A PARALLEL ALGORITHM FOR TWO PHASE MULTICOMPONENT CONTAMINANT TRANSPORT

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ABSTRACT

We discuss the formulation of a simulator in three spatial dimensions for a multicomponent, two phase (air, water) system of groundwater flow and transport with biodegradation kinetics and wells with multiple screens. The simulator has been developed for parallel, distributed memory, message passing machines. The numerical procedures employed are a fully implicit expanded mixed finite element method for flow and either a characteristics-mixed method or a Godunov method for transport and reactions of dissolved chemical species in groundwater. Domain decomposition, symmetric and nonsymmetric solvers have been developed for solving the systems of equations resulting from the discretization of the model. Results from applying this simulator to a bioremediation field problem with several injection and production wells each having multiple screens are presented.

1. INTRODUCTION

Microbial biodegradation (the decomposition of contaminants by microorganisms) is an important process for rendering certain contaminants harmless. It is a natural process that can be accelerated to protect a potable water supply. U.S. Environmental Protection Agency studies [20] have shown that this strategy can result in almost complete removal of contaminants, whereas many alternative restoration strategies have not proven as effective. Biodegradation technologies are being employed at several U.S. Department of Energy Laboratories in an effort to remove or contain volatile organic compounds [5,8,11,12,13,15,18,19,20,22].

Biological decontamination is physically and chemically complex. It involves flow and transport in both unsaturated soils and the aquifer, and the interaction of hydrocarbons, microbes, oxygen, nitrogen, and various other chemical compounds. Numerical simulation of these processes is a critical step in understanding and designing biorestoration applications [5,8,13,22]. Indeed, without applying numerical simulation, wide-scale in situ biodegradation of contaminants is impractical.

In attempting to model these physical systems, one encounters certain difficulties. The physical, chemical and geologic definition of the problem is always incomplete and imprecise. In addition, the chemical processes involve interphase mass transfer as well as a host of intraphase chemical reactions, including dissolution, aqueous phase complexation, ion exchange, adsorption, precipitation, oxidation/reduction, and even biological degradation kinetics. The extent of mass transfer and chemical reaction is ultimately limited by thermodynamic equilibrium, but compositions far from equilibrium often arise locally because of kinetic and surface area constraints. Additional complexities arise in scaling since parameters derived in laboratory experiments are not always applicable to the field scale aquifer.

Parallel computing offers an opportunity for building detailed models of the chemical and physical processes and in providing the capability of solving larger, more realistic and practical problems faster and more economically. This includes the ability to use an adequately refined discretization mesh, to incorporate complex chemical and physical effects associated with the transport of both hydrocarbons and organic contaminants in porous media, and to employ stochastic or conditional simulation. The latter is essential for simulating a realistic geologic aquifer, since much of the data needed to characterize it cannot be quantified accurately.

The outline of the paper is as follows. In §2 we describe the governing flow and transport equations with biodegradation in an unsaturated/saturated porous medium. For simplicity, we assume linear sorption and aerobic conditions. More general kinetics such as Michaelis-Menton can be treated with the numerical techniques described in this paper. In §3, we describe the parallel implementation of the model, and in §4 we present three dimensional, parallel, bioremediation simulation results. Conclusions and current directions on parallel implementation are given in §5.

2. TWO PHASE FLOW AND CONTAMINANT TRANSPORT WITH BIODEGRADATION

We first present the two phase flow model. It is very similar to the well known black oil model from petroleum engineering as described by Peaceman [17] and the formulation presented by Parker [16]. The coupled equations are:

Water Phase
$$\frac{\partial(\phi\rho_w s_w)}{\partial t} + \nabla\cdot(\rho_w u_w) = Q_w + \gamma_w; \tag{1}$$

Air Phase
$$\frac{\partial(\phi\rho_a s_a)}{\partial t} + \nabla\cdot(\rho_a u_a) = Q_a + \gamma_a; \tag{2}$$

Equations of State
$$\rho_w = \rho_w^0 e^{c_w p_w}, \quad \rho_a = \rho_a^0 e^{c_a p_a}; \tag{3}$$

Darcy's Law
$$u_w = -\frac{K k_{rw}(s_w)}{\mu_w}(\nabla p_w - \rho_w g \nabla z), \tag{4}$$
$$u_a = -\frac{K k_{ra}(s_a)}{\mu_a}(\nabla p_a - \rho_a g \nabla z); \tag{5}$$

Capillary Pressure
$$p_c(s_w) = p_a - p_w; \tag{6}$$

Volume Balance
$$s_w + s_a = 1. \tag{7}$$

Here ϕ is porosity, p phase pressure, ρ phase density, K absolute permeability, k phase relative permeability, μ phase viscosity, s phase saturation, c phase compressibility, g gravitational constant, z depth, Q an external phase source or sink, and γ are source or sink terms due to mass transfer between phases (subscripts have been omitted for simplicity).

Multicomponent transport and biodegradation are governed by a system of advection-diffusion-reaction equations consisting of m_s electron donors (substrates) and m_n electron acceptors or nutrients, and a system of m_x ordinary differential equations involving microbial mass (transport of microbes can be treated also if one assumes instead a system of advection-diffusion-reaction equations for the microbes). They can be written in terms of the concentration dissolved in water, $C_i = C_i^w$, as:

Electron Donor (Substrate)
$$\frac{\partial(\phi_i C_i)}{\partial t} - \nabla \cdot (D_i \nabla C_i - u_i C_i) = \phi \chi_i + g_i, \quad i = 1, \ldots, m_s; \tag{8}$$

Electron Acceptor (Nutrient)
$$\frac{\partial(\phi_i C_i)}{\partial t} - \nabla \cdot (D_i \nabla C_i - u_i C_i) = \phi \chi_i + g_i, \quad i = m_s + 1, \ldots, m_s + m_n; \tag{9}$$

Microbial Mass
$$\frac{\partial(\phi C_i)}{\partial t} = \phi \chi_i, \quad i = m_s + m_n + 1, \ldots, m_s + m_n + m_x. \tag{10}$$

Since we assume that mass transfer between phases is based on equilibrium partitioning among the phases, we have

Equilibrium Phase Partitioning
$$C_i^a = \Gamma_{ia} C_i^w, \quad C_i^s = \Gamma_{is} C_i^w \quad i = 1, \ldots, m_s + m_n, \tag{11}$$

where Γ_{ia} and Γ_{is} are the equilibrium phase partitioning constants between an air/water system and a soil/water system, respectively, for component i. Here we define

$$\begin{gathered} \phi_i = \phi(s_w + s_a \Gamma_{ia}) + \Gamma_{is}, \quad u_i = u_w + u_a \Gamma_{ia}, \\ D_i = \phi(s_w D_{iw} + s_a \Gamma_{ia} D_{ia}), \end{gathered} \tag{12}$$

where $D_{iw}(u_w)$ is the hydrodynamic diffusion/dispersion tensor, and $D_{ia}(u_a)$ is defined similarly for the air phase. The χ_i are possibly nonlinear kinetic terms which account for biodegradation of contaminants, utilization of nutrients, and growth and decay of microorganisms. The number and complexity of specific metabolic pathways or chemical reactions varies with the application. The source/sink terms g_i represent production and injection wells.

3. PARALLEL IMPLEMENTATION

Our two-phase flow and reactive transport code involves the coupling of flow and transport/reaction modules. The latter module was developed to simulate the transport and reactions of dissolved chemical species in the groundwater. This fully parallel code is based on time splitting for advection, diffusion, and reactions. Either the method of characteristics or a higher order Godunov method is employed for treating advection. The mixed finite element method is used to treat diffusion. Reactions are handled separately as a differential algebraic system. The Godunov scheme is especially useful when the reactive time steps are on the order of a CFL time step. The characteristics-mixed method allows for much larger time steps, since no CFL restriction is needed for stability. The Godunov mixed finite element scheme and the characteristic-mixed method for advection/diffusion were introduced and analyzed by Dawson [9, 10] and Arbogast and Wheeler [4, 5] respectively.

The transport/reaction module handles an arbitrary number of component chemical species, as well as microbial mass and radionuclide decay. The code also incorporates equilibrium and nonequilibrium biological and geochemical kinetics and treats an arbitrary number of phases including the solid phase (adsorption). Each component is dissolved in one or more of these phases. The distribution of mass in the phases is assumed to follow the linear Raoult's or Henry's Law. This code achieves almost linear parallel scaling [5,3]; thus, it is highly effective when run on a parallel machine. Application to contaminant transport in single phase groundwater flow can be found in [1] and [5].

The flow module is a fully implicit two phase flow code with fully coupled wells. Capillary pressure and relative permeability are functions of water saturation and formation type. Functional forms can be defined by tables or by definition as piecewise C^2 splines. Equations (1)–(2) and (4)–(5) are discretized using an expanded mixed finite element method with the Raviart Thomas lowest order approximating spaces. The trapezoidal quadrature rule is used to obtain a finite difference scheme for the unknowns. This expanded mixed finite element method with quadrature was developed and analyzed in [6,7,2] for single phase flow. Constitutive laws (3), (6) and (7) are used to close the system. The resulting nonlinear equations are treated by Newtonian iteration. Here p_a and s_a are chosen as primary variables. A preconditioned domain decomposition GMRES procedure has been developed for treating the nonsymmetric system.

We now describe briefly how the combined modules solve the model (1)–(12). The flow module first approximates (1)–(7). Given the saturations and phase velocities the transport module is called. Here equations (8)–(12) are solved. One global time step of the transport module involves the following three sequential steps:

(A) Pure transport. For each electron donor or acceptor, the characteristics of the flow are tracked or Godunov fluxes found to treat the advection terms. In the former case, the characteristics are traced backwards in time to locate their

origin at the previous time level, and fluid is transported directly forward. This may be done by taking small micro time steps. This solves (8)–(9) without the reaction terms χ_i and the dispersion terms D_i.

(B) Reactions. The coupled system of reaction equations (i.e., (8)–(10) without the two divergence terms and without the g_i source terms) are approximated using a fourth order Runge-Kutta procedure. Initial conditions are the cell averages from (A) for acceptors and donors, and the previous time step concentrations for the microbes. Many small time steps may be taken to improve the accuracy.

(C) Diffusion and dispersion. The diffusion/dispersion step involves approximating a parabolic system for each donor or acceptor using initial data from (B) and applying the mixed finite element method, again implemented as a cell-centered finite difference method. A tensor product trapezoidal rule is used in treating the diffusion/dispersion term. A finite stencil is obtained for each component, nine points in two dimensions and nineteen in three. The discrete system is solved using a Jacobi preconditioned conjugate gradient algorithm. Details may be found in [1,5,6].

After having completed the transport and reactive step, mass transfer source and sink terms γ_p are computed. The time step is then incremented and the flow subroutine is called to obtain new saturations and phase velocities.

4. MULTIPLE WELL BIOREMEDIATION RESULTS

Rice University and Pacific Northwest Laboratory (PNL) began a collaborative research effort in 1992 that involves laboratory, field, and simulation work directed toward validating remediation strategies. We discuss below some preliminary computational results based on some recent microbial CCl_4 destructive kinetics developed by Skeen and Chan of PNL [19].

The model has six components: electron acceptors nitrate NO_3^-, nitrite NO_2^-, and acetate CH_3COO^-, CCl_4, microbial mass $C_5H_9O_3N$, and a nonreactive tracer. We also assume that the retardation factor for acetate is 1.8. The chemical reactions for this system are:

$$\begin{aligned}
8NO_3^- + 2CH_3COO^- + 2H^+ &\rightarrow 4CO_2 + 8NO_2^- + 4H_2O,\\
8NO_2^- + 3CH_3COO^- + 11H^+ &\rightarrow 6CO_2 + 4N_2 + 10H_2O,\\
7CH_3COO^- + 2NO_3^- + 9H^+ &\rightarrow 4CO_2 + 6H_2O + 2C_5H_9O_3N,\\
13CH_3COO^- + 4NO_2^- + 17H^+ &\rightarrow 6CO_2 + 10H_2O + 4C_5H_9O_3N,
\end{aligned}$$

and bioremediation is described by

$$\frac{d(CCl_4)}{dt} = \frac{-\mu\,(CCl_4)\,(C_5H_9O_3N)}{1 + k_i(\,(NO_3^-) + (NO_2^-)\,)}$$

for the two parameters μ and k_i.

An unsaturated/saturated domain with 3 wells was simulated. The physical domain was $[0, 123] \times [0, 123] \times [220, 305]$ feet. The vertical wells were placed arealy in a straight line running from the lower left corner to the upper right corner of the domain with the inner well as injection and the outer 2 wells as extraction, with approximately 6 meter spacing between the wells. The production 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. A schematic drawing of a vertical cross-section containing all the wells along with the location of the water table is given in Figure 1. The domain had heterogeneous layered permeabilities in the vertical direction dominated by two tight streaks with low permeability ($\approx$ 10 milliDarcy) as sketched in Figure 2. A constant porosity of 0.25 was assumed.

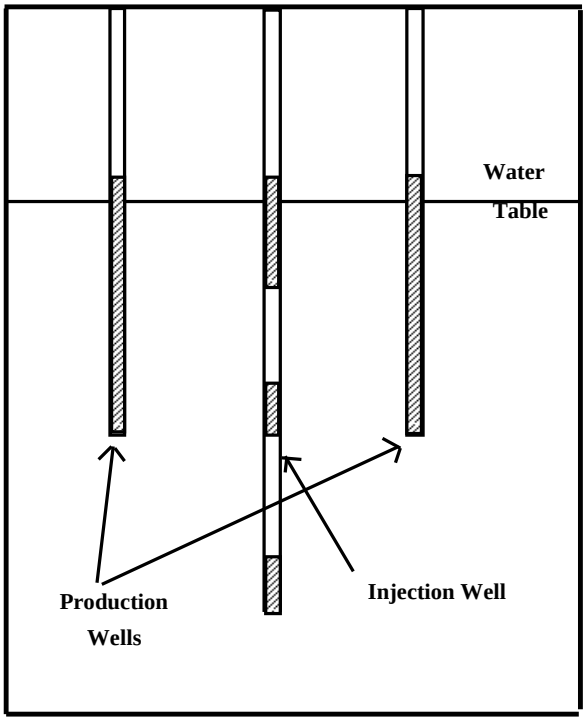

Fig. 1. Location of injection and production wells.

Background concentrations of 2000 ppb for carbon-tetrachloride, 300 ppm for nitrate, and $1.27*10^{-9}$ for microbes were 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.

Cross-sectional plots of the carbon-tetrachloride, nitrate, nitrite, microbe, and acetate solutions are given in Figures 3–7. These plots show the solutions in a vertical slice of the domain which passes through the wells. The carbon-tetrachloride

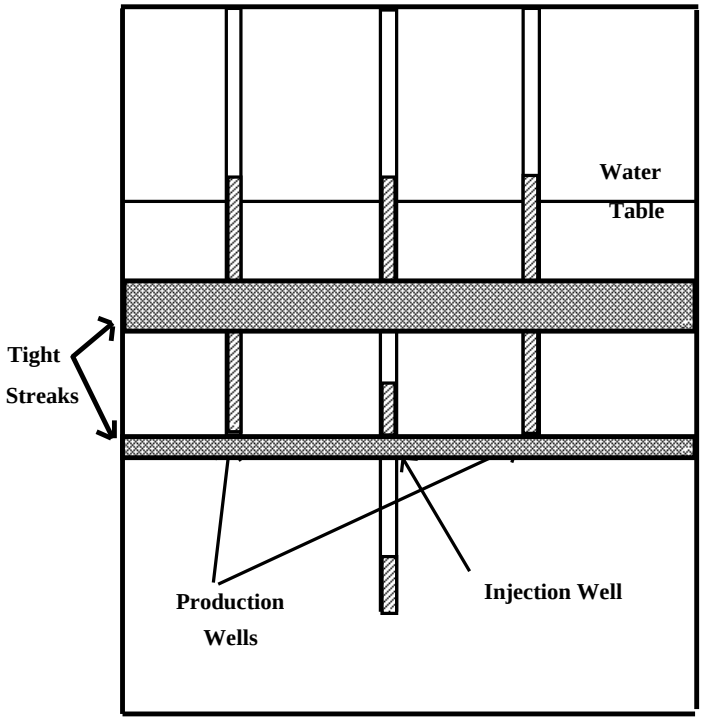

Fig. 2. Position of tight permeability streaks in relation to wells.

solution at 1, 3, 5, and 7.5 days is given in Figure 3. This figure shows that carbontetrachloride is being removed from the area near the injection well. The nitrate, nitrite, microbe, and acetate solutions at 7.5 days are given in Figures 4–7. Note that microbial growth is occurring near the injection well, indicating biological activity. Nitrite is also being produced as a byproduct of biodegradation. Moreover, the acetate front movement is retarded relative to the nitrate front due to adsorption.

5. CONCLUSIONS AND FUTURE DIRECTIONS

A parallel algorithm for modeling three dimensional groundwater reactive multiphase flow and transport has been presented. A code has been under development at Rice University. Its purpose is to simulate the flow and transport of reacting chemical species in the groundwater. This code is based on combining locally conservative schemes: an expanded mixed finite element method for flow with a characteristics or higher order Godunov method for advection coupled with a mixed finite element method for diffusion/dispersion. Computational experiments indicate that this approach is useful in solving grand challenge problems such as bioremediation and that the code achieves good parallel scaling.

We are presently modifying the flow module to treat three phases (air, nonaqueous phase liquid, and water). Logically rectangular grids on general geometry are being tested for the multiphase simulator. Current work also includes the

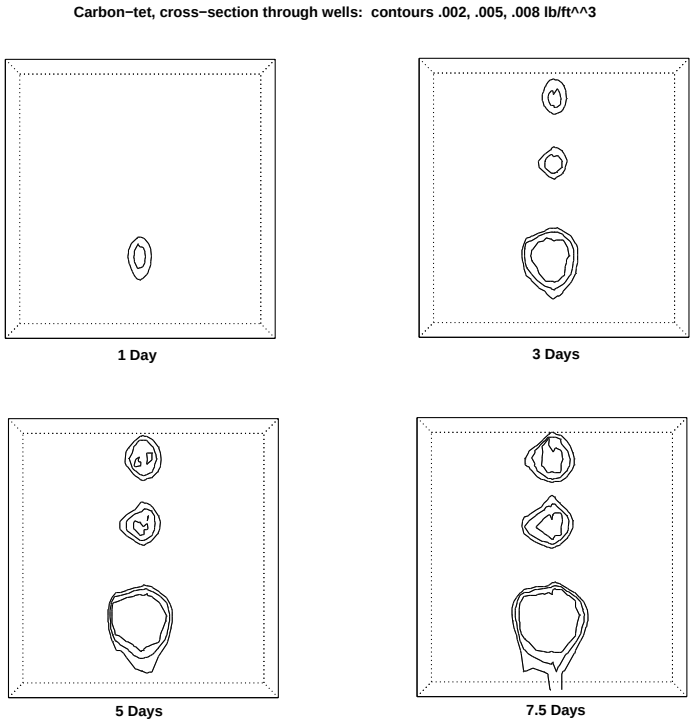

Fig. 3. Carbon-tetrachloride solution at 1, 3, 5, and 7.5 days.

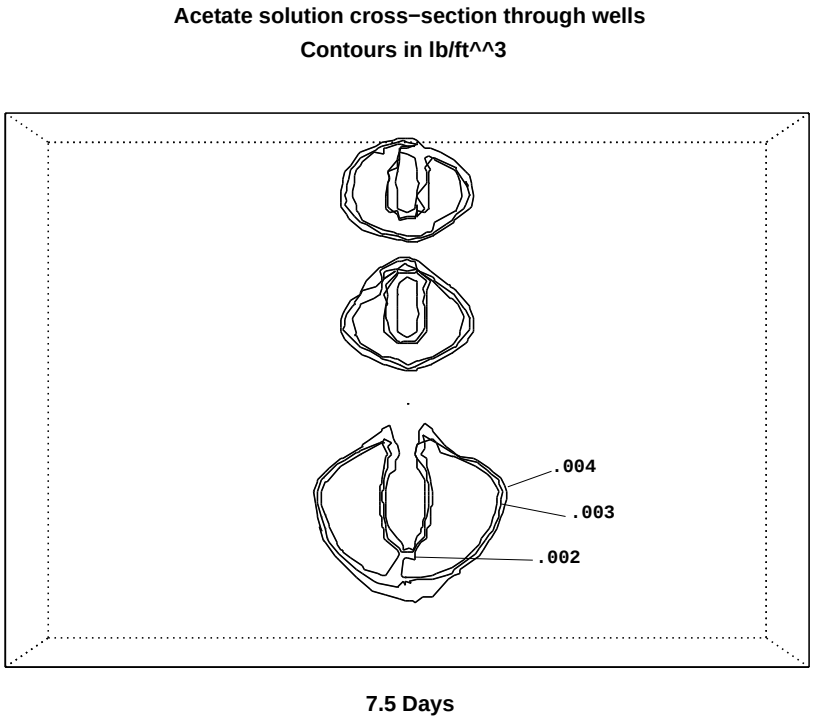

Fig. 4. Acetate solution at 7.5 days.

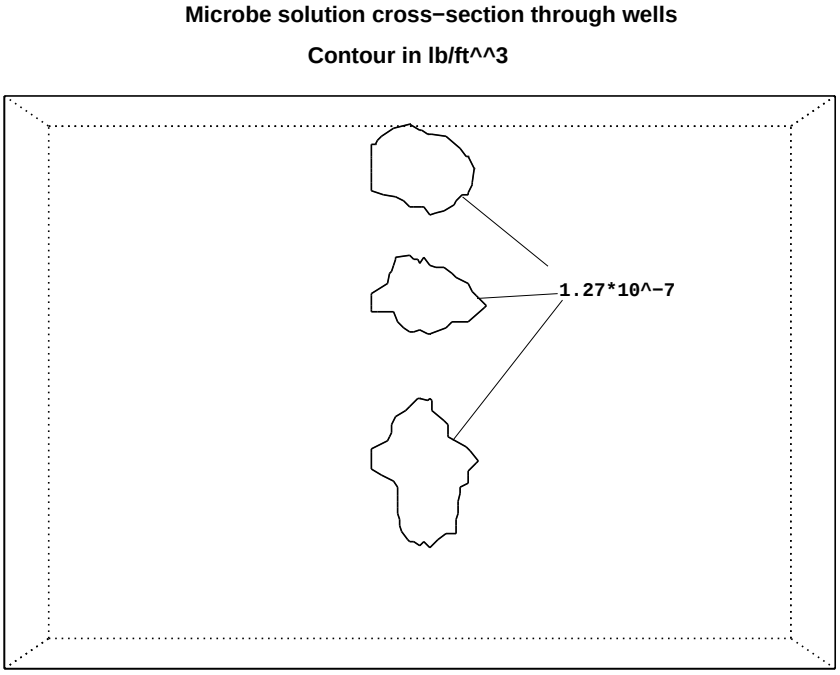

Fig. 5. Microbe solution at 7.5 days.

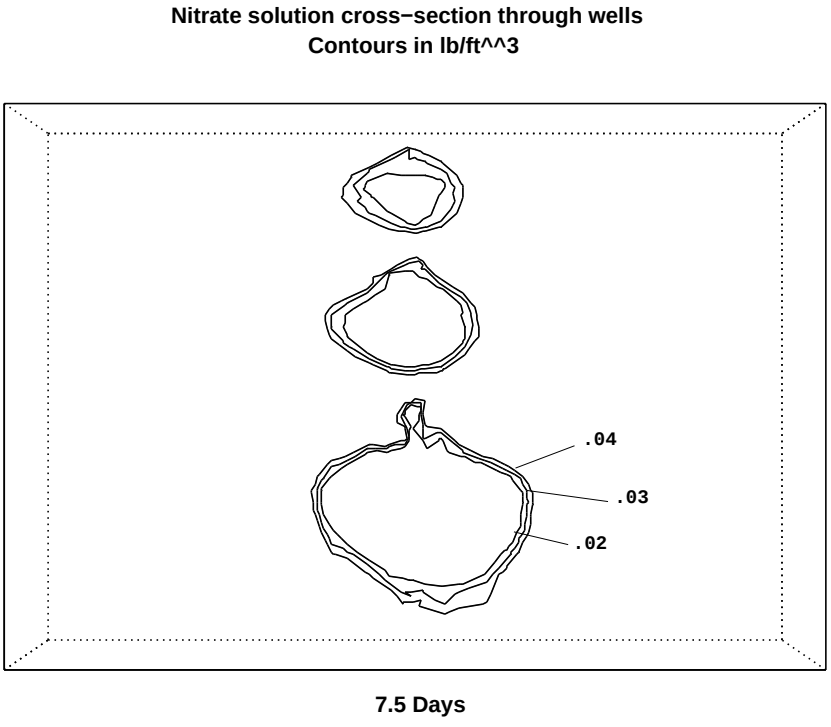

Fig. 6. Nitrate solution at 7.5 days.

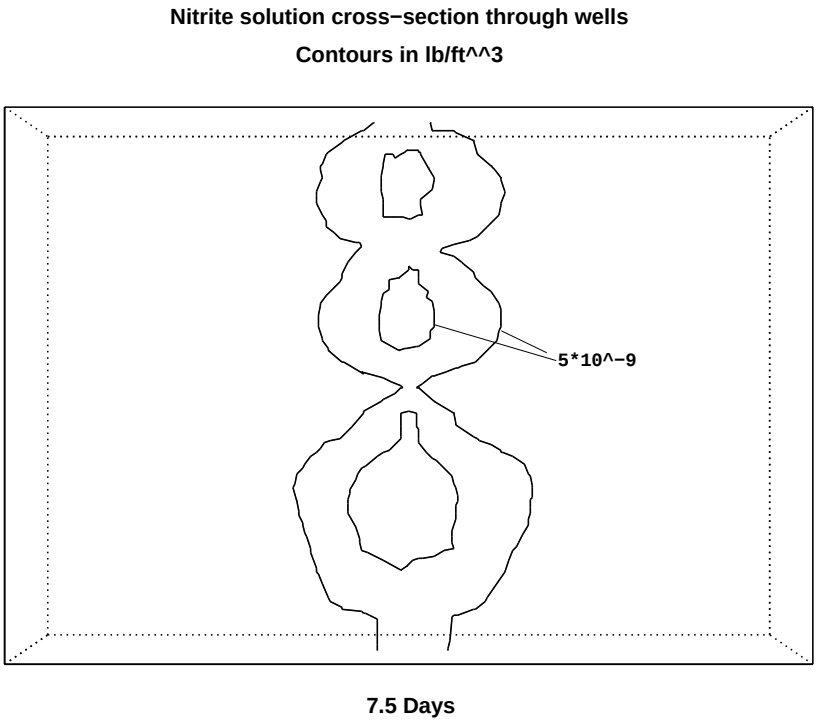

Fig. 7. Nitrite solution at 7.5 days.

testing and development of robust differential algebraic solvers for the equilibrium and nonequilibrium reactions and mass transfer.

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