WATER RESOURCES RESEARCH, VOL. 25, NO. 6, PAGES 1141–1148, JUNE 1989

Contaminant Transport and Biodegradation
A Numerical Model for Reactive Transport in Porous Media

MICHAEL A. CELIA

Department of Civil Engineering, Massachusetts Institute of Technology, Cambridge

J. SCOTT KINDRED

Golder Associates Inc., Redmond, Washington

ISMAEL HERRERA

Instituto de Geofisica, National Autonomous University of Mexico, Mexico City

A new numerical solution procedure is presented for simulation of reactive transport in porous media. The new procedure, which is referred to as an optimal test function (OTF) method, is formulated so that it systematically adapts to the changing character of the governing partial differential equation. Relative importance of diffusion, advection, and reaction are directly incorporated into the numerical approximation by judicious choice of the test, or weight, function that appears in the weak form of the equation. Specific algorithms are presented to solve a general class of nonlinear, multispecies transport equations. This includes a variety of models of subsurface contaminant transport with biodegradation.

1. INTRODUCTION

A proper description of contaminant transport is important in many aqueous systems. For subsurface flows, description of the flow physics must often be augmented by chemical and/or biological considerations. This generally leads to advective–diffusive–reactive transport equations. When multiple species are present in the aqueous phase, the governing equations form a set of partial differential equations that are coupled through reaction terms. These equations generally need to be solved numerically.

The transport equation is one for which numerical solution procedures continue to exhibit significant limitations for certain problems of physical interest. The most widely cited example is the case of advection domination. In this case, one is usually forced to choose between nonphysical oscillations or excessive (numerical) diffusion. While a variety of methods have been developed specifically for advection-dominated flows [*Leonard*, 1979; *Hughes and Brooks*, 1982; *Tezduyar and Ganjoo*, 1986; *Baptista*, 1987], only partial success can be reported to date.

A key to providing reliable numerical simulations is recognition of the changing nature of the governing equation. Diffusion domination implies behavior analogous to that predicted by model parabolic partial differential equations; advection domination implies behavior analogous to first-order hyperbolic partial differential equations; and reaction domination implies first-order ordinary differential equation (in time) behavior. A numerical procedure that fails to accommodate these disparate behaviors cannot be expected to produce reliable numerical solutions.

Paper number 89WR00271.
0043-1397/89/89WR-00271$05.00

The recent work of *Herrera* [1984, 1985*a*, *b*], *Herrera et al.* [1985], and *Celia et al.* [1989*a*] provides a systematic framework in which numerical solutions to general second-order equations can be obtained. The procedure leads to numerical approximations that automatically change as the governing partial differential equation changes. This is achieved by choosing test functions, which are present in a weak form of the original governing equation, to satisfy specific, rigorously derived criteria. No arbitrary parameters are involved. It is the purpose of this paper to develop a solution algorithm, based on this procedure, for systems of advective–diffusive–reactive transport equations. In a companion paper [*Kindred and Celia*, this issue] the methodology is applied to a specific model of transport in biologically reactive porous media.

The presentation in this paper begins by exposing the underlying numerical algorithm for the case of a single advective–diffusive–reactive transport equation with constant coefficients. This allows the salient features of the method to be explained in a simple mathematical setting. The procedure is then extended to the case of spatially variable coefficients, and finally to the case of multiple equations that are coupled through nonlinear reaction terms. Example calculations are presented to demonstrate the numerical procedure and to provide a direct link to the biodegradation model that is developed in the companion paper [*Kindred and Celia*, this issue].

. NUMERICAL ALGORITHM—SINGLE SPECIES TRANSPORT WITH CONSTANT COEFFICIENTS

The numerical development begins by examining a single species, advective–diffusive–reactive transport equation

$$R\,\partial u/\partial t + V\,\partial u/\partial x - D\,\partial^2 u/\partial x^2 + Ku = f(x, t) \qquad (1)$$

$$0 \leq x \leq L \qquad t > 0$$

$$u(0, t) = g_0 \qquad t > 0$$

$$\partial u/\partial x(L, t) = g_L \qquad t > 0$$

$$u(x, 0) = u_0(x) \qquad 0 \leq x \leq L$$

defined over the finite spatial domain $\Omega \equiv [0, L]$. Any boundary conditions can be accommodated in the numerical algorithm; the conditions given above provide a typical example. Nomenclature is such that R is a retardation coefficient (dimensionless); V is fluid velocity (L/T); D is a diffusion coefficient (L^2/T); K is a first-order reaction coefficient ($1/T$); f is a given forcing function; and $u(x, t)$ is the dependent scalar of interest, which in this case is a measure of concentration of a dissolved substance. The forcing function $f(x, t)$ is a source/sink term that may include reaction terms that are not dependent on the unknown function u. To begin the numerical development, let the coefficients R, V, D, and K be assumed constant. The numerical procedure that is to be applied to (1) consists of application of the algebraic theory of *Herrera* [1984, 1985*a*, *b*] in space, thereby producing a semidiscrete system of ordinary differential equations in time. This resulting set of ordinary differential equations is then integrated in time using standard methods.

Let (1) be rewritten in the form

$$\mathcal{L}_x u \equiv D\,\partial^2 u/\partial x^2 - V\,\partial u/\partial x - Ku = R\,\partial u/\partial t - f(x, t) \qquad (2)$$

where the operator $\mathcal{L}_x$ incorporates both the spatial derivatives and the reaction term. The weak form of (2) is then formed by multiplying the equation by a weight, or test, function, $w(x)$, and integrating over the domain $[0, L]$

$$\int_0^L (D\,\partial^2 u/\partial x^2 - V\,\partial u/\partial x - Ku)w(x)\,dx = \int_0^L (R\,\partial u/\partial t - f)w(x)\,dx \qquad (3)$$

Next, let the spatial domain $[0, L]$ be subdivided into E subintervals $\{[x_0, x_1], [x_1, x_2], \cdots, [x_{E-1}, x_E]\}$, with $x_0 = 0$, $x_E = L$. These subintervals, or elements, are separated by the $E + 1$ node points $\{x_0, x_1, \cdots, x_E\}$. If the solution u is assumed to be at least $\mathbb{C}^1$ continuous, $u \in \mathbb{C}^1[0, L]$(that is, u and $\partial u/\partial x$ are continuous functions over $0 \leq x \leq L$), and $w(x)$ is at least $\mathbb{C}^{-1}$ continuous, $w \in \mathbb{C}^{-1}$ $[0, L]$ (that is, $\int_0^x w(x')\,dx'$ is a continuous function over $0 \leq x \leq L$), then the integral on the left side of (3) can be written equivalently as

$$\int_0^L (D\,\partial^2 u/\partial x^2 - V\,\partial u/\partial x - Ku)w(x)\,dx = \sum_{j=0}^{E-1} \int_{x_j}^{x_{j+1}} (D\,\partial^2 u/\partial x^2 - V\,\partial u/\partial x - Ku)w(x)\,dx \qquad (4)$$

The equality (4), which introduces elementwise integration, is permissible due to the continuity constraints on u and w. The case of lower continuity on u has been treated by *Herrera* [1984, 1985*a*, *b*]; for the present development, $u \in \mathbb{C}^1$ will suffice. Also, let any discontinuities that occur in $w(x)$ be restricted to node points. Within each $[x_j, x_{j+1}]$, it is assumed that $w(x) \in \mathbb{C}^2$.

The first key to the numerical procedure is application of integration by parts twice to each term of the summation in (4). For each element integration, the first integration by parts produces

$$\int_{x_j}^{x_{j+1}} (\mathcal{L}_x u)w(x)\,dx = \int_{x_j}^{x_{j+1}} \left(D\frac{\partial^2 u}{\partial x^2} - V\frac{\partial u}{\partial x} - Ku\right)w\,dx = \left[D\frac{\partial u}{\partial x}w - Vuw\right]_{x_j}^{x_{j+1}} + \int_{x_j}^{x_{j+1}} \left(-D\frac{\partial u}{\partial x}\frac{dw}{dx} + Vu\frac{dw}{dx} - Kuw\right)dx$$

Application of an additional integration by parts then yields

$$\int_{x_j}^{x_{j+1}} (\mathcal{L}_x u)w\,dx = \left[D\frac{\partial u}{\partial x}w - Du\frac{dw}{dx} - Vuw\right]_{x_j}^{x_{j+1}} + \int_{x_j}^{x_{j+1}} \left(D\frac{d^2 w}{dx^2} + V\frac{dw}{dx} - Kw\right)u\,dx$$

$$= \left[D\frac{\partial u}{\partial x}w - Du\frac{dw}{dx} - Vuw\right]_{x_j}^{x_{j+1}} + \int_{x_j}^{x_{j+1}} (\mathcal{L}_x^* w)u\,dx \qquad (5)$$

where $\mathcal{L}_x$ is the original spatial operator and $\mathcal{L}_x^*$ is its formal adjoint.

The second key to the numerical procedure is to recognize that the original integral (on the left side) of (5) can be replaced by nodal evaluations by choosing $w(x)$ such that $\mathcal{L}_x^* w = 0$ within each $[x_j, x_{j+1}]$. That is to say, proper choice of the test function $w(x)$ effectively concentrates information at node points and eliminates interior element integrations. In addition, the concentration of information at node points is accomplished in the absence of any trial function definition (as would be the case in a standard finite element formulation). Both the special choice of test function and the lack of a trial function distinguish this numerical formulation from standard finite element or Petrov-Galerkin methods.

Consider a choice of $w(x)$ that satisfies $\mathcal{L}_x^* w = 0$ within each $[x_j, x_{j+1}]$, $j=0, 1, \cdots, E-1$. Furthermore, allow $w(x)$ the ability to exhibit discontinuities at node points. Given such a definition of $w(x)$, (4) and (5) can be combined and restated in terms of known coefficients and unknown nodal values of the dependent variable. In light of (5) and the fact that $\mathcal{L}_x^* w = 0$, (4) can be rewritten as

$$\sum_{j=0}^{E-1} \int_{x_j}^{x_{j+1}} (\mathcal{L}_x u)w\,dx = \sum_{j=0}^{E-1} \left\{\left[\left(-D\frac{dw}{dx} - Vw\right)u + (Dw)\frac{\partial u}{\partial x}\right]_{x_j}^{x_{j+1}}\right\}$$

$$= \sum_{j=1}^{E-1} \left\{\left[D\frac{dw}{dx} + Vw\right]_{x_j} u_j - [[Dw]]_{x_j}\frac{\partial u}{\partial x}j\right\} + \left[\left(-D\frac{dw}{dx} - Vw\right)u + Dw\frac{\partial u}{\partial x}\right]_0^L \qquad (6)$$

In (6), the double bracket denotes a jump operator, which is defined by $[[\cdot]]_{x_j} \equiv \lim_{\varepsilon \to 0} [(\cdot)_{x_j+\varepsilon} - (\cdot)_{x_j-\varepsilon}]$. Since D, V, and

w are are all known, the only unknowns in (6) are the $2E$ + 2 nodal values $\{u_j, (\partial u/\partial x)_j\}_{j=0}^{E}$. These nodal values correspond to the function u and its spatial derivative. These values are unique at each node by the continuity assumption $u \in \mathbb{C}^1[0, L]$. Equation (6) can be written more succinctly as a simple linear combination of known coefficients and unknown nodal values

$$\int_0^L (\mathcal{L}_x u)w \, dx = \sum_{j=0}^{E} A_j u_j + B_j \frac{\partial u}{\partial x} j \qquad (6')$$

For the operator $\mathcal{L}_x$ of (2), the formal adjoint operator is, according to (5),

$$\mathcal{L}_x^* \equiv D d^2/dx^2 + V d/dx \quad K \qquad (7)$$

The homogeneous solutions corresponding to $\mathcal{L}_x^*$ are given by

$$\Psi_1(x) = \exp[(\alpha + \beta)x] \qquad (8a)$$

$$\Psi_2(x) = \exp[(\alpha - \beta)x] \qquad (8b)$$

where $\alpha \equiv -V/2D$ and $\beta \equiv (1/2D)(V^2 + 4KD)^{1/2}$. Equations (8$a$) and (8$b$) represent the two fundamental solutions of the homogeneous adjoint equation. Any linear combination of these solutions also satisfies the homogeneous adjoint equation. The computational procedure proposed herein uses as test functions two nonzero solutions to $\mathcal{L}_x^* w = 0$ defined in each element and formed as linear combinations of solutions (8a) and (8b). These functions are defined such that they are nonzero only within the element of interest, and zero in all other elements. As such, each $w(x) \in \mathbb{C}^{-1}[0, L]$. For any element e, defined by $[x_j, x_{j+1}]$, the test functions are defined by

$$w_1^e(x) = C_{11} \exp[(\alpha + \beta)x] + C_{12} \exp[(\alpha - \beta)x] \qquad (9a)$$

$$x_j < x < x_{j+}$$

$$w_1^e(x) = 0 \qquad x < x_j \quad x > x_{j+}$$

$$w_2^e(x) = C_{21} \exp[(\alpha + \beta)x] + C_{22} \exp[(\alpha - \beta)x] \qquad (9b)$$

$$x_j < x < x_{j+}$$

$$w_2^e(x) = 0 \qquad x < x_j \quad x > x_{j+1}$$

The constants C_{11}, C_{12}, C_{21}, and C_{22}, are chosen, for convenience, to satisfy the conditions $w_1^e(x_j) = 1$, $w_1^e(x_{j+1}) = 0$, $w_2^e(x_j) = 0$, and $w_2^e(x_{j+1}) = 1$. Therefore $C_{11} = -\exp[-(\alpha+\beta)x_j - 2\beta(\Delta x)]/\{1-\exp[-2\beta(\Delta x)]\}$, $C_{12} = \exp[-(\alpha-\beta)x_j]/\{1-\exp[-2\beta(\Delta x)]\}$, $C_{21} = -\exp[-(\alpha-\beta)x_{j+1} - 2\beta x_j]/\{1-\exp[2\beta(\Delta x)]\}$, and $C_{22} = \exp[-(\alpha-\beta)x_{j+1}]/\{1-\exp[2\beta(\Delta x)]\}$, with $\Delta x \equiv x_{j+1} - x_j$. Any other linear combination of the fundamental solutions (8) would be equally acceptable. Since there are E elements, $2E$ equations are produced corresponding to the $2E$ linearly independent test functions, $\{w_1^e(x), w_2^e(x)\}_{e=1}^{E}$. The undetermined nodal values that appear in (5) are the function u and the spatial derivative $\partial u/\partial x$, forming the set of $2E+2$ unknowns $\{u_j, (\partial u/\partial x)_j\}_{j=0}^{E}$. Two boundary conditions provide the two additional equations needed to close the system.

For steady state conditions, $\partial u/\partial t = 0$ and (1) reduces to an ordinary differential equation. After evaluation of the right side forcing term $\int_0^L f(x)w(x)\,dx$ and imposition of the two boundary conditions, $2E+2$ linear algebraic equations result for the $2E+2$ nodal unknowns. Solution of this set of equations produces exact nodal values, since no approximation has been introduced, and the set of test functions is T complete [see *Herrera*, 1984]. Detailed algorithms for the case of constant coefficient, ordinary differential equations are presented by *Herrera et al.* [1985].

When $\partial u/\partial t \neq 0$, the time dimension must be included. Examination of (3) indicates that a spatial integral of the product of $(\partial u/\partial t)(x,t)$ and $w(x)$ must be evaluated. To perform this integration, $\partial u/\partial t$ is approximated using a polynomial expansion that involves the nodal values appearing in the expression on the right side of (6). The natural choice for the approximation developed above is a piecewise cubic Hermite polynomial interpolation in space, since this involves nodal values of u and $\partial u/\partial x$, namely,

$$\partial u/\partial t \simeq \partial \hat{u}/\partial t \equiv \sum_{j=0}^{E} \{U_j(t)\phi_{0j}(x) + (\partial U/\partial x)_j(t)\phi_{1j}(x)\} \qquad (10)$$

In (10), $\{U_j, (\partial U/\partial x)_j\}_{j=0}^{E}$ are time-dependent nodal values of function and spatial derivative, and ϕ_{0j}, ϕ_{1j} are standard cubic Hermite polynomials (see, for example, *Carey and Oden* [1983, pp. 63–65]). Substitution of expansion (10) into the integral of interest yields

$$\int_0^L \frac{\partial u}{\partial t} w \, dx \simeq \sum_{j=0}^{E} \left\{ \frac{d}{dt}[U_j(t)] \int_0^L \phi_{0j}(x)w(x)\,dx + \frac{d}{dt}\left[\frac{\partial U_j}{\partial x}(t)\right] \int_0^L \phi_{1j}(x)w(x)\,dx \right\} \qquad (11)$$

Given that $\phi_{0j}(x)$, $\phi_{1j}(x)$, and $w(x)$ are each well defined and known functions, the integrals can be evaluated directly and (11) can be written, with inclusion of the coefficient R, as

$$R \int_0^L \frac{\partial u}{\partial t} w(x)\,dx \simeq \sum_{j=0}^{E} \left\{ \alpha_j \frac{d}{dt}(U_j) + \beta_j \frac{d}{dt}\left(\frac{\partial U_j}{\partial x}\right) \right\} \qquad (11')$$

Thus the resulting approximation that derives from (11), (6), and (3) is

$$\sum_{j=0}^{E} \left\{ \alpha_j \frac{d}{dt}(U_j) + \beta_j \frac{d}{dt}\left(\frac{\partial U_j}{\partial x}\right) - A_j U_j - B_j \frac{\partial U_j}{\partial x} \right\} = \int_0^L f(x,t)w(x)\,dx \qquad (12)$$

An equation of the form of (12) is written for each of the $2E$ choices of $w(x)$ given in (9). The two boundary conditions required for the second-order equation (1) provide two additional equations, so that $2E+2$ equations result for the $2E+2$ nodal values. This provides the semidiscrete system of equations

$$\mathbf{P} \cdot d\mathbf{U}/dt - \mathbf{Q} \cdot \mathbf{U} = \mathbf{F} \qquad (13)$$

where matrix $\mathbf{P}$ contains the α_j, β_j coefficients of (11), $\mathbf{Q}$ contains the coefficients A_j, B_j of (6), and the vector $\mathbf{U}$ contains nodal values of U and $\partial U/\partial x$. The structure of the coefficient matrices $\mathbf{P}$ and $\mathbf{Q}$ is exactly analogous to that of standard cubic Hermite collocation. This structure is illus-

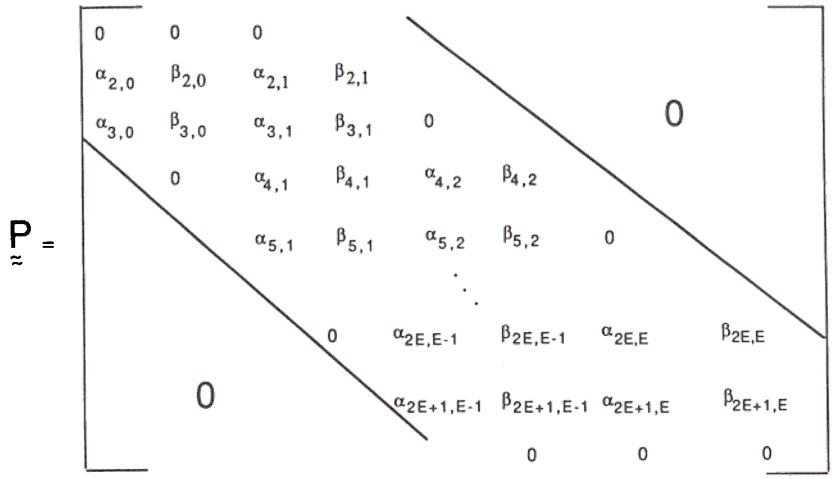

Fig. 1. Typical five-diagonal matrix structure. Matrix P of (13) is shown. Matrix Q has the same structure. First and last rows correspond to boundary conditions.

trated in Figure 1. Computational requirements for this optimal test function (OTF) method are very similar to those for Hermite collocation algorithms.

Equation (13) can be solved by any time integrator of choice. A simple scheme is the variably weighted Euler method.

$$\mathsf{P} \cdot (\mathbf{U}^{n+1} - \mathbf{U}^n)/\Delta t - \mathsf{Q} \cdot [\theta \mathbf{U}^{n+1} + (1-\theta)\mathbf{U}^n] = \mathbf{F}^{n+\theta} \tag{14a}$$

or

$$[(1/\Delta t)\mathsf{P} - \theta \mathsf{Q}] \cdot \mathbf{U}^{n+1} = [(1/\Delta t)\mathsf{P} + (1-\theta)\mathsf{Q}] \cdot \mathbf{U}^n + \mathbf{F}^{n+\theta} \tag{14b}$$

where θ is a weighting parameter, usually taken as $0 \leq \theta \leq 1$. Imposition of the initial conditions and subsequent marching through time yields the discrete approximation of interest.

This development, for both steady state and transient cases, requires the equation to be second order in space, that is, $D \neq 0$. If the equation is purely advective, then solution of the homogeneous adjoint operator equation is no longer given by (8), and the entire development must be reformulated. This is consistent with the formal change from a parabolic to a hyperbolic equation. While the procedure for pure advection is analogous to that presented above, the present formulation only considers the case of $D \neq 0$.

3. Optimal Test Functions

The choice $w(x)$ given by (9) derives from a rigorous and exact mathematical treatment of the spatial operator in the governing equation. The test functions reflect all of the physical processes that are described by the governing differential operator. Furthermore, the formulas of (9) indicate that the test functions respond automatically to changes in the coefficients D, V, and K. Figure 2 illustrates three different sets of functions, one each for the cases of diffusion domination, advection domination, and reaction domination. When diffusion dominates, the functions approach piecewise linear forms (analogous to finite element "hat" functions, although the current functions are fully discontinuous). Since diffusion is a symmetric process that has spatial coupling, these functions are seen to correspond to the dominant physical process. When advection dominates, the functions exhibit an upstream bias. This corresponds to the physically asymmetric process of advective transport. The amount of the upstream bias, or "upstream weighting," is directly related to the parameters of the governing equation and involves no arbitrary parameters or coefficients. This is in contrast to traditional upstream finite difference or finite element methods, wherein the degree of upstreaming is generally related to an arbitrary parameter. Finally, when reaction dominates, the functions are weighted toward the nodes, and spatial coupling is diminished. This is consistent with the spatial derivatives in the governing equation being unimportant, and the point process (in space) of the first-order reaction being dominant.

This automatic shifting of the test functions in accordance with the physics inherent in the governing partial differential equation implies a certain optimality of the test functions. Examination of the equality of (5) reinforces the optimality claim in the sense that the differential equation is written in

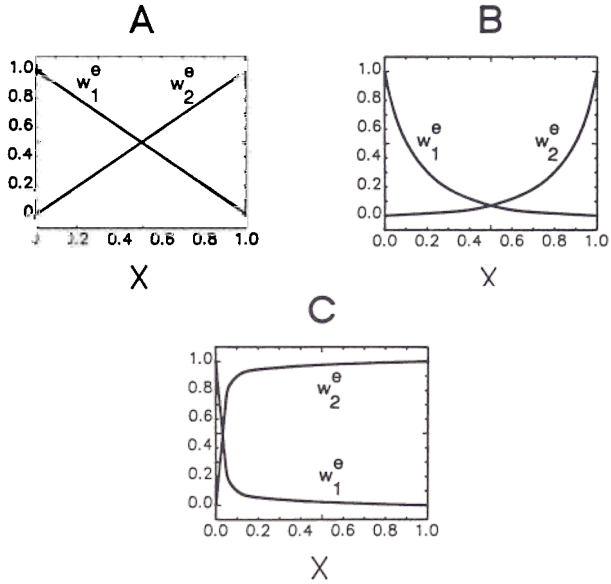

Fig. 2. Typical test functions, plotted over one element for the cases of (*a*) diffusion domination, (*b*) reaction domination, and (*c*) advection domination.

terms of nodal values in a mathematically precise way. Furthermore, optimal accuracy occurs for steady state equations in both one dimension (exact nodal solutions for equation (1) when $R = 0$) and two dimensions (see Discussion in section 8). The numerical algorithm presented above is therefore referred to as an OTF method.

4. Treatment of Nonconstant Coefficients

When the coefficients in (1) exhibit spatial variability, it is generally not possible to exactly satisfy the homogeneous adjoint equation, $\mathcal{L}_x^* w = 0$. In this case, an approximation procedure is required to provide good estimates to w, so that $\mathcal{L}_x^* w \simeq 0$.

Two approaches have been developed to treat the variable coefficient case. The first, which is used herein, involves replacement of the coefficients in (1) with piecewise Lagrange polynomials. The approximate coefficients have different polynomial definitions in each element and are generally discontinuous across element boundaries. The basic idea is that with these approximate coefficients, the adjoint equation is simply an ordinary differential equation with polynomial coefficients. As such, two independent series solutions can be developed for the homogeneous adjoint equation using standard techniques (see, for example, *Hildebrand* [1976]). *Celia and Herrera* [1987] have shown that through judicious choice of interpolation points within each element, piecewise nth degree Lagrange interpolants can provide $0((\Delta x)^{2n+2})$ accuracy in the numerical solution. The arguments used to develop this theory are analogous to those used to choose collocation point locations in the collocation finite element method (see, for example, *Prenter* [1975]). The interpolation points in the OTF method, and the collocation points in the collocation finite element method, both turn out to be the Gauss-Legendre integration points within each element [*Celia and Herrera*, 1987]. An alternative approach for developing test functions uses a local (elementwise) collocation solution for the homogeneous adjoint equation. This again yields two independent solutions for $w(x)$ within each element. Details of this local collocation procedure are provided by *Herrera* [1987].

For the current treatment, consider approximation of the coefficients by piecewise constants. That is, the coefficients are constant within each element and can change from one element to the next. Since $\mathcal{L}_x^* w = 0$ within each element separately, the adjoint equation in any element involves constant coefficients. Therefore simple analytical solutions can be obtained for the test functions. By the error estimate cited above, this provides $0((\Delta x)^2)$ accuracy in the approximation. If $D(x)$, $V(x)$, and $K(x)$ are replaced by $\bar{D}(x)$, $\bar{V}(x)$, and $\bar{R}(x)$, with overbarred quantities referring to piecewise constant approximations, then the test functions remain as defined in (9) with D, V, and K, interpreted to be the values within the element of interest.

5. Treatment of Nonlinear Equations

When the governing partial differential equation is nonlinear, some linearization technique must be applied to allow for tractable numerical solution. This is true of any numerical approximation, including the optimal test function method. The linearization may or may not involve iteration, depending on the severity of the nonlinearity and the preference of the analyst.

For the optimal test function method, a linearization is performed prior to derivation of the adjoint operator. For an equation of the form of (1), where the coefficients are functions of the unknown u, linearization involves evaluation of the coefficients using previous (known) values of the solution. These can be values of previous iterations or values at previous time steps. In either case, the linearized governing equation is analogous to a variable coefficient problem. Techniques discussed in the previous section therefore pertain.

Linearization can take one of several forms. For time marching problems, nonlinear coefficients can be estimated from solutions at previous time steps, allowing for solution at the new time level exclusive of iteration. Conversely, progressively improved solutions at the new time level can be obtained through iterative solution procedures. These iterative procedures include simple (Picard) iteration, Newton-Raphson iteration, and various modifications of each. The linearization that is chosen herein for the case of nonlinear reactive transport uses a noniterative time marching algorithm coupled with a second-order projection technique for estimating the nonlinear coefficients. Estimates of nonlinear coefficients are based on solutions at the previous two time levels. For a time weighting parameter θ, as used in (14), the appropriate projected value is given by

$$u^{n+\theta} \simeq (1+\theta)u^n - \theta u^{n-1} \tag{15}$$

This is a second-order (in time) estimate for $u^{n+\theta}$. This very simple linearization was chosen because of the relatively mild nonlinearities and the very good numerical results that were subsequently produced. As stated previously, application of the optimal test function method is indifferent to the linearization chosen; OTF is applicable to any linearization procedure.

6. Sets of Coupled Equations–Reactive Transport of Multiple Species

Mathematical description of transport of multiple species in flowing groundwater involves a set of coupled, advective–diffusive–reactive transport equations. Depending on the nature of both the flow system and the chemical or biological reactions, different forms of equations pertain. *Rubin* [1983] provided a detailed overview of various types of chemical reactions and their concomitant mathematical descriptions. *Kindred and Celia* [this issue], in a companion to this paper, discuss biologically reactive media and its related mathematical description.

The set of transport equations chosen for the current presentation has the following form:

$$\frac{\partial c_1}{\partial t} + V_1 \frac{\partial c_1}{\partial x} - D_1 \frac{\partial^2 c_1}{\partial x^2} + K_1(c_1, \cdots, c_N, X_1, \cdots, X_M)c_1 = f_1(c_1, \quad , c_N, X_1,$$

$$\frac{\partial c_2}{\partial t} + V_2 \frac{\partial c_2}{\partial x} - D_2 \frac{\partial^2 c_2}{\partial x^2} + K_2(c_1, \cdots, c_N, X_1, \quad \cdot, X_M)c_2 = f_2(c \quad \cdots, c_N, X_1, \cdots, X_M) \tag{16a}$$

$$\frac{\partial c_N}{\partial t} + V_N \frac{\partial c_N}{\partial x} - D_N \frac{\partial^2 c_N}{\partial x^2} + K_N(c_1, \cdot \quad, c_N, X_1, \cdots, X_M)c_N = f_N(c_1, \quad , c_N, X_1, \quad , X_M)$$

$$\frac{\partial X_1}{\partial t} + G_1(c_1, \quad , c_N, X_1, \quad X_M)X_1$$

$$= F_1(c_1, \quad , c_N, X_1, \quad , X_M) \qquad (16b)$$

$$\frac{\partial X_M}{\partial t} + G_M(c_1, \quad c_N, X_1, \quad X_M)X_M$$

$$= F_M(c \quad c_N, X_1, \quad , X_M)$$

In (16), $c_1, c_2, \cdots, c_N$ are measures of aqueous concentrations of N dissolved species, each of which is hydrodynamically transported and has the ability to react with other constituents. The variables $X_1, X_2, \cdots, X_M$ are concentration measures of reactive species that are stationary. This set of equations is taken to generally correspond to various models of biodegradation discussed by *Kindred and Celia* [this issue]. The present objective is to describe the overall numerical algorithm proposed to solve the set (16). *Kindred and Celia* [this issue] provide derivation and physical motivation for the equation forms as well as additional computational details.

The solution procedure adopted herein utilizes the optimal test function concepts developed in the earlier sections of this paper. To proceed from one time step to the next, a simple, noniterative linearization is employed. Equation (15) is used to provide required estimates of the solution for evaluation of the nonlinear reaction coefficients and forcing functions. The projection is applied to each c_i, $i=1, 2, \cdots, N$, as well as each X_i, $i=1, 2, \cdots, M$. Let the projected values be denoted with an asterisk. The linearized version of (16) is thus written

$$\frac{\partial c_i}{\partial t} + V_i \partial c_i/\partial x - D_i \partial^2 c_i/\partial x^2 + K_i(c_1^*, \quad , c_N^*, X_1^*, \quad X_M^*)c_i$$

$$= f_i(c_1^*, \quad c_N^*, X_1^*, \quad X_M^*) \qquad (17a)$$

$$\partial X_i/\partial t + G_i(c_1^*, \quad c_N^*, X_1^*, \quad X_M^*)X_i$$

$$= F_i(c_1^*, \cdots, c_N^*, X_1^*, \cdots, X_M^*) \qquad (17b)$$

These equations are used to move from the level n to $n+1$. Given known values c_i^*, X_i^* each K_i, G_i, f_i, and F_i are known functions of space. These spatially variable coefficients are next approximated by piecewise constants, with each coefficient taken as constant within any element. Given these piecewise constant values, the adjoint operator is obtained for each element. Homogeneous solutions of the adjoint equation are subsequently obtained and used as test function in the optimal test function algorithm. Each transport equation has its own set of test functions, and each equation is solved separately.

The equations for $X_i(x, t)$ have no spatial derivatives, implying no coupling in space. As such, these equations are solved for each node in space, with no coupling between nodes. Linearization is again based on the projection technique of (15). Use of constant values of G_i and F_i over a time step, based on the values c_i^*, X_i^*, allows (17b) to be solved analytically.

7. EXAMPLE CALCULATIONS

Several example calculations are presented to demonstrate the viability of OTF methods for advective–diffusive–reactive transport systems. A variety of problems related specifically to biodegradation are solved in the companion paper [*Kindred and Celia*, this issue] using the techniques developed herein. Additional test problems for the specific case of advection dominated, nonreactive transport are reported by *Celia et al.* [1989*a*]. *Bouloutas and Celia* [1988] provide an in-depth numerical analysis of a related OTF algorithm for nonreactive transport of a single species.

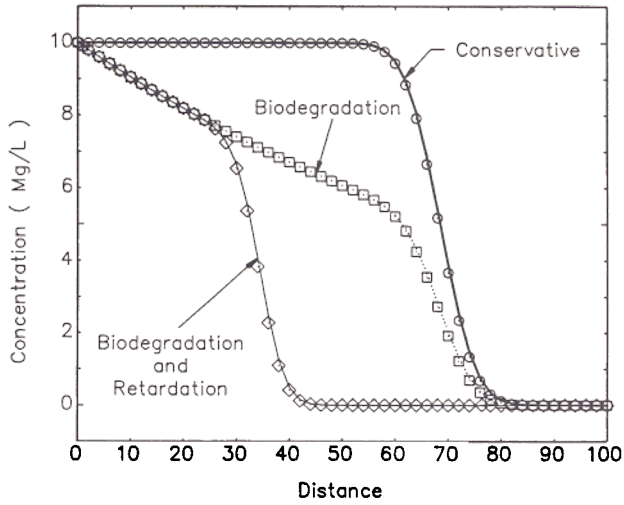

Fig. 3. Comparison of numerical solutions to analytical solutions. Solid curves indicate OTF numerical solutions; symbols indicate analytical solution values.

7.1. *Comparison to Analytical Solutions*

Equation (1), with constant coefficients, is solved for several different combinations of the coefficients. Three cases are considered: (1) $R = 1$, $K = 0$; (2) $R = 1$, $K = 0.01$; and (3) $R = 2$, K = 0.01. Each case uses $V = 1.0$, $D = 0.2$, $f(x,t) = 0.0$, and $\Delta x = 2.0$, implying a grid Peclet number of 10. Initial conditions are fixed as $u_0(x) = 0$, and boundary conditions are $g_0 = 10$, $g_L = 0$. Figure 3 shows numerical results for each case, as well as the respective analytical solutions. Agreement is excellent in each case. Numerical mass balance errors are less than 1% for the first two solutions and approximately 1.5% for the third solution.

7.2. *Two-Species Transport*

A second example is presented that involves transport of two species, coupled through the reaction terms. One stationary component is included, but it is assumed to be temporally static. One physical analogy for this system is transport of two substrates in the presence of a stationary biological population. Dissolved species might be an organic contaminant and dissolved oxygen, leading to an aerobic biodegradation transport problem. Simulations that include temporal dynamics of the stationary species are included in the work by *Kindred and Celia* [this issue].

Governing equations for this system take the form

$$\partial c_1/\partial t + V\, \partial c_1/\partial x - D\, \partial^2 c_1/\partial x^2 + K_1(c_1, X_1)c_1 = f_1(c_2, X_1)$$

$$\partial c_2/\partial t + V\, \partial c_2/\partial x - D\, \partial^2 c_2/\partial x^2 + K_2(c_2, X_1)c_2 = f_2(c_1, X_1)$$

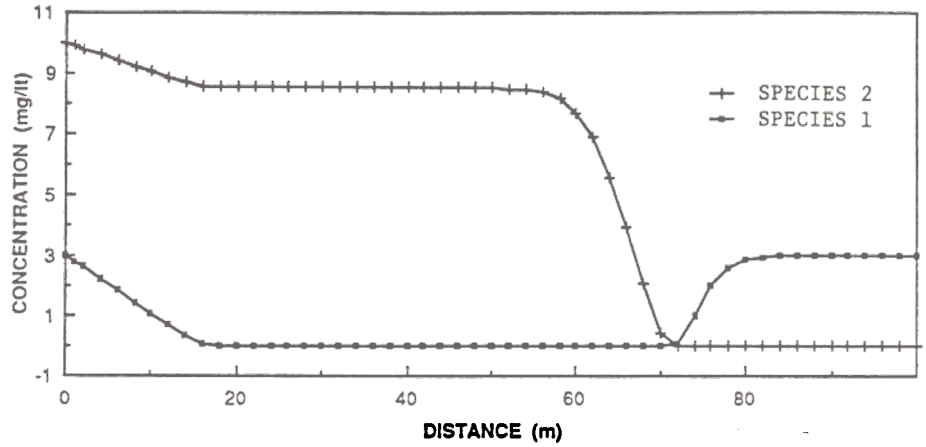

Fig. 4. Numerical solution of (18) and (19) using OTF. Solutions are plotted at time t = 68 days.

Specific functional forms for the nonlinear coefficients are chosen, based on the analogy to biodegradation, as follows:

$$K_1(c_1, X_1) = (V_m^1 X_1/(K_h^1 + c_1))\delta_1 \quad (19a)$$

$$K_2(c_2, X_1) = (V_m^2 X_1/(K_h^2 + c_2))\delta_2 \quad (19b)$$

$$f_1(c_2, X_1) = -\kappa_{12}(V_m^2 X_1/(K_h^2 + c_2))\delta_2 c_2 = -\kappa_{12} K_2 c_2 \quad (19c)$$

$$f_2(c_1, X_1) = -\kappa_{21}(V_m^1 X_1/(K_h^1 + c_1))\delta_1 c_1 = -\kappa_{21} K_1 c_1 \quad (19d)$$

where physical interpretations are that V_m^i is the maximum uptake rate for species i, K_h^i, the half-saturation constant for species i, κ_{ij} is the yield ratio coefficient for species i when species j is limiting, and δ_i is equal to 1 if species i is limiting the reactions and zero otherwise. Species 1 and 2 are assumed to react in a fixed ratio; this is reflected in the coefficients κ_{ij}. Equations (18) allow either of the species to be limiting. There is no bacterial growth in this equation (G_1 = 0), so the stationary species has a fixed value X_1. Derivation and discussion of these equations is provided in the companion paper [*Kindred and Celia*, this issue].

Parameter values are assigned as follows: V_m^i = 1.0 days^{-1}, i = 1, 2; K_h^i = 0.1 mg/L, i = 1, 2; κ_{12} = 2.0, κ_{21} = 0.5. Initial conditions are $c_1(x, 0) = 3.0$, $c_2(x, 0) = 0.0$. Imposed boundary conditions are $c_1(0, t) = 3.0$, $c_2(0, t) = 10.$, $\partial c_1/\partial x\,(L, t) = \partial c_2/\partial x\,(L, t) = 0$, where L = 100 m. The stationary species is fixed at X_1 = 0.2 mg/L. Flow parameters are V = 1.0 m/day and D = 0.2 m^2/day. The system described by these parameters corresponds to a step introduction of species c_2 at the left boundary. This propagates into the domain by advection and diffusion. Its presence instigates uptake of both species 1 and 2. Figure 4 shows plots of concentration as a function of distance for time t = 68 days, for both species 1 and 2, calculated using the OTF algorithm with grid spacing Δx = 2 m and time step Δt = 0.2 days. The reaction occurs until species 1, which is limiting to the left of the invading front, disappears, at which point reaction ceases. To the right of the front, species 2 is limiting, due to its initial concentration of zero. The grid Peclet number for this example is 10. This small to intermediate value of Grid Peclet number is easily accommodated by the OTF method. This example is expanded in the companion paper of *Kindred and Celia* [this issue] to include both inhibited and uninhibited bacterial growth.

Mass balance errors for this two-species example were approximately 5% for species 1 and approximately 3% for species 2. This error is not a consequence of the time stepping algorithm, because the solution was insensitive to time step reductions. Reduction of the space step Δx from 2 m to 1 m reduced the mass balance errors to less than 3% for species 1 and less than 1% for species 2. The actual solutions for Δx = 2 and Δx = 1 are virtually indistinguishable at t = 68 days, with only a slight change evident at the interacting concentration fronts (the fronts are displaced by approximately 1 m). This appears to be a consequence of the piecewise constant approximation of the spatially variable (nonlinear) reaction coefficient, which is a relatively poor approximation in the vicinity of the sharp concentration fronts. Implementation of the high-order spatial procedures of *Celia and Herrera* [1987] or reduction of the space step (as indicated above) will alleviate the mass balance discrepancy. While the mass balance approaches unity as Δx decreases, the numerical solutions for concentrations remain virtually indistinguishable from those presented in Figure 4.

8. Discussion and Conclusions

This paper presents a new numerical method for solution of reactive transport problems. The technique derives from judicious mathematical manipulation of the weak form of the governing equations. Special choice of the test functions, based on solution of the homogeneous adjoint equation, leads to an optimal approximation technique. The method has the desirable property of automatic adjustment of the approximation to accommodate varying degrees of diffusion, advection, and reaction domination.

For one-dimensional, steady state problems (ordinary differential equations with constant coefficients), the method produces exact nodal values for the unknown function and, if desired, its first derivative. Procedures of arbitrarily high order, on fixed grids, have been developed for the case of variable coefficients [*Celia and Herrera*, 1987; *Herrera*, 1987]. In addition, tensor product test functions applied to the two-dimensional Laplace equation lead again to an optimal approximation. This latter case can be shown to produce a sixth-order approximation using only nine node points [*Celia et al.*, 1989*b*]. *Collatz* [1960] has shown that this is the highest possible order of approximation for a nine point approximation to the Laplace equation. The OTF approach therefore appears to be a very promising numerical method.

Current efforts are focusing on improved treatment of the time domain as well as extensions to multiple spatial dimensions. As indicated above, initial efforts in multiple dimensions using tensor product test functions have produced very encouraging results. We plan to extend these results to the case of multidimensional reactive transport. We are also investigating several formulations that apply the OTF concept to the full space-time equation. The companion paper to this one [*Kindred and Celia*, this issue] uses the OTF simulator developed herein as a numerical tool to demonstrate behavior of various biologically reactive subsurface transport systems.

Acknowledgments. This work was supported in part by the National Science Foundation under grant 8657419-CES and by the Massachusetts Institute of Technology under Sloan Foundation grant 26950.

REFERENCES

Baptista, A. M., Solution of advection-dominated transport by Eulerian-Lagrangian methods using the backward methods of characteristics, Ph.D. thesis, Dep. of Civ. Eng., Mass. Inst. of Technol., Cambridge, Mass., 1987.

Bouloutas, E. T., and M. A. Celia, An analysis of a class of Petrov-Galerkin and Optimal Test Functions methods, in *Proc. Seventh Int. Conf. Computational Methods in Water Resources*, edited by M. A. Celia et al., pp. 15–20, Elsevier Science, New York, 1988.

Carey, G. F., and J. T. Oden, *Finite Elements: A Second Course*, volume 2, *The Texas Finite Element Series*, Prentice-Hall, Englewood Cliffs, N.J., 1983.

Celia, M. A., and I. Herrera, Solution of general ordinary differential equations by a unified theory approach, *Num. Methods Partial Differential Equations*, *3*(2), 117–129, 1987.

Celia, M. A., I. Herrera, E. T. Bouloutas, and J. S. Kindred, A new numerical approach for the advective-diffusive transport equation, *Num. Methods Partial Differential Equations*, in press, 1989*a*.

Celia, M. A., I. Herrera, and E. T. Bouloutas, Adjoint Petrov-Galerkin methods for multi-dimensional flow problems, in *Proc. Seventh Int. Conf. on Finite Element Methods in Flow Problems*, pp. 953–958, UAH Press, Huntsville, Ala., 1989*b*.

Collatz, L., *Numerical Treatment of Differential Equations*, 3rd ed., Springer, New York, 1960.

Herrera, I., *Boundary Methods: An Algebraic Theory*, Pitman, London, 1984.

Herrera, I., Unified approach to numerical methods, I, Green's formula for operators in discontinuous fields, *Numer. Methods Partial Differential Equations*, *1*(1), 25–44, 1985*a*.

Herrera, I., Unified approach to numerical methods, II, Finite elements, boundary elements, and their coupling, *Numer. Methods Partial Differential Equations*, *1*(3), 159–186, 1985*b*.

Herrera, I., The algebraic theory approach for ordinary differential equations: Highly accurate finite differences, *Numer. Methods Partial Differential Equations*, *3*(3), 199–218, 1987.

Herrera, I., L. Chargoy, and G. Alducin, Unified approach to numerical methods, III, Finite differences and ordinary differential equations, *Numer. Methods Partial Differential Equations*, *1*(4), 241–258, 1985.

Hildebrand, F. B., *Advanced Calculus for Applications*, 2nd ed., Prentice-Hall, Englewood Cliffs, N.J., 1976.

Hughes, T. J. R., and A. Brooks, A theoretical framework for Petrov-Galerkin methods with discontinuous weighting functions: Applications to the streamline-upwind procedure, in *Finite Elements in Fluids*, vol. 4, edited by R. H. Gallagher et al., pp. 47–65, John Wiley and Sons, New York, 1982.

Kindred, J. S., and M. A. Celia, Contaminant transport and biodegradation, 2, Conceptual model and test simulations, *Water Resour. Res.*, this issue.

Leonard, B. P., A stable and accurate convective modelling procedure based on quadratic upstream interpolation, *Comp. Meth. Appl. Mech. Eng.*, *19*, 55–98, 1979.

Prenter, P. M., *Splines and Variational Methods*, 323 pp., John Wiley and Sons, San Diego, Calif., 1975.

Rubin, J., Transport of reacting solutes in porous media: Relation between mathematical nature of problem formulation and chemical nature of reactions, *Water Resour. Res.*, *19*(5), 1231–1252, 1983.

Tezduyar, T. E., and D. K. Ganjoo, Petrov-Galerkin formulations with weighting functions dependent upon spatial and temporal discretization: Application to transient convective-diffusion problems, *Comp. Method Appl. Mech. Eng.*, *59*, 49–71, 1986.

M. A. Celia, Parsons Laboratory, Room 48-207, Department of Civil Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139.

I. Herrera, Instituto de Geofisica, National Autonomous University of Mexico, Apdo. Postal 22-582, 14000 Mexico D.F., Mexico.

J. S. Kindred, Golder Associates Inc., 4104 148th Avenue Northeast, Redmond, WA 98052.

(Received April 21, 1988;
revised January 16, 1989;
accepted January 31, 1989.)