Split Operator Methods for Reactive Chemical Transport in Groundwater

D. A. Barry, Department of Environmental Engineering, Centre for Water Research, University of Western Australia, Nedlands WA 6907 Australia (email: barry@cwr.uwa.edu.au)

C. T. Miller, Department of Environmental Sciences and Engineering, University of North Carolina, Chapel Hill, NC 27599-7400 USA (email: casey_miller@unc.edu)

P. J. Culligan, Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge MA 02139-4307 USA (email: trishch@mit.edu)

K. Bajracharya, Department of Environmental Engineering, Centre for Water Research, University of Western Australia, Nedlands WA 6907 Australia (email: bajracha@cwr.uwa.edu.au)

Abstract   Coupled solute transport and reaction models are computationally demanding when multispecies, multidimensional simulations are considered. Split operator methods approximate solutions to the reactive solute transport problem that are both relatively efficient to compute and to construct. The transport and reaction operators are split into two separate computational steps. Split operator schemes are introduced in the context of single species sorption to the soil, with an emphasis on the splitting errors that are induced. For standard two step methods, the splitting error is proportional to Δt, the temporal step size of the numerical scheme. The alternating split operator scheme, in which the order of the operations is switched at succeeding time steps, apparently does not remove the splitting error for nonlinear reactions, whereas it is removed for linear cases. An alternative to the standard time discretisation approaches is presented. The transport step is assumed to be solved by any available groundwater transport code, while the reaction model is formulated as a system of coupled ordinary differential equations and solved using an ODE solver. Two variants of the standard two step/ODE approach are presented. The efficiency of these latter schemes is compared with a standard split operator approach.

1. INTRODUCTION

Operator splitting is an efficient decoupling technique for solving porous media flow problems involving coupled chemical transport and reaction. In general, most approaches to the fully coupled model involve, in discrete form, the solution of $N \times n$ nonlinear algebraic equations at each time step, where N is the number of chemical species (or components) and n is the number of nodes in the spatial grid. The computational burden can quickly become prohibitively large for multidimensional, multispecies simulations.

The most straightforward implementation of operator splitting is the two-step method, which consists of solving first the chemical transport, followed by the chemical reactions. The decoupled problem consists of N linear transport equations, each with n unknowns, and n nonlinear algebraic equations describing the chemical reactions, each with N unknowns. Thus, N + n equations are solved in all, N of them being linear systems. The splitting method is efficient also because existing computer codes for reaction and transport can be combined relatively easily, substantially reducing programmer time in comparison to devising and implementing a numerical solution to the fully coupled problem.

These efficiency gains come with a cost, however. Because reactions involve temporal derivatives, there is usually an $O(\Delta t)$ splitting error introduced as a result of the splitting, where Δt is the time step used in the numerical scheme. Typically, numerical schemes are formulated with $O(\Delta t^2)$ accuracy, this accuracy being sacrificed for the convenience of operator splitting.

An error analysis of a typical operator splitting scheme as applied to a nonlinear reaction model is performed. The analysis applies to arbitrary spatial transport operators in any number of dimensions, and with any boundary conditions. This analysis extends and generalises previous work based on the linear retardation model and radioactive decay in one dimension with specified boundary conditions. Further, the analysis is extended to transport of two reactive species.

Another type of operator-splitting scheme is the alternating operator method, involving switching the order of the transport and reaction steps every second time step in the numerical solution. For linear reactions it has been shown that this method is always $O(\Delta t^2)$ accurate so long as the correct choice of initial condition is made in each reaction step.

There are many single species (usually tracer) transport codes available. Some simple ways to improve the coupling between the transport and reaction steps, as well as the computation of the reaction portion of calculations, are considered. These methods are based on formulation of the reaction step as a system of ODEs, so that any publicly available solver can be used.

2. ERROR ANALYSIS

We first consider the error induced by operator splitting. For simplicity the analysis will focus initially on a single reactive species. The governing transport/reaction model is (e.g., Bajracharya and Barry, 1994):

$$\frac{\partial c}{\partial t} + \frac{\partial s}{\partial t} = L(c), \quad (1)$$

where L is the n-dimensional advective/diffusive transport operator, c is the liquid phase concentration and s is the solid phase concentration (i.e., a sorption reaction is occurring) expressed in liquid phase concentration units. Equation (1) is subjected to a spatial discretisation scheme (e.g., finite differences) giving (e.g., Barry et al., 1995)

$$\frac{dc}{dt} + \frac{ds}{dt} = Ac + b, \quad (2)$$

where c is a vector (length n) of concentrations at each node in the spatial grid, s is the corresponding vector of sorbed solute concentrations, A is a sparse matrix ($n \times n$) resulting from the discretisation of the spatial operator, L, and b is a vector resulting from the application of the boundary conditions together with the spatial discretisation scheme.

The solute reaction may be time dependent (nonequilibrium) or effectively instantaneous (equilibrium). The difference between these two cases depends on the Damköhler number, $\alpha l/v$, where α is the characteristic reaction rate, l is the typical macroscopic domain length scale, and v is the characteristic advection rate through the system. If the Damköhler number is much greater than 1, then the reaction is in equilibrium relative to the advection time characteristic of the system (e.g., Barry and Li, 1994). The mathematical description of the former (nonequilibrium) case is

$$\frac{\partial s}{\partial t} = f(c, s), \quad (3)$$

whereas in the latter (equilibrium) it is

$$s = g(c), \quad (4)$$

where f and g are arbitrary functions. After taking into account the spatial discretisation, (3) and (4) become, respectively,

$$\frac{ds}{dt} = f(c, s) \quad (5)$$

and

$$s = g(c). \quad (6)$$

2.1. Crank-Nicolson Temporal Differencing

Crank-Nicolson differencing of (2) yields the following $O(\Delta t^2)$ numerical scheme:

$$A_L c^{k+1} + s^{k+1} = s^k + A_R c^k + [b^{k+1} + b^k] \frac{\Delta t}{2}, \quad (7)$$

where c^k is the numerical solution at the kth time step, $A_L = I - A\Delta t/2$ and $A_R = I + A\Delta t/2$. Similarly, (5) gives:

$$s^{k+1} = s^k + \frac{\Delta t}{2}(f^{k+1} + f^k), \quad (8)$$

where $f^k = f(c^k, s^k)$. Equation (6) or (8) is solved in conjunction with (7) at each time step to give the "exact", i.e., $O(\Delta t^2)$ numerical solution.

2.2. Two Step Solution

The Crank-Nicolson scheme is solved, approximately, in two steps. First there is the transport step:

$$c^{*(k+1)} = A_L^{-1}\{A_R c^k + [b^{k+1} + b^k]\frac{\Delta t}{2}\}, \quad (9)$$

followed by the reaction step:

$$c^{k+1} + s^{k+1} = s^k + c^{*(k+1)}. \quad (10)$$

The advantage of (9) and (10) is that the transport and reaction operations are completely separated. In large scale problems, this separation is responsible for the savings in programmer time and computation that are the main advantages of the two step scheme. As will be shown below, however, this scheme is $O(\Delta t)$, rather than $O(\Delta t^2)$. Observe that (9) and (10) would reproduce (7) if (10) was replaced by

$$A_L c^{k+1} + s^{k+1} = s^k + A_L c^{*(k+1)}. \quad (11)$$

2.3. Taylor Series Analysis

After eliminating $c^{*(k+1)}$ between (9) and (10) a Taylor series expansion in powers of Δt is performed about t = $(k + 1/2)\Delta t$. For the purpose of illustration, we consider a nonlinear equilibrium reaction, (4). Linear, nonequilibrium reactions were considered in detail by Barry et al. (1995).

The difference between the usual Taylor series for c^{k+1} and the corresponding Taylor series from (9) and (10) is, to $O(\Delta t)$:

$$H\frac{dc}{dt} = Ac + b + \frac{\Delta t}{2}A(Ac + b - \frac{dc}{dt}), \quad (12)$$

where

$$H = I + \frac{dg}{dc}. \quad (13)$$

The term dg/dc indicates the $n \times n$ matrix derived by computing dg/dc at each node in the spatial grid. Note

that only the diagonal of this matrix contains nonzero elements, reflecting the fact that the sorption reaction is local. Elimination of the temporal derivative on the right side of (12) yields, to $O(\Delta t)$:

$$\mathbf{H}\frac{dc}{dt} = \mathbf{A}c + \mathbf{b} + \frac{\Delta t}{2}\mathbf{A}\mathbf{H}^{-1}\frac{dg}{dc}(\mathbf{A}c + \mathbf{b}). \qquad (14)$$

Equation (14) differs from (2) by the $O(\Delta t)$ term in the former, i.e., the two step scheme (9) and (10) is first order accurate in the time step.

Equation (14) is now put in the more familiar form of a partial differential equation. The matrix $\mathbf{A}$ represents the continuous differential operator L in discrete form. At any node then, (14) corresponds to:

$$(1+\frac{dg}{dc})\frac{\partial c}{\partial t} = L(c) + \frac{\Delta t}{2}L\left[\frac{\frac{dg}{dc}}{1+\frac{dg}{dc}}L(c)\right], \qquad (15)$$

where L operates on all terms in its argument. Equation (15) is a general result and applies for 1, 2 or 3 dimensions. For g linear in c it reduces to an expression given by Barry et al. (1995). In 1 dimension, L is given by:

$$L \equiv D\frac{\partial^2}{\partial x^2} - v\frac{\partial}{\partial x}, \qquad (16)$$

where D is the dispersion coefficient and v is the advection rate. In truncation error analysis the lowest order derivative is assumed to dominate, so only the second term of (16) is applied to (15), with the result:

$$(1+\frac{dg}{dc})\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} + E, \qquad (17)$$

where the error term, E, is given by

$$E = \frac{v^2\Delta t}{2}\left[\frac{\frac{dg}{dc}}{1+\frac{dg}{dc}}\frac{\partial^2 c}{\partial x^2} + \frac{\frac{d^2 g}{dc^2}}{(1+\frac{dg}{dc})^2}(\frac{\partial c}{\partial x})^2\right]. \qquad (18)$$

For the case of linear retardation, (18) reduces to the expression given by Herzer and Kinzelbach (1989). In that case, numerical dispersion of constant magnitude is induced. For nonlinear g, each term in (18) is expected to vary with c, with the possibility that either term may dominate. For example, for the Freundlich isotherm (e.g., Barry, 1992), this term will dominate for small c, unless the spatial gradient is sufficiently small.

As an example of nonlinear equilibrium transport we consider the exact analytical solution of Barry and Sander (1991). Their one dimensional, exact solution is valid for the isotherm:

$$g(c) = \frac{\sum\limits_{i=0}^{2} a_i c^i}{\kappa A_2(v-1) - vA_2 A_3 - a_2 c}, \qquad (19)$$

where the a_is are functions of the A_is, and are given by Barry and Sander (1991).

In Figure 1, breakthrough curves computed at a position 5 cm along the one-dimensional transport domain are plotted for the isotherm in (19). Initially, no solute is in the soil, and influent at unit concentration is added (third-type boundary condition). The isotherm used to obtain the results in Figure 1 corresponds to a real soil (Barry et al., 1991).
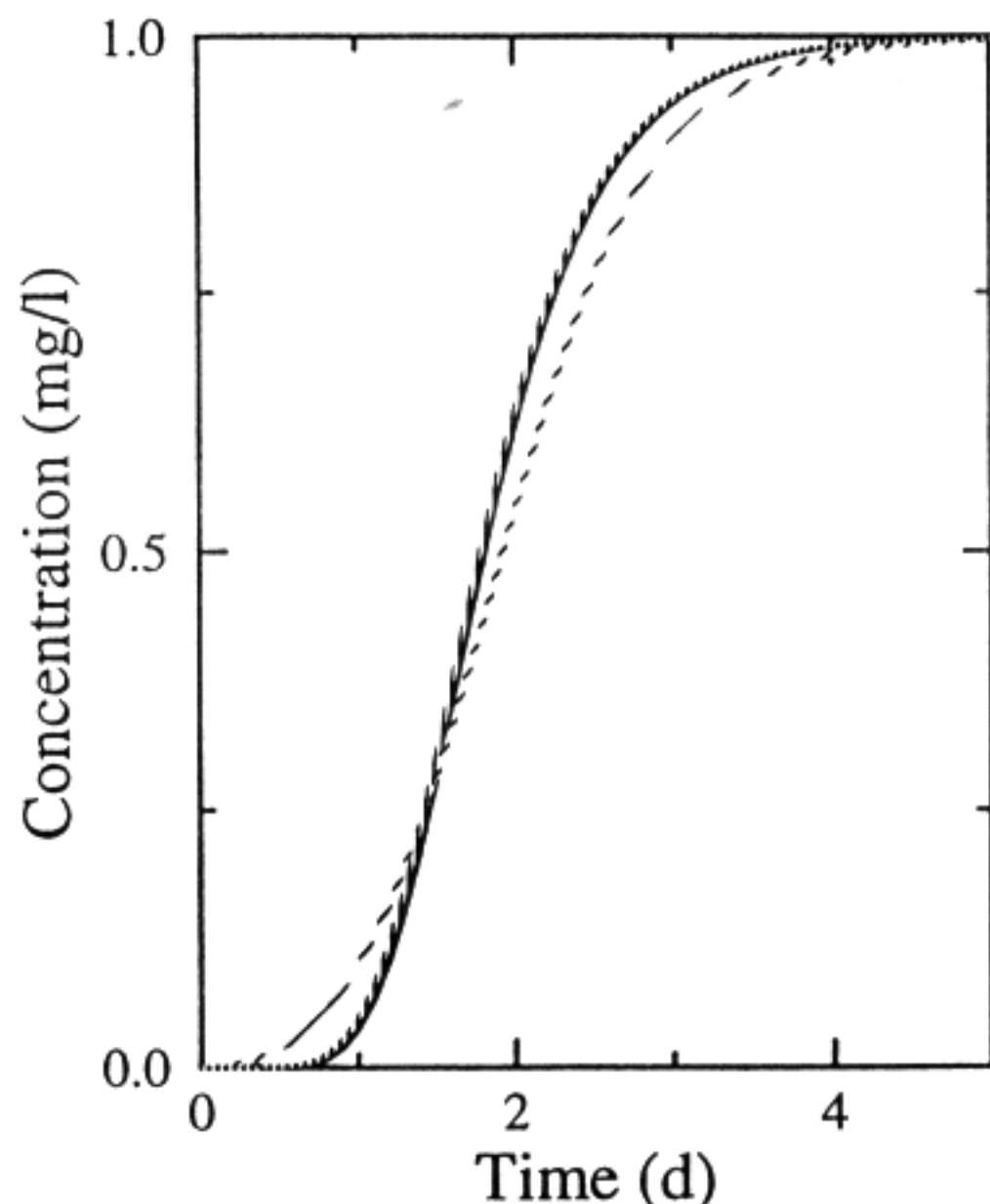

Figure 1. Exact (solid line) and standard two step breakthrough curves for a nonlinear equilibrium problem. Sloping dashes ($\Delta t = 0.2$ d) and vertical dashes ($\Delta t = 0.01$ d) are the standard two step solutions. Parameter values used are: D = 3.3524 cm²/d, v = 5.8677 cm/d, κ = 2.1257, A_1 = 0.2594, A_2 = 0.3295, A_3 = 0.3124, v = 0.0473.

For the parameter values used in the present problem, the results clearly indicate that numerical dispersion is induced when larger time steps are used. By using smaller time steps, numerical dispersion can be eliminated. However, the position of the numerically computed fronts do not exactly coincide with the exact breakthrough curve. The front is always ahead of the exact breakthrough curve, although the difference reduces with Δt.

The error (E) computed at a distance of 5 cm is plotted in Figure 2. The purpose of this figure is to show the variation in E with c. An examination of the magnitude of each of the terms on the right side of (18) reveals that the first term usually dominates the error. Clearly, the nonlinear nature of (18) precludes the option of correcting

the error induced by the operator splitting. On the other hand, if g is linear in c, then E becomes constant, as already mentioned. In this case the numerical dispersion induced by the splitting is easily corrected in the numerical solution.
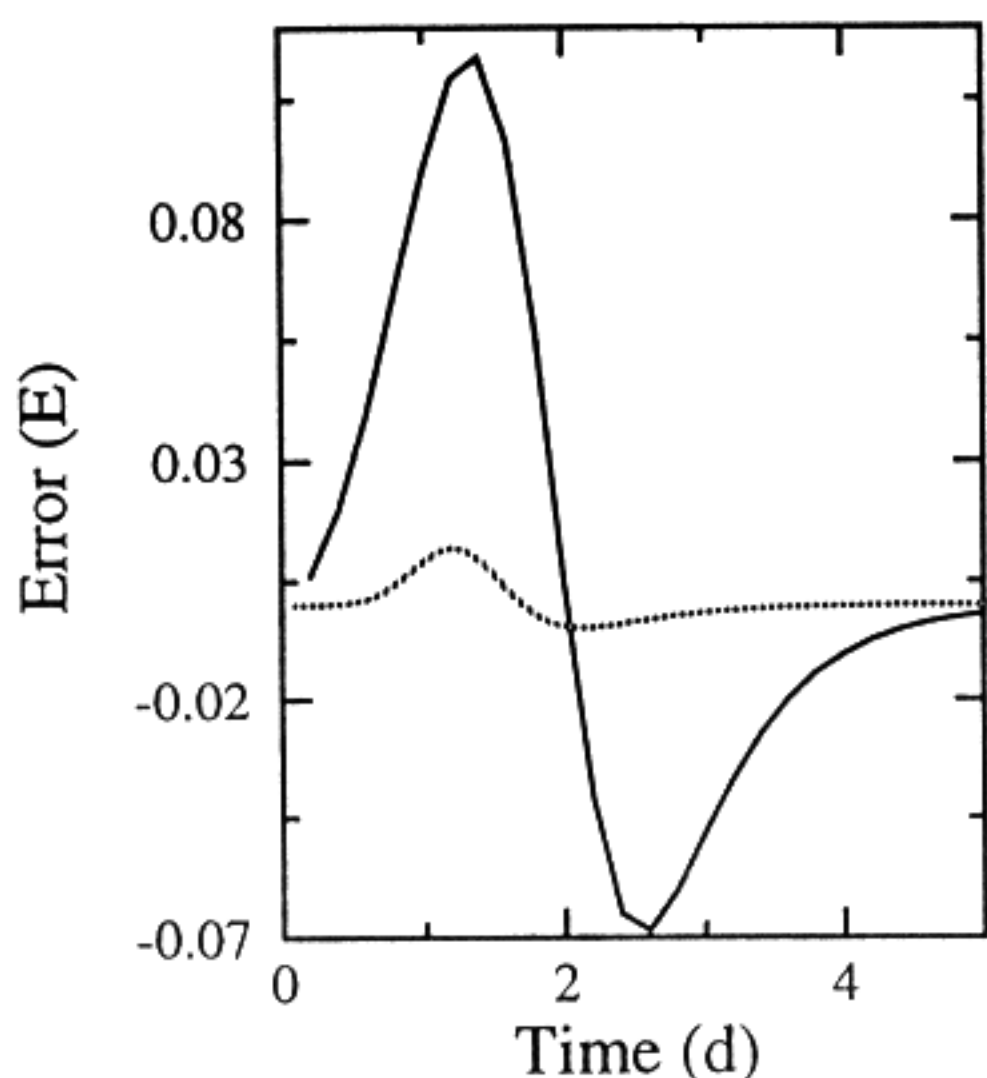

Figure 2. Equation (18) error term plotted as a function of time for the example in Figure 1. The solid line corresponds to the time step of 0.2 d and the broken line corresponds to the time step of 0.01 d.

2.4. Alternating Split Operator Scheme

This scheme was introduced by Strang (1968), who considered splitting of spatial operators. Miller and Rabideau (1993) implemented a version of the scheme for reactive transport problems. Essentially, their scheme consists of (9) over a step of $\Delta t/2$, then performing (10) over Δt, followed by another half time step of (9). A theoretical analysis of the scheme for linear reactions was given by Barry et al. (1995). They showed that the alternating scheme is always $O(\Delta t^2)$ accurate, i.e., the $O(\Delta t)$ splitting error is removed. However, the numerical results of Miller and Rabideau (1993) suggest that for nonlinear reactions the scheme is still $O(\Delta t)$. Thus, it appears that the $O(\Delta t^2)$ accuracy reported by Barry et al. (1995) does not extend to nonlinear isotherms. Further work is underway to examine this point.

2.5. Two Species Transport

The above analysis can be extended to more than one solute species. The two species case will be considered here. For detailed derivations of the governing multispecies transport/reaction models see, e.g., Kirkner and Reeves (1988), Yeh and Tripathi (1989, 1991) or Zysset et al. (1994).

Assume that two exchangeable cations are being transported through a porous medium. Equation (2) applies to each species, with the concentration variables subscripted by a 1 or 2 to denote species 1 or species 2. Assume that the operator L remains unchanged for each species. The total exchange capacity of the soil is the CEC, in which case

$$s_1 + s_2 = CEC. \tag{20}$$
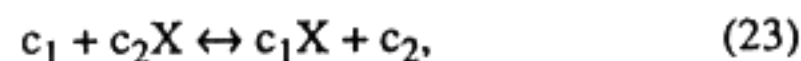
For equilibrium ion exchange, characterised by the selectivity coefficient, K, the equilibrium exchange isotherms are:

$$s_1 = \frac{Kc_1 CEC}{Kc_1 + c_2} = g_1 \tag{21}$$

and

$$s_2 = \frac{c_2 CEC}{Kc_1 + c_2} = g_2. \tag{22}$$

Equations (21) and (22) are based on a homovalent, heterogeneous fast cation exchange reaction of form:

$$c_1 + c_2 X \leftrightarrow c_1 X + c_2, \tag{23}$$

where X is the exchanging solid medium. Barry and Bajracharya (1994) offer a generalisation of the homovalent model presented here. A more general case is where (21) and (22) are replaced by the arbitrary expressions:
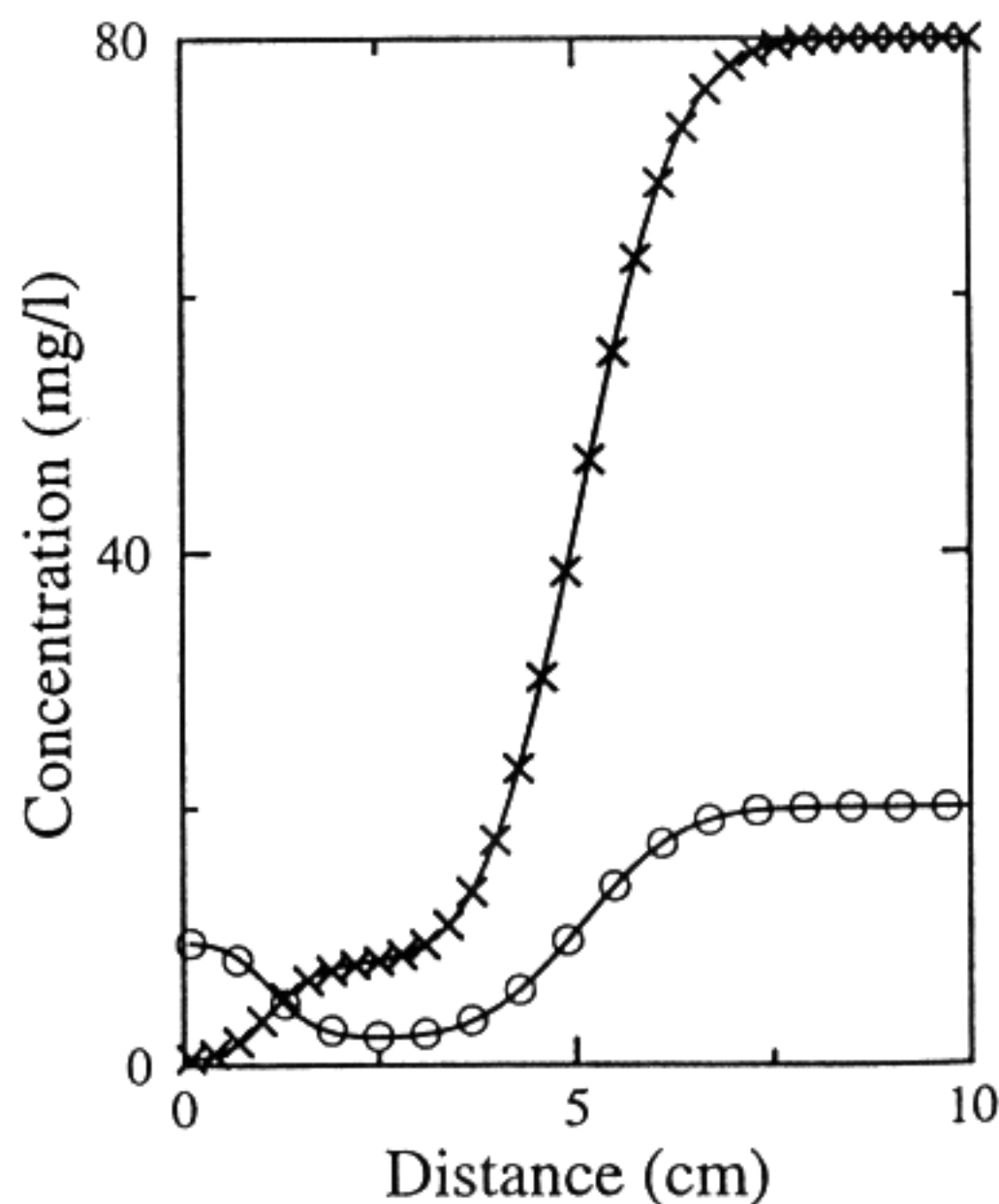
$$s_i = g_i(c_1, c_2), \ i = 1,2. \tag{24}$$

Figure 3. Crank-Nicolson (solid lines) and standard two step solutions (crosses and circles) for a multispecies ion exchange problem. Parameters used are v = 1 cm/d, D = 0.1 cm²/d, K = 1, CEC = 36mg/l. The profiles were generated at t = 5 d. Spatial and time steps used in the two-step solution were 0.1 cm and 0.05 d, respectively. Initial and boundary conditions used were: $c_1(0,t) = 9.5$ mg/l, $c_2(0,t) = 0.5$ mg/l, $c_1(x,0) = 20$ mg/l, $c_2(x,0) = 80$ mg/l.

A similar splitting error analysis to that in §2.3 is performed; the details are unimportant and are omitted. The corresponding expression to (15) is, for species 1:

$$\frac{\partial c_1}{\partial t} + \frac{\partial s_1}{\partial t} = L(c_1) + \frac{\Delta t}{2} L(E_1), \qquad (25)$$

where

$$E_1 = \frac{L(c_1)\dfrac{dg_1}{dc_1} - L(c_2)\dfrac{dg_2}{dc_2}}{1 + \dfrac{dg_1}{dc_1} + \dfrac{dg_2}{dc_2}}. \qquad (26)$$

Similar expressions to (15) and (26) can be written for species 2. Equation (26) reduces to the corresponding portion of (15) when the second species is not exchanged, i.e., $g_2 = 0$.

The sign difference in (26) may act to improve two species transport simulations compared with the numerical errors arising in single species simulation, as shown by (15). In Figure 3, a one-dimensional two-species example is displayed. The chemical reaction equations are given by (20) - (22), with parameter values shown in the caption. The two-step solution is compared with an "exact" Crank-Nicolson solution (Barry et al., 1983, 1987). Note that grid independent Crank-Nicolson results are plotted. The two step method results are excellent in this case perhaps because $K = 1$ and so $dg_1/dc_1 = dg_2/dc_2$. Doubling the time step in the two step method gave virtually the same results.

3. STABILITY ANALYSIS

Standard stability analyses of the two step method for single species transport are straightforward so long as the governing reaction equations are linear in c. Two cases were considered. The first was that of linear retardation, i.e., (4) is written as

$$s = (R - 1)c, \qquad (27)$$

where R is the retardation factor. The second case considered was radioactive decay:

$$\frac{\partial s}{\partial t} = \mu c, \qquad (28)$$

where μ is the decay rate. For both these cases, a von Neumann stability analysis (Noye, 1982) was performed. The analyses showed the two step method to be unconditionally stable.

4. ALTERNATIVE NUMERICAL SOLUTION

We shall consider schemes that maintain separation of the reaction and transport components of the solution. In particular, the Method of Lines (Brenan et al., 1989) approach will be adopted. This method has recently been shown to provide efficient and accurate solutions for the strongly nonlinear Richards' equations describing single phase unsaturated flow in porous media (Tocci et al., 1995).

The Method of Lines (MoL) can be applied directly to (2) and (5), or their generalisations. The unknown variables are collected in a vector $\mathbf{u} = [c,s]^T$. The ds/dt term in (2) is replaced using (5) and the MoL is invoked in a

straightforward fashion. In the case of equilibrium reactions, (6), the system of first order ODEs becomes a differential/algebraic system of equations. Again, the MoL can be used to obtain such solutions efficiently. A disadvantage is that the use of (2) precludes usage of the available computer codes for water flow and tracer transport as the first step of a two step solution strategy. Below we examine methods that maintain the separation of solute transport and reaction steps, but make use of ODE solvers for the reaction step.

4.1. Two Step ODE Solution

We presume in general that a multispecies reaction/transport problem is under consideration. As discussed above, the transport step is left untouched, i.e., transport of each species is handled independently by a given transport code. However, for the reaction step we must deal with a system of nonlinear algebraic equations, i.e., in the standard two step method we must solve N coupled nonlinear algebraic equations of the form given by (10). Alternatively, the "exact" solution to the original Crank-Nicolson formulation of the problem involves solving N equations of the form (11).
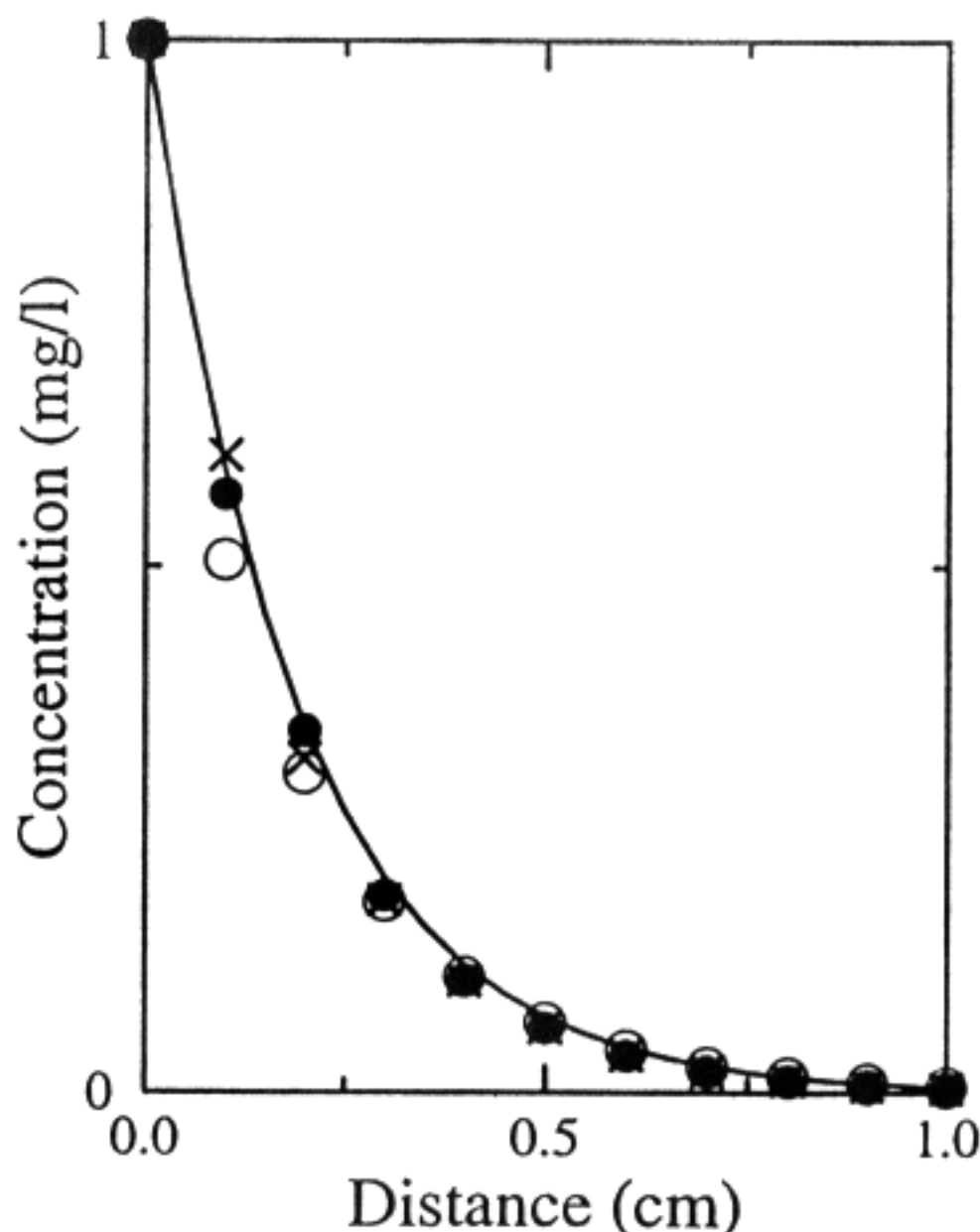

Figure 4. Exact (line), standard two step (open circles), modified two step [with one additional term in the Taylor series expansion] (crosses) and modified two step [with two extra terms in the Taylor series expansion, (30)] (solid circles) solutions for a first order decay problem ($\mu = 4$/d, $v = 1$ cm/d, $D = 0.1$ cm^2/d). The spatial and time steps used in the two step solutions were, respectively, 0.1 cm and 0.04 d. The profiles were generated at time = 10 d.

We seek to formulate the problem as a system of ODEs, so as to make use of an ODE solver. The reaction equations themselves are often stiff (Miller and Rabideau, 1993). Thus, publicly available stiff ODE solvers such as LSODE (Hindmarsh, 1983) can be employed. Note that the mass balance statement, (10), is obtained from (11) by setting $A_L = I$. The latter equation can be thought of

as a discretised version of:

$$A_L \frac{dc}{dt} = -\frac{ds}{dt}, \quad k\Delta t < t < (k+1)\Delta t. \qquad (29)$$

Equations (5) and (29) may be solved using available ODE solvers. Such codes are easily obtainable on the World Wide Web (using, in Australia, the following URL as a starting point: http://www.cs.uow.edu.au/netlib/master/readme.html).

Two cases of (29) will be compared below. First, let $A_L = I$; this is a version of the standard two step method. Second, replace A_L by an approximation to its inverse on the right side of (29):

$$\frac{dc}{dt} = -(I + A\frac{\Delta t}{2} + A^2\frac{\Delta t^2}{4} + \ldots)\frac{ds}{dt}. \qquad (30)$$

Keeping one term in the Taylor series expansion in (30) is, of course, the two step method; we also ran cases where two or three terms were kept. In all cases reported here an order 4 Runge-Kutta ODE solver was used.
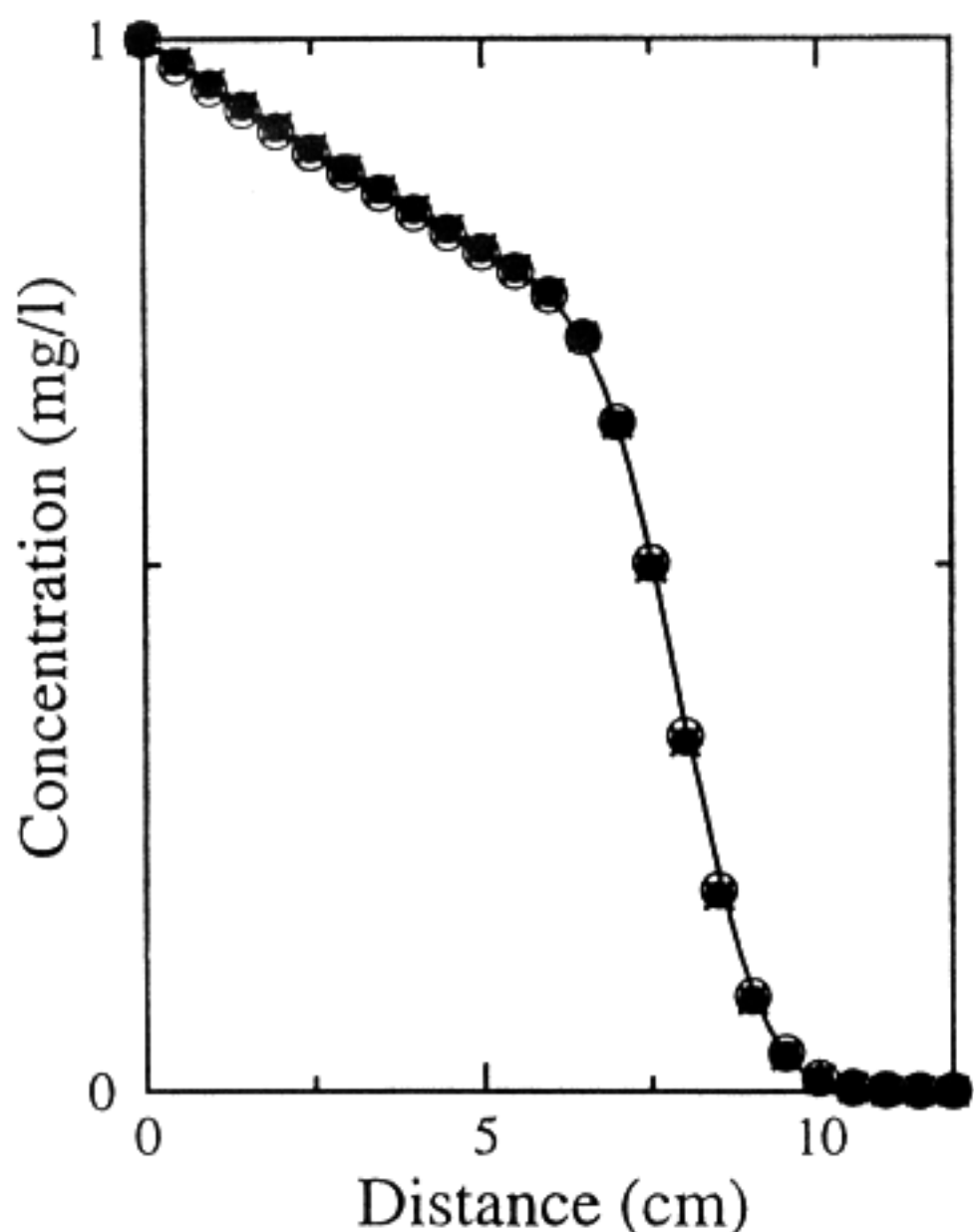

Figure 5. Exact (line), standard two step (open circles), modified two step [with one additional term in the Taylor series expansion] (solid circles) and modified two step [with two additional terms in the Taylor series expansion] (crosses) solutions for a first-order decay problem ($\mu = 9/d$, $v = 2$ cm/d, $D = 0.1$ cm^2/d, $\alpha = 0.01/d$). The spatial and time steps used in the two step solutions were, respectively, 0.1 cm and 0.08 d. The profiles were generated at $t = 4$ d.

In Figure 4, results of a one-dimensional radioactive decay problem, modelled by (28), are shown. An initially solute free soil profile was considered, with a unit concentration, first-type boundary condition applied as the influent condition. The present example shows the advantage of the modified scheme. For the same time step of 0.04 d, the modified solution gives better results than the standard two step method. With smaller time steps, however, all the solutions merge to the exact solution (results not shown). The improved results obtained with the coarser time steps come at the cost of slightly increased computation time (discussed further below). The standard two step method is more efficient but less accurate than the modified scheme. Also, at larger time steps, the modified solutions show some signs of instability, in that oscillations were observed at the influent boundary. The solution in which two terms of the Taylor series expansion are included tends to be more unstable than the solution in which only one term is included. The standard two step method, however, is stable for all time step sizes.

The next example is that of a kinetic reaction, with a reaction term given by (e.g., Parker and van Genuchten, 1984; Rinaldo, 1988):

$$\frac{\partial s}{\partial t} = \alpha [(R-1)c - s]. \qquad (31)$$

The exact solution to (1), (16) and (31) was calculated using the CXTFIT code (Parker and van Genuchten, 1984). Results for two different time step sizes are displayed. In Figure 5, all three methods based on (30) perform well (standard two step, as well as two and three term approximations). In Figure 6, which differs from Figure 5 in the temporal step size only, all methods perform equally poorly. Note the minor oscillation near the influent boundary in Figure 6, as well as the flattening of concentration profile at the top of the front.
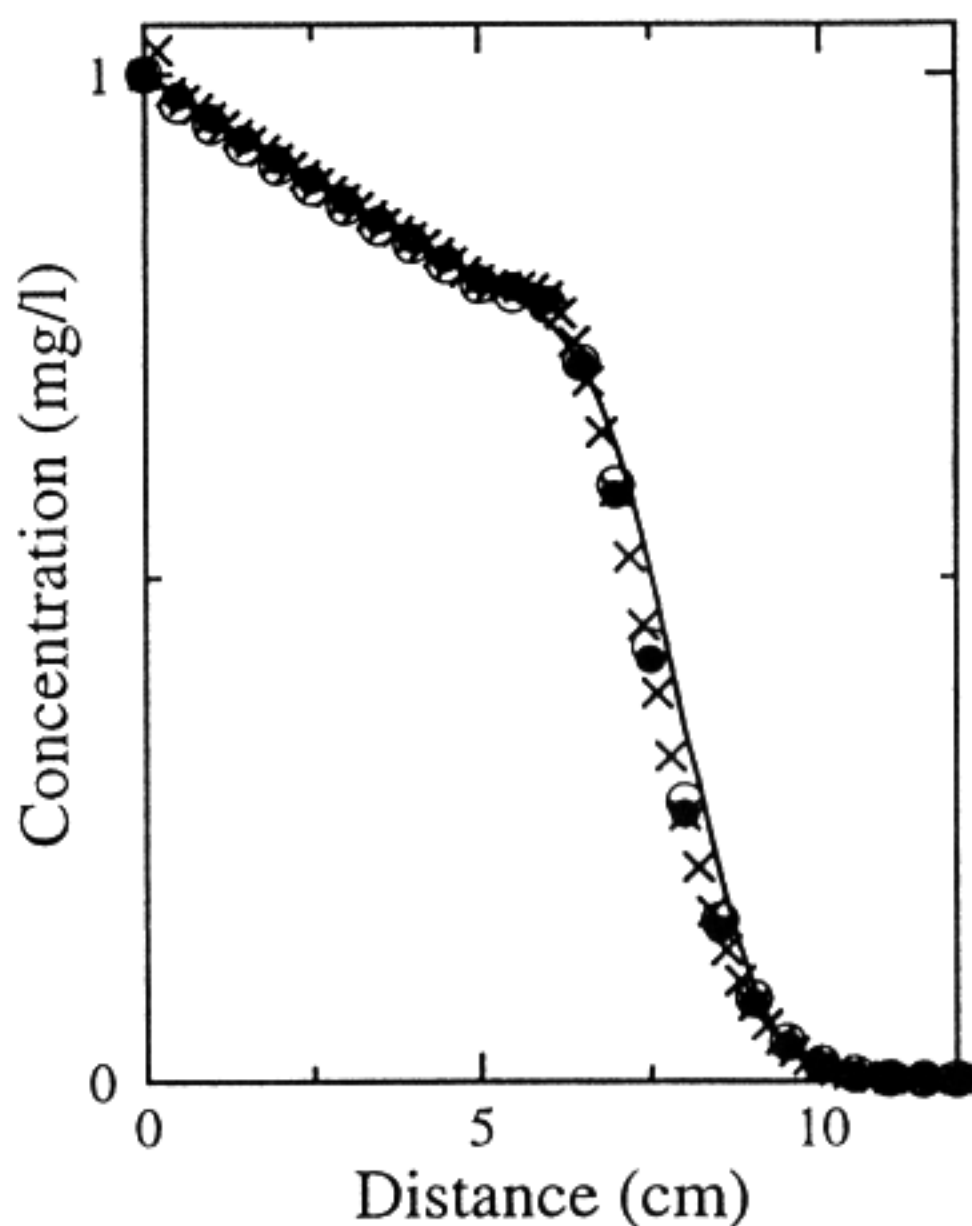

Figure 6. Same as Figure 5 except that $\Delta t = 0.2$ d.

To compare the methods, a measure of the error of the numerical solutions was computed. The error is defined by:

$$Error = \frac{1}{n} \sum_{i=1}^{n} [c(i\Delta x, t) - c_{ex}(x, t)]^2, \quad (32)$$

where c_{ex} is the exact solution. This error was computed for the standard two step method, as well as for the two term modified two step model, based on (30). The results are shown in Figure 7.

At larger time steps (shorter CPU time), the standard two step method shows slightly less error. At smaller time steps (intermediate values), the modified two step method gives results that are an order of magnitude better for similar computational times. At very small time steps (greatest CPU time), both methods result in larger errors. The standard two step method again gives less errors in comparison to the modified two step method.
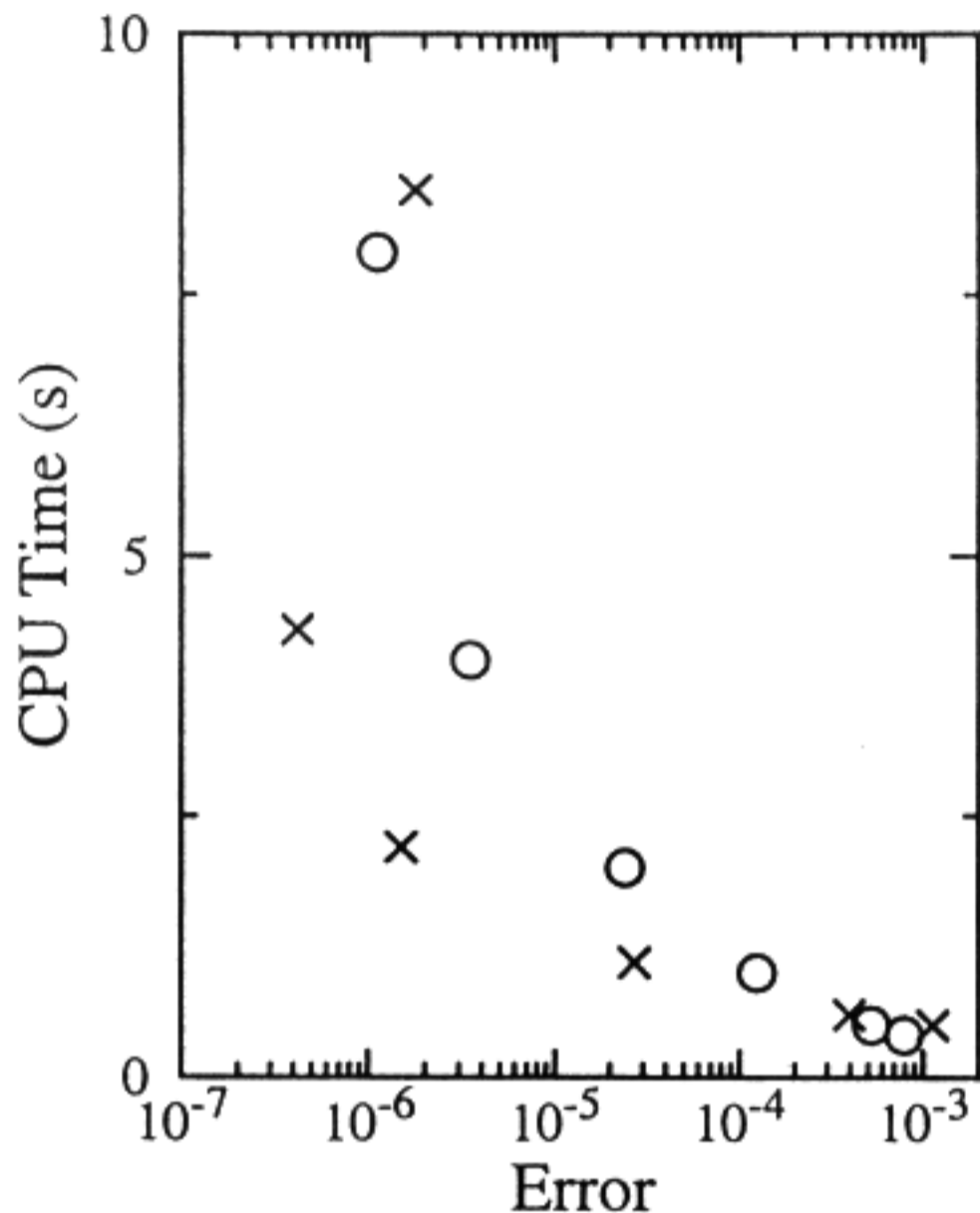

Figure 7. Plot of CPU time (for a Sun Sparc 1) versus accuracy of the standard two step method (open circles) and the modified two step method (crosses).

5. SUMMARY AND CONCLUSIONS

From the point of view of programmer efficiency, split operator solutions to transport/reaction problems offer the advantage that existing, independent transport and reaction modules can be coupled together with relatively little effort. The main disadvantage is that an $O(\Delta t)$ splitting error is introduced, necessitating small time step sizes for accurate results. Computational efficiency is reduced, therefore.

We have analysed the splitting error that arises for non-linear equilibrium, single species transport, in an arbitrary spatial domain. Unlike the case of linear equilibrium, the numerical dispersion induced by the splitting cannot be removed as it depends on the dependent variable, c. This analysis was extended to two competing species with a similar result, i.e., the splitting error is again proportional to Δt. However, unlike the single species case, the two species error expression contains terms that may approximately cancel under some circumstances. This deduction was supported by an example that revealed that very accurate results could be obtained using the standard two step approach.

Finally, we briefly investigated an alternative approach to solving the reaction portion of the two step scheme. This step can be formulated as a system of ODEs, or as a system of differential/algebraic equations (only the former case was considered here). In either case, publicly available software can be used to obtain solutions. Although we have not done so here, equations of the form of (29) can be solved directly using, for example, the LSODI code (Hindmarsh, 1983). Rather, we focused directly on the errors inherent in the two step scheme, for example, setting $A_L = I$ in (29), or using as well the second and third terms in the Taylor series expansion of A_L^{-1}. A CPU time check (Figure 7) suggests that keeping a single additional term in the Taylor series expansion is computationally efficient.

6. NOTATION

a_i	parameters in sorption isotherm, $i = 0,2$
A_i	parameters in sorption isotherm, $i = 1,2,3$
A	spatial discretisation matrix, $1/T$
A_L	$I - A\Delta t/2$
A_R	$I + A\Delta t/2$
b	boundary value vector, $M/L^3 T$
c	liquid phase solute concentration, M/L^3
c	liquid phase solute concentration vector, M/L^3
CEC	cation exchange capacity, M/L^3
D	dispersion coefficient, L^2/T
E	$O(\Delta t)$ error term defined by (18)
f	arbitrary function, $M/L^3 T$
f	vector of f at each node in the spatial grid, $M/L^3 T$
g	arbitrary function, M/L^3
g	vector of g at each node in the spatial grid, M/L^3
H	matrix defined by (13)
I	identity matrix
k	time step number
l	characteristic macroscopic length scale, L
L	advection/dispersion operator, $1/T$
n	number of nodes in the numerical solution
n	number of dimensions
MoL	Method of Lines
N	number of chemical species
ODE	ordinary differential equation
R	retardation factor
s	solid phase solute concentration, M/L^3
s	solid phase solute concentration vector, M/L^3
t	time, T
u	contains c and s, M/L^3
v	advection rate, L/T
x	position, L
X	soil exchanger, M/L^3

6.1. Greek

α	reaction rate, $1/T$
Δt	time discretisation, T
κ	parameter in sorption isotherm
μ	decay rate, $1/T$
ν	parameter in sorption isotherm

6.2. Other

$\cdot_{ex}$	exact solution
$\cdot_i$	the ith chemical species, $i = 1, 2$
$\cdot_T$	transpose of the vector $\cdot$

intermediate value of ·

7. REFERENCES

Bajracharya, K., and D. A. Barry. Note on common mixing cell models, *J. Hydrol.*, 153, 189-214, 1994.

Barry, D. A. Modelling contaminant transport in the subsurface: Theory and computer programs, in *Modelling Chemical Transport in Soil: Natural and Applied Contaminants*, edited by H. Ghadiri and C. W. Rose, pp. 105-144, Lewis Publishers, Boca Raton, Florida, 1992.

Barry, D. A., and K. Bajracharya. Application of an improved mixing cell model to equilibrium and nonequilibrium multispecies transport, in *Proceedings of the Sixth Biennial Conference on Computational Techniques and Applications: CTAC93*, edited by D. Stewart, H. Gardner, and D. Singleton, World Scientific, Singapore, pp. 103-111, 1994.

Barry, D. A., and L. Li. Physical basis of nonequilibrium solute transport in soil. *Fifteenth International Congress of Soil Science, Transactions*, Acapulco, Mexico, 10-16 July, International Society of Soil Science and Mexican Society of Soil Science. 2a, 86-105, 1994.

Barry, D. A., C. T. Miller, and P. J. Culligan-Hensley. Temporal discretisation errors in non-iterative split-operator approaches to solving chemical reaction/groundwater transport models, *J. Contam. Hydrol.*, In Press, 1995.

Barry, D. A., J.-Y. Parlange, and J. L. Starr. Numerical analysis of the precursor effect, *Soil Sci.*, 143, 309-317, 1987.

Barry, D. A., and G. C. Sander. Exact solutions for water infiltration with an arbitrary surface flux or nonlinear solute adsorption, *Water Resour. Res.*, 27, 2667-2680, 1991.

Barry, D. A., G. C. Sander, and I. R. Phillips. Modelling solute transport, chemical adsorption and cation exchange, *International Hydrology and Water Resources Symposium*, The Institution of Engineers, Australia, National Conference Publication Number 91/22, Preprints of Papers 3, 913-918, Perth, 2-4 October, 1991.

Barry, D. A., J. L. Starr, J.-Y. Parlange, and R. D. Braddock, Numerical analysis of the snow-plow effect. *Soil Sci. Soc. Am. J.*, 47, 862-868, 1983.

Brenan, K. E., S. L. Campbell, and L. R. Petzold. *The Numerical Solution of Initial Value Problems in Differential-Algebraic Systems*, Elsevier, New York, 1989.

Herzer, J., and W. Kinzelbach. Coupling of transport and chemical processes in numerical transport models, *Geoderma*, 44, 115-127, 1989.

Hindmarsh, A. ODEPACK, A systemized collection of ODE solvers, in *Scientific Computing*, edited by R. Stepleman, pp. 55-64, North-Holland, New York, 1983.

Kirkner, D. J., and H. Reeves. Multicomponent mass transport with homogeneous and heterogeneous chemical reactions: Effect of the chemistry on the choice of numerical algorithm, 1. Theory, *Water Resour. Res.*, 24, 1719-1729, 1988.

Miller, C. T., and Rabideau, A. J. Development of split-operator, Petrov-Galerkin methods to simulate transport and diffusion problems, *Water Resour. Res.*, 29, 2227-2240, 1993.

Noye, J. Finite difference methods for partial differential equations, in *Numerical Solutions for Partial Differential Equations*, edited by J. Noye, pp. 3-137, North Holland, New York, 1982.

Parker, J. C., and M. Th. van Genuchten. *Determining Transport Parameters from Laboratory and Field Tracer Experiments*, Virginia Agricultural Experiment Station, Bull. 84-3, Blacksburg, Virginia, 1984.

Rinaldo, A. Solute lifetime distributions in soils and the two-component convection-dispersion equation, in *Validation of Flow and Transport Models for the Unsaturated Zone*: Conference Proceedings, May 23-26, Ruidoso, New Mexico, eds. P. J. Wierenga and D. Bachelet, Dept. of Agronomy and Horticulture, New Mexico State University, Las Cruces, New Mexico, pp. 340-345, 1988.

Strang, G. On the construction and comparison of difference schemes, *SIAM J. Numer. Anal.*, 5, 506-517, 1968.

Tocci, M. D., C. T. Kelley, and C. T. Miller. Accurate and economical solution of the pressure-head form of Richards' equation by the method of lines, Submitted to *Adv. Water Resour.*, 1995.

Yeh, G. T., and V. S. Tripathi. A critical evaluation of recent developments in hydrogeochemical transport models of reactive multichemical components, *Water Resour. Res.*, 25, 93-108, 1989.

Yeh, G. T., and Tripathi, V. S. A model for simulating transport of reactive multispecies components: Model development and demonstration, *Water Resour. Res.*, 27, 3075-3094, 1991.

Zysset, A., Stauffer, F., and Dracos, T. Modeling of chemically reactive groundwater transport, *Water Resour. Res.*, 30, 2217-2228, 1994.