry's Law. The reactions can be at equilibrium or may follow biological, geochemical and radio-nuclear decay kinetics, as discussed in the next section.

The equation describing transport of an aqueous chemical species of concentration c_i takes the general form

$$\frac{\partial(\phi c_i)}{\partial t} + \nabla \cdot (\mathbf{u}_w c_i - \mathbf{D}_i(\mathbf{u}_w) \nabla c_i) = \phi R_i(c_1, \dots, c_N), \quad (8)$$

with appropriate initial and boundary conditions, where $\mathbf{D}_i(\mathbf{u}_w)$ is the diffusion and dispersion tensor and R_i is the rate of appearance or disappearance of species i due to chemical reaction, decay, and/or mass transfer.

To solve these equations numerically, we use a time splitting scheme that allows us to take different time step sizes for advection, diffusion, and reactions as appropriate for the time scale on which each occurs. The flow module first approximates (1)–(7). Given the saturations, phase velocities, and approximate solutions at time t^n , the transport module advances to time t^{n+1} as follows.

First consider the advection-diffusion problem in the absence of reactions

$$\frac{\partial(\phi c_i)}{\partial t} + \nabla \cdot (\mathbf{u}_w c_i - \mathbf{D}_i(\mathbf{u}_w) \nabla c_i) = 0. \quad (9)$$

We have developed the characteristics-mixed method to solve this problem [12, 13, 14]. It approximates advection, that is,

$$\frac{\partial(\phi c_i)}{\partial t} + \nabla \cdot (\mathbf{u}_w c_i) = 0, \quad (10)$$

by explicitly tracing characteristics using a series of small sub-time-steps. This is followed by the diffusion/dispersion step, which solves

$$\frac{\partial(\phi c_i)}{\partial t} - \nabla \cdot (\mathbf{D}_i(\mathbf{u}_w) \nabla c_i) = 0 \quad (11)$$

over the full time-step by a mixed finite element method. (The mixed method is again approximated as a cell-centered finite difference scheme as we did for the flow equations.) The scheme allows large overall time steps to be used, since no Courant-Friedrich-Lewy (CFL) restriction is needed for stability.

When reactions are present, we interpose the reaction step, as described in the next section, between the advection and diffusion/dispersion steps. That is, the advected concentrations, \tilde{c}^{n+1} , are reacted locally in space, and then diffused. We have found that when the reaction time steps are on the order of a CFL time step, it is better to use the Godunov mixed finite element scheme of Dawson [15, 16]. It approximates advection by an explicit higher order Godunov method, and diffusion/dispersion again by a mixed finite element method.

Both advection-diffusion schemes are conservative and accurate, and both incorporate a slope limiting technique to prevent oscillatory behavior. Thus, for example, negative concentrations do not arise. This is quite important for the reaction step.

Because the two advection schemes are explicit, each computation requires only spatially local information, and very little parallel overhead is seen. Moreover, diffusion and dispersion are small effects, so they can be solved efficiently with simply the Jacobi preconditioned conjugate gradient algorithm. In fact, both advection-diffusion schemes achieve almost linear parallel speed-up [14, 17]. (Applications to contaminant transport in single phase groundwater flow can be found in [12] and [14], and to two-phase flow in [18].)

4 Solving for Local Chemical Compositions

To carry out a reaction step we take advantage of the fact that the mass of each (stable) chemical element is conserved. From the stoichiometry of the chemical species, their radioactivity, and their advected concentrations \tilde{c}^{n+1} as initial conditions to the time-step, the elemental masses at time t^{n+1} can be calculated. The task is then to re-distribute the elemental totals among the species in a manner consistent with the reaction expressions.

Let us assume that a set of $M \leq N$ *components* has been identified. Components form “a set of chemical entities that permits a complete description of the stoichiometry of a system” [19]. The local, governing equations for the reactive system are a mixed problem of differential and algebraic equations of the form

$$\frac{dc_i}{dt} = R_i(c_1, \dots, c_N) \quad \text{for the kinetic species or,} \quad (12)$$

$$F_j(c_1, \dots, c_N) = 0 \quad \text{for the equilibrium species,} \quad (13)$$

where the R_i are known *kinetic* reaction rate expressions and the F_j are nonlinear *equilibrium* expressions. The F_j arise when some reactions occur at effectively infinite rates, thereby creating an algebraic rather than a differential relationship among the concentrations. The F_j are generally of the form

$$F_j = a_j - K_j \prod_{k=1}^{N_a} a_k^{q_{j,k}}, \quad (14)$$

where the a_j are the *activities*, which are either known functions of composition in the non-ideal case, or equal to the concentrations in the ideal case, and the $q_{j,k}$ are stoichiometric coefficients. This description allows us to handle aqueous complexation and interactions between aqueous solution and solid phases, including the formation of pure condensed phases, i.e., minerals.

Equations (12)–(13) are subject to elemental mass-balances, or stoichiometry, of the form

$$\mathbf{Q} \mathbf{c} = \mathbf{b}, \quad (15)$$

where $\mathbf{Q} \in \mathbb{R}^{M \times N}$ is the stoichiometric matrix and the vectors $\mathbf{c} \in \mathbb{R}^N$ and $\mathbf{b} \in \mathbb{R}^M$ represent total concentrations of the species and components, respectively, resulting from the transport step.

Not necessarily all the concentrations are linearly independent, so the transport equations (8) corresponding to the dependent ones are replaced by (13) or (15).

The system (12)–(15) can be difficult to solve. One reason is that the species concentrations and rate parameters can differ by many orders of magnitude [20]. Another is the physical requirement that species concentrations be nonnegative. The non-differentiable character of the equilibria for precipitation-dissolution reactions adds a particular complication: the possibility that a mineral can be present imposes an inequality constraint on the species concentrations, which becomes an equality only when the mineral is actually present. To handle such constraints requires iteration through different combinations of minerals. This iteration introduces a variety of problems regarding convergence, efficiency, robustness and stability. The lack of a robust algorithm, i.e., one which converges for (almost) any set of elemental totals and for (almost) any initial guess for the composition, is a serious drawback for a reactive flow simulator, which must solve (12)–(15) at each time step in every grid block of the spatial domain.

Some of the difficulties in solving (12)–(15) can be avoided by rewriting the equilibrium conditions as an equivalent free-energy minimization problem:

$$\begin{aligned} & \min G_{\text{tot}}(c_1, \dots, c_N) \\ & \text{subject to } \mathbf{Q} \mathbf{c} = \mathbf{b} \quad (\text{element mass-balance}) \\ & \text{and, for each } i, c_i \geq 0 \quad (\text{concentrations are nonnegative}) \end{aligned}$$

where G_{tot} is the total free energy written to include all the possible mineral phases. The problem of identifying the correct set of mineral phases remains, however, unless the non-negativity constraints are rigorously incorporated into the formulation. Other workers have considered various ways of including such constraints [21]; our approach will be based on the Interior Point method [22], a new non-linear programming algorithm particularly suitable for dealing with a large number of inequality constraints.

In this Interior Point framework, iterative tests for the appearance or disappearance of mineral phases or, more generally, for any phase, are no longer required. Instead, an *a priori* specification of possible minerals is made, and the algorithm attempts to find the correct assemblage. Although this strategy increases the size of the problem to be solved, we have found it to be more robust and expect it ultimately to be more efficient. Furthermore, this approach should provide similar benefits in phase equilibrium calculations (“flash calculations”) that arise when species are soluble in multiple phases.

We close this section by noting that the reaction subproblems can be solved efficiently in parallel. Because our time splitting approach handles reactions locally (independently of spatial movement), the reaction subproblems in the grid cells are independent of each other, and so they are naturally suited to parallel computation.

5 Applications

5.1 Multiple Well Bioremediation Results

In a collaborative effort with the Pacific Northwest National Laboratory (PNNL) we simulated a field test of biodegradation, using microbial carbon-tetrachloride (CCl_4) destructive kinetics developed by Skeen and Chan of PNNL [23]. The model has six components: electron acceptors nitrate NO_3^- , nitrite NO_2^- , and acetate CH_3COO^- , and CCl_4 , microbial mass $\text{C}_5\text{H}_9\text{O}_3\text{N}$, and a non-reactive tracer. Four redox reactions have been identified, resulting in a rate of biodegradation described by

$$\frac{d(\text{CCl}_4)}{dt} = -\frac{\alpha(\text{CCl}_4)(\text{C}_5\text{H}_9\text{O}_3\text{N})}{1 + \beta[(\text{NO}_3^-) + (\text{NO}_2^-)]}$$

for the two parameters α and β .

An unsaturated/saturated domain with 3 vertical wells was simulated. The physical domain was $[0, 123] \times [0, 123] \times [220, 305]$ feet. The wells were placed approximately 6 meters apart on a straight line (aerial view) near the center of the domain. The inner well is an injector and the outer 2 wells are extractors. The extraction wells had one screened interval from 240 to 279 feet, while the injection well was screened at 3 intervals: 240 to 257 feet, 274 to 279 feet, and 294 to 299 feet. The flow rates at the production wells were 0.3125 gpm/meter (gallons per minute per meter) well screen and at the injection well 0.625 gpm/meter well screen. The domain had heterogeneous layered permeabilities in the vertical direction dominated by two tight streaks with low permeability (≈ 10 milliDarcy). A constant porosity of 0.25 was assumed. The retardation factor for acetate was taken to be 1.8.

Background concentrations of 2000 ppb for carbon-tetrachloride and 300 ppm for nitrate were assumed. A small background concentration for *in situ*, native microbes were also assumed. Acetate was injected twice a day at 1000 ppm over a 1 hour duration, with a 12 hour frequency, starting from time zero. Nitrate was injected twice a day at 1400 ppm over a 1 hour duration with a 12 hour frequency, starting at 1 hour.

The simulations showed steady microbial growth near the injection well, with consequent reduction of CCl_4 levels and increased nitrite (due to reaction of acetate and nitrate). The acetate front movement is retarded relative to the nitrate front due to adsorption. The simulations provide concentration profiles at various times which can be compared with measurements in monitoring wells. This permits validation of the physical and chemical models of the site, as well as a means for evaluating the effectiveness of different remediation strategies. For more details, see [18, 14].

5.2 Radio-nuclide Transport

The effect of sorption is a critical factor determining the propagation of heavy metals and radio-nuclide contaminants such as strontium and cobalt. Simulation can be

a useful tool in developing such an understanding, and in studying the effects of various geological and chemical parameters. For example, heavy metals tend to be very insoluble at high pH, and so one strategy for immobilizing them in waste pits is to add a strong base to the pit.

We simulated the migration of such species from highly basic sources into neutral pH groundwater/soil in various simple geometrical arrangements. The chemistry model in these simulations accounts for aquatic and surface complexation and precipitation-dissolution. Even for a relatively simple case of strontium plus common background aqueous species, a total of 74 species were involved in the calculations. The adsorption model used accounts for the electrostatic interactions between the surface and aqueous species (after Dzombak and Morel [24]). In the simulation the assumption was made that all reactions reach thermodynamic equilibrium.

The simulations for migration of Sr generally showed significant retardation. A remarkable result, however, was that when the source was above a certain pH, a pulse of Sr formed and propagated very rapidly, nearly at tracer velocity. This unexpected behavior is consistent with field observations of Sr migration. Further studies are underway to determine the conditions for this bimodal propagation.

6 Conclusions

By using a variety of advanced computational techniques, one can simulate accurately and effectively the complex set of physical, geochemical, and biological phenomena that arise in groundwater contamination problems. We have described methods that use parallel computers with nearly maximum efficiency, i.e., runtime is inversely proportional to number of processors used. This permits significant increases in problem size and resolution, and decreases in simulation turnaround time. Preliminary results support the robustness of the interior point method for solving the local chemistry problem. Such robustness is critical to obtaining a practical tool for environmental applications. A computer code incorporating these concepts has already proven useful in modeling and understanding field behavior.

Acknowledgments

The authors acknowledge the contributions of Ashokkumar Chilakapti, Lawrence Cowsar, Hector Klie, Doug Moore, Carol San Soucie, John Wheeler, and Ivan Yotov to this work. We thank Kyle Roberson and Brian Wood of Pacific Northwest National Laboratory, and Laura Toran and Gary Jacobs of Oak Ridge National Laboratory for providing data for the applications. We also thank George Yeh of Penn State University for providing us with his KEMOD code [25].

This work was funded in part by grants from the Department of Energy through the Partnership in Computational Science, Oak Ridge National Laboratory (Martin Marietta), and a contract with Pacific Northwest Laboratory (Batelle). Further

support came from the National Science Foundation through the Center for Research in Parallel Computation and from the State of Texas Governor's Energy Office.

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