

Generalized solution to multispecies transport equations coupled with a first-order reaction network

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Abstract. A generalized solution methodology is presented for deriving analytical solutions to multispecies transport equations coupled with multiparent, serial, parallel, converging, diverging, and/or reversible first-order reactions. The method is flexible for solving one-, two-, or three-dimensional advection-dispersion equations that are coupled with a set of first-order reactions. However, a major limitation is that the method cannot be used for solving multispecies transport equations with different retardation factors. Mathematical steps are provided to illustrate how the general solution method can be derived using linear transformation principles and to show why the method would fail when the retardation factors are different. Derivations are also presented to demonstrate how the *Sun et al.* [1999b] method for solving sequential reactive transport problems, which was previously presented without any fundamental analysis, can be deduced from the general solution. The results of the presented solution scheme for a test problem compare well with the numerical solution computed using the RT3D code. The proposed methodology is useful for developing simple analytical models that can be used to perform screening simulations and can be used to test complex multispecies transport codes.

1. Introduction

Analytical models are useful tools for predicting the fate and transport of groundwater contaminant plumes [Domenico, 1987; Chilakapati and Yabusaki, 1999]. Although numerous analytical models are available in the literature for solving single-species transport problems, these models have limited use at complex field sites because most field problems involve multiple reactive contaminants. Examples include nuclear waste sites contaminated with radioactive species and their daughter products and hazardous waste sites contaminated with chlorinated solvents such as PCE (tetrachloroethylene) and TCE (trichloroethylene) and their biodegradation products [Clement *et al.*, 1998, 2000].

Analytical solutions to multispecies transport equations are currently available only for a limited number of first-order-kinetics coupled reactive transport equations [van Genuchten, 1985; Lunn *et al.*, 1996; Khandelwal and Rabideau, 1999]. Also, almost all the multispecies analytical solutions published in the literature can only be used for solving one-dimensional systems, which greatly restricts their use. Recently, *Sun et al.* [1999a] presented a transformation format to solve multiple reactive transport equations that are coupled with a sequential, first-order reaction network. This method is general enough to solve the reactive transport of any number of sequential reactive species in one, two, or three dimensions. *Sun et al.* [1999b] extended the method to analyze serial and parallel reaction networks. *Sun and Clement* [1999] further generalized the solution and proposed a numbering scheme for systematically solving multiple serial-parallel reactions. In addition, they also presented two- and three-dimensional validation results for the solution strategy. However, the basic solution format used in

all these manuscripts was presented without any fundamental analysis. Although the validity of the transformation format was tested extensively by comparing it against numerical and other analytical solutions [Sun and Clement, 1999], the fundamental principles behind the solution strategy were never discussed. Also, the solution strategy cannot be used to solve problems with complex reactions such as reversible reactions, converging reactions, and multiparent reactions.

The objective of this work is to develop a general methodology for solving multispecies transport equations that are coupled with any type of first-order reactions. As a part of this work, necessary mathematical steps will also be presented to demonstrate how *Sun et al.*'s [1999b] solution, which is a subset of the presented general solution scheme, can be deduced using linear transformation principles. The mathematical derivations will be used to answer the following three key questions concerning the *Sun et al.* [1999b] solution strategy: (1) Is there a fundamental basis for the *Sun et al.* [1999b] transformation format? (2) How and why does the transformation format work? (3) Why does it not work when the transport equations have different retardation values?

2. Mathematical Problem

Assuming a uniform flow velocity in the x direction, the three-dimensional transport equation for predicting the fate and transport of a chemical species in a system having multiple reactive contaminants, which are coupled by a set of first-order reactions, can be written as

$$R_i \frac{\partial c_i}{\partial t} + v \frac{\partial c_i}{\partial x} - D_x \frac{\partial^2 c_i}{\partial x^2} - D_y \frac{\partial^2 c_i}{\partial y^2} - D_z \frac{\partial^2 c_i}{\partial z^2} = \sum_{j=1}^{i-1} y_{ij} k_j c_j - k_i c_i + \sum_{j=i+1}^n y_{ij} k_j c_j \quad \forall i = 1, 2, \dots, n, \quad (1)$$

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where c is the i th species concentration [$M L^{-3}$]; y_{ij} is the effective yield factor which describes the mass of a species i produced from another species j [$M M^{-1}$]; k_i is the first-order contaminant destruction rate constant of the i th species [T^{-1}]; v is the seepage velocity [$L T^{-1}$]; D_x , D_y , and D_z are the dispersion coefficients [$L^2 T^{-1}$]; and n is the total number of species in the reaction network. Equation (1) applies only when degradation is limited to the liquid phase, but other situations can be modeled by appropriately redefining the degradation rate terms [van Genuchten, 1985]. However, as illustrated in section 3, the solution strategy to be discussed here is applicable only when the values of R_i are identical for all the transported species, but the degradation rate constant k_i can be different for each of the species.

If the reactions are assumed to follow a simple sequential pattern (e.g., $PCE \rightarrow TCE \rightarrow DCE \rightarrow VC$), the transport equations can be simplified as [Sun et al., 1999b]

$$\begin{aligned} R_i \frac{\partial c_i}{\partial t} + v \frac{\partial c_i}{\partial x} - D_x \frac{\partial^2 c_i}{\partial x^2} - D_y \frac{\partial^2 c_i}{\partial y^2} - D_z \frac{\partial^2 c_i}{\partial z^2} \\ = y_i k_{i-1} c_{i-1} - k_i c_i \quad \forall i = 1, 2, \dots, n, \end{aligned} \quad (2)$$

where y_i is the amount of species i produced from its immediate parent species $i - 1$. It should be pointed out that in typical sequential reaction problems, the values of k_0 and y_0 are assumed to be equal to zero; that is, there is no production term for the first species in the decay chain [Sun et al., 1999b]. The focus of this paper is to develop a general solution procedure for solving (1) and demonstrate how the Sun et al. [1999b] solution to (2) falls out naturally from this general solution.

The coupled reactive transport system described by (1) can be compactly represented by using matrix notation as

$$\mathbf{R} \hat{\mathbf{c}}' + v \hat{\mathbf{c}}'_x - D_x \hat{\mathbf{c}}_x^2 - D_y \hat{\mathbf{c}}_y^2 - D_z \hat{\mathbf{c}}_z^2 = \mathbf{K} \hat{\mathbf{c}}, \quad (3)$$

where bold letters are used to represent square matrices and the circumflex is used to represent column matrices (or vectors); $\hat{\mathbf{c}}$ is the concentration vector; $\hat{\mathbf{c}}'$ is the temporal derivative of the concentration vector; $\hat{\mathbf{c}}'_x$ is the x component of the first spatial derivative of the concentration; $\hat{\mathbf{c}}_x^2$ is the x component of the second spatial derivative of the concentration vector (similar notations are used for the y and z components); \mathbf{R} is the retardation matrix; and \mathbf{K} is the reaction coefficient matrix. Matrices in (3) can be explicitly assembled for any type of first-order reactive transport system having any number of species. As an example, for a four-component sequential reactive transport system (e.g., $PCE \rightarrow TCE \rightarrow DCE \rightarrow VC$) the matrix equation can be written as

$$\begin{bmatrix} R_1 & 0 & 0 & 0 \\ 0 & R_2 & 0 & 0 \\ 0 & 0 & R_3 & 0 \\ 0 & 0 & 0 & R_4 \end{bmatrix} \begin{bmatrix} \frac{\partial c_1}{\partial t} \\ \frac{\partial c_2}{\partial t} \\ \frac{\partial c_3}{\partial t} \\ \frac{\partial c_4}{\partial t} \end{bmatrix} + \begin{bmatrix} v \frac{\partial c_1}{\partial x} \\ v \frac{\partial c_2}{\partial x} \\ v \frac{\partial c_3}{\partial x} \\ v \frac{\partial c_4}{\partial x} \end{bmatrix} - \begin{bmatrix} D_x \frac{\partial^2 c_1}{\partial x^2} \\ D_x \frac{\partial^2 c_2}{\partial x^2} \\ D_x \frac{\partial^2 c_3}{\partial x^2} \\ D_x \frac{\partial^2 c_4}{\partial x^2} \end{bmatrix}$$

$$\begin{aligned} & - \begin{bmatrix} D_y \frac{\partial^2 c_1}{\partial y^2} \\ D_y \frac{\partial^2 c_2}{\partial y^2} \\ D_y \frac{\partial^2 c_3}{\partial y^2} \\ D_y \frac{\partial^2 c_4}{\partial y^2} \end{bmatrix} - \begin{bmatrix} D_z \frac{\partial^2 c_1}{\partial z^2} \\ D_z \frac{\partial^2 c_2}{\partial z^2} \\ D_z \frac{\partial^2 c_3}{\partial z^2} \\ D_z \frac{\partial^2 c_4}{\partial z^2} \end{bmatrix} \\ & = \begin{bmatrix} -k_1 & 0 & 0 & 0 \\ y_2 k_1 & -k_2 & 0 & 0 \\ 0 & y_3 k_2 & -k_3 & 0 \\ 0 & 0 & y_4 k_3 & -k_4 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix}, \end{aligned} \quad (4)$$

where the concentration terms c_1 , c_2 , c_3 , and c_4 are temporally and spatially variable unknown concentrations of the transported species.

Since the reaction coefficient matrix (\mathbf{K} matrix) on the right-hand side of (3) will usually have several cross-coupling terms (as shown in (4)), the set of coupled partial differential equations must be solved simultaneously to evaluate the unknown concentrations. However, for special cases when the \mathbf{K} matrix is in a diagonal form, the partial differential equations will become uncoupled, and under this condition each transport equation can be solved independently. The analytical solution strategy developed in this paper attempts to achieve this unique uncoupled condition for a generic set of coupled transport equations. The technique simply uses a series of judiciously chosen linear transformations to (3) to transform the coupled system into a new domain where \mathbf{K} will be in a diagonal form. In this transformed domain the uncoupled transport equations are solved individually to compute concentrations. Later, an inverse transformation equation is used to transform the concentrations back to the original domain. It should be pointed out that the basic linear transformation technique used in this paper is not new. It is a standard technique discussed in several linear algebra textbooks [e.g., Johnson and Riess, 1981] where a similar solution procedure is used for solving systems of ordinary differential equations. Aris [1965] used a similar technique to analyze batch reactions. In this work, we demonstrate the use of this technique for solving a system of coupled, advection-dispersion equations. Although the solution method is a straightforward application of linear transformation principles, to our knowledge, no one has demonstrated its use for deriving analytical solutions to reactive multispecies transport equations.

3. Solution Procedure

As a first step in the solution strategy, let us assume an arbitrary $n \times n$ transformation matrix \mathbf{S} and use its inverse matrix to perform the following linear transformation:

$$\hat{\mathbf{b}} = \mathbf{S}^{-1} \hat{\mathbf{c}}. \quad (5)$$

Conversely, the transformation equation can also be written in an inverse form:

$$\hat{\mathbf{c}} = \mathbf{S} \hat{\mathbf{b}}. \quad (6)$$

Note the transformation matrices \mathbf{S}^{-1} and \mathbf{S} are used to transform the original concentration vector $\hat{\mathbf{c}}$ into a transformed "b" domain or to convert the transformed concentration vector $\hat{\mathbf{b}}$ back to the original "c" domain, respectively.

Using principles of linear transformation, we can also transform the temporal derivatives of $\hat{\mathbf{c}}$ to the “b” domain using the relation

$$\hat{\mathbf{b}}' = \mathbf{S}^{-1}\hat{\mathbf{c}}', \quad (7)$$

where matrix \mathbf{S} is assumed to be independent of both temporal and spatial variations. Also, spatial derivatives of the \mathbf{c} vector can be transformed using the expression

$$\hat{\mathbf{b}}_x^2 = \mathbf{S}^{-1}\hat{\mathbf{c}}_x^2. \quad (8)$$

Similar expressions can be written for the y and z components of $\hat{\mathbf{c}}$ and also for $\hat{\mathbf{c}}_x^1$. Using expressions (5) through (8), (3) can be transformed as

$$\mathbf{RS}\hat{\mathbf{b}}' + v\mathbf{S}\hat{\mathbf{b}}_x^1 - D_x\mathbf{S}\hat{\mathbf{b}}_x^2 - D_y\mathbf{S}\hat{\mathbf{b}}_y^2 - D_z\mathbf{S}\hat{\mathbf{b}}_z^2 = \mathbf{KS}\hat{\mathbf{b}}. \quad (9)$$

Premultiplying the inverse matrix \mathbf{S}^{-1} to every term in (9), we can obtain the following expression:

$$\mathbf{S}^{-1}\mathbf{RS}\hat{\mathbf{b}}' + v\hat{\mathbf{b}}_x^1 - D_x\hat{\mathbf{b}}_x^2 - D_y\hat{\mathbf{b}}_y^2 - D_z\hat{\mathbf{b}}_z^2 = \mathbf{S}^{-1}\mathbf{KS}\hat{\mathbf{b}}. \quad (10)$$

Now, if we assume that $\mathbf{S}^{-1}\mathbf{R} = \mathbf{RS}^{-1}$ and if $\mathbf{S}^{-1}\mathbf{KS} = \tilde{\mathbf{K}}$, where $\tilde{\mathbf{K}}$ will be a diagonal matrix (validity of these two assumptions will be discussed later), then

$$\mathbf{R}\hat{\mathbf{b}}' + v\hat{\mathbf{b}}_x^1 - D_x\hat{\mathbf{b}}_x^2 - D_y\hat{\mathbf{b}}_y^2 - D_z\hat{\mathbf{b}}_z^2 = \tilde{\mathbf{K}}\hat{\mathbf{b}}. \quad (11)$$

Note that the format of (11) is similar to (3); however, since $\tilde{\mathbf{K}}$ is a diagonal matrix, (11) represents a set of n independent (uncoupled) transport equations that can be explicitly solved to evaluate the concentration vector $\hat{\mathbf{b}}$ in the transformed “b” domain. A standard analytical solution can be used to solve these uncoupled advection-dispersion equations with an “appropriate” first-order decay term. The initial and boundary conditions must be transformed to the “b” domain before obtaining the analytical solution. After computing the concentrations in the “b” domain, (6) can be used to transform the concentrations back to the “c” domain.

Depending on the dimensionality and initial and boundary conditions of the considered problem, several standard analytical solutions to (11) can be employed to solve the uncoupled transport equations in the transformed “b” domain. For example, the *Bear* [1979] solution can be used to solve one-dimensional problems with constant concentration boundary conditions; the *Wilson and Miller* [1978] solution can be used to solve two-dimensional problems with mass injection boundary conditions; and the *Kim et al.* [1988] or the *Domenico* [1987] solution can be used to solve three-dimensional problems with mass injection or constant concentration boundary conditions.

At this stage the validity of the assumptions used in deriving (11) must be established. The two relevant questions that need to be addressed are the following: (1) Under what conditions can we assume $\mathbf{S}^{-1}\mathbf{R} = \mathbf{RS}^{-1}$ in order to simplify the first term in (10)? (2) How can we compute the transformation matrix \mathbf{S} that would satisfy the relationship $\mathbf{S}^{-1}\mathbf{KS} = \tilde{\mathbf{K}}$, where $\tilde{\mathbf{K}}$ must be a diagonal matrix?

The answer to the first question is straightforward. Since matrix multiplication is not, in general, a commutative operation $\mathbf{S}^{-1}\mathbf{R}$ can be guaranteed to be equal to \mathbf{RS}^{-1} if and only if \mathbf{R} is a diagonal matrix and the diagonal entries of \mathbf{R} are identical. This requirement implies that the solution strategy is applicable only when the transport equations have identical retardation values, which is clearly a major limitation of this solution strategy.

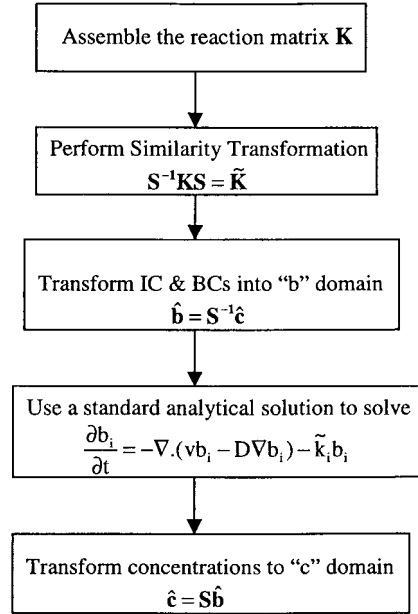


Figure 1. Algorithm for the generalized solution procedure.

To answer the second question, we will use the following matrix properties related to similarity transformation of matrices [Johnson and Riess, 1981]:

If \mathbf{P} is a square matrix whose column vectors are the eigenvectors of a matrix \mathbf{A} , then $\mathbf{P}^{-1}\mathbf{A}\mathbf{P} = \mathbf{D}$, where \mathbf{D} will be a diagonal matrix; also, the diagonal entries of \mathbf{D} are nothing but the eigenvalues of \mathbf{A} . The matrices \mathbf{A} and \mathbf{D} are known to be similar matrices. The process of decomposing a square matrix \mathbf{A} into a $\mathbf{P}\mathbf{D}\mathbf{P}^{-1}$ form is known as the similarity transformation.

On the basis of these matrix properties we can conclude that our problem of finding \mathbf{S} and \mathbf{S}^{-1} reduces to performing a similarity transformation analysis of the \mathbf{K} matrix. Several general-purpose numerical computer algorithms are available for solving the similarity transformation problem [Press et al., 1992]. One of these algorithms can be used to numerically evaluate the \mathbf{S} and \mathbf{S}^{-1} matrices for a given \mathbf{K} matrix. Once \mathbf{S}^{-1} is known, the initial and boundary conditions of the problem can be transformed to the “b” domain using (5), and then the uncoupled transport equations can be independently solved in the “b” domain. Later, the \mathbf{S} matrix can be used to transform the concentrations back to the “c” domain by employing (6). Note the \mathbf{K} matrix can be used to represent any combination of first-order reaction, including multiparent reactions, converging, and/or reversible reactions, provided all the reaction steps follow first-order kinetics. A general computer algorithm for implementing this solution strategy is shown in Figure 1. Application of this algorithm for solving a four-component example problem is discussed in section 4.

4. Example Problem

A schematic of the reaction network considered in this example is given in Figure 2. As shown in Figure 2, the network consists of a system of serial, parallel, and reversible reactions. Assuming one-dimensional transport with no adsorption and first-order reaction kinetics, the reactive transport equations for the system can be written using matrix notations as

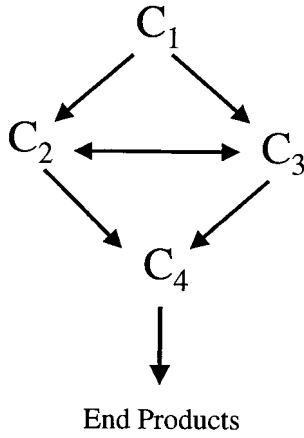


Figure 2. Schematic of the reaction network.

$$\begin{aligned}
 & \begin{bmatrix} \frac{\partial c_1}{\partial t} \\ \frac{\partial c_2}{\partial t} \\ \frac{\partial c_3}{\partial t} \\ \frac{\partial c_4}{\partial t} \end{bmatrix} + \begin{bmatrix} v \frac{\partial c_1}{\partial x} \\ v \frac{\partial c_2}{\partial x} \\ v \frac{\partial c_3}{\partial x} \\ v \frac{\partial c_4}{\partial x} \end{bmatrix} - \begin{bmatrix} D \frac{\partial^2 c_1}{\partial x^2} \\ D \frac{\partial^2 c_2}{\partial x^2} \\ D \frac{\partial^2 c_3}{\partial x^2} \\ D \frac{\partial^2 c_4}{\partial x^2} \end{bmatrix} \\
 & = \begin{bmatrix} -k_1 & 0 & 0 & 0 \\ F_{c_2/c_1} Y_{c_2/c_1} k_1 & -k_2 & F_{c_2/c_3} Y_{c_2/c_3} k_3 & 0 \\ F_{c_3/c_1} Y_{c_3/c_1} k_1 & F_{c_3/c_2} Y_{c_3/c_2} k_2 & -k_3 & 0 \\ 0 & F_{c_4/c_2} Y_{c_4/c_2} k_2 & F_{c_4/c_3} Y_{c_4/c_3} k_3 & -k_4 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix}, \quad (12)
 \end{aligned}$$

where the decay fraction F_{c_j/c_i} is the mass fraction of a parent compound c_i decaying into a daughter product c_j and Y_{c_j/c_i} is the stoichiometric yield value of the reaction. To conserve mass balance, the decay fractions should satisfy the following constraints:

$$F_{c_2/c_1} + F_{c_3/c_1} = 1.0, \quad (13)$$

$$F_{c_3/c_2} + F_{c_4/c_2} = 1.0, \quad (14)$$

$$F_{c_2/c_3} + F_{c_4/c_3} = 1.0. \quad (15)$$

Note that in (13)–(15), the product FY may be combined into an effective yield value (y) or the product FYk can also be combined as an effective reaction rate. However, keeping these terms separate would help better illustrate the underlying reaction mechanisms of the kinetic framework.

The above reactive transport problem was solved using the computational algorithm shown in Figure 1. An eigenvalue decomposition routine available in EISPACK [Smith, 1976] was used to numerically evaluate the \mathbf{S} , \mathbf{S}^{-1} , and $\bar{\mathbf{K}}$ matrices for this example problem. Since transport is assumed to be one-dimensional, the Bear [1979] analytical solution, which can predict the movement of a radioactive tracer in a semi-infinite column, was used as the basis solution for computing concentrations in the transformed domain. The column was assumed to have uniform initial concentrations and constant inlet concentrations. These boundary conditions are similar to those used in deriving the Bear [1979] solution. The length of the column was assumed to be 40 m, and the initial concentrations

Table 1. Transport and Reaction Parameters Used in the Example Problem

Parameter	Value
Column length L	40 m
Dispersion coefficient D	$0.08 \text{ m}^2 \text{ d}^{-1}$
Velocity v	0.4 m d^{-1}
Reaction rate k_1	0.075 d^{-1}
Reaction rate k_2	0.05 d^{-1}
Reaction rate k_3	0.02 d^{-1}
Reaction rate k_4	0.045 d^{-1}
Yield Y (all of them)	1.0 mol mol^{-1}
F_{c_2/c_1}	0.75
F_{c_3/c_1}	0.25
F_{c_3/c_2}	0.5
F_{c_4/c_2}	0.5
F_{c_4/c_3}	0.2
F_{c_2/c_3}	0.8

of all the species were set to zero. The inlet concentration of species 1 was fixed to be equal to 1 mol L^{-1} , and the inlet concentrations of all other species were set to zero. Other physical and chemical transport parameters used in this problem are summarized in Table 1. Simulations were completed to predict the reactive transport in the column for a period of 50 days.

The performance of the analytical solution strategy was evaluated by comparing the results of the presented solution scheme with the results predicted using the finite difference numerical reactive transport solver RT3D [Clement, 1997]. Figure 3 shows the predicted concentration profiles of all four species across the column after 50 days of reactive transport calculated by using the presented analytical approach and by using the RT3D code. The results indicate that the concentration profiles predicted by both methods are almost identical.

5. Analytical Analysis of the Sequential Reaction Problem and Comparison With the Sun et al. [1999b] Solution

It is possible to derive general analytical expressions for the \mathbf{K} matrix transformation matrices \mathbf{S} and \mathbf{S}^{-1} for simple reaction systems, such as the sequential decay system. In this section we will first derive analytical expressions for the elements of \mathbf{S} and \mathbf{S}^{-1} for the four-species sequential decay problem described by (4) and will later use these results to deduce the format of \mathbf{S} and \mathbf{S}^{-1} matrices for a general sequential reaction system. As a first step, the following matrix equation is solved to compute the eigenvalues and eigenvectors for the \mathbf{K} matrix of (4):

$$\begin{bmatrix} -k_1 & 0 & 0 & 0 \\ y_2 k_1 & -k_2 & 0 & 0 \\ 0 & y_3 k_2 & -k_3 & 0 \\ 0 & 0 & y_4 k_3 & -k_4 \end{bmatrix} \begin{bmatrix} s_{1,1} \\ s_{2,1} \\ s_{3,1} \\ s_{4,1} \end{bmatrix} = \lambda_1 \begin{bmatrix} s_{1,1} \\ s_{2,1} \\ s_{3,1} \\ s_{4,1} \end{bmatrix}, \quad (16)$$

where the $\hat{s}_{i,1}$ vector is the eigenvector corresponding to one of the eigenvalues (λ_i) of the reaction coefficient matrix \mathbf{K} . To solve this eigenvalue problem, we will use the following matrix property [Cullen, 1979]: “if a square matrix \mathbf{A} is a triangular matrix (as our \mathbf{K} matrix) then its eigenvalues are displayed on the diagonal.” From this matrix property we can conclude that the \mathbf{K} matrix used in this example will have four distinct eig-

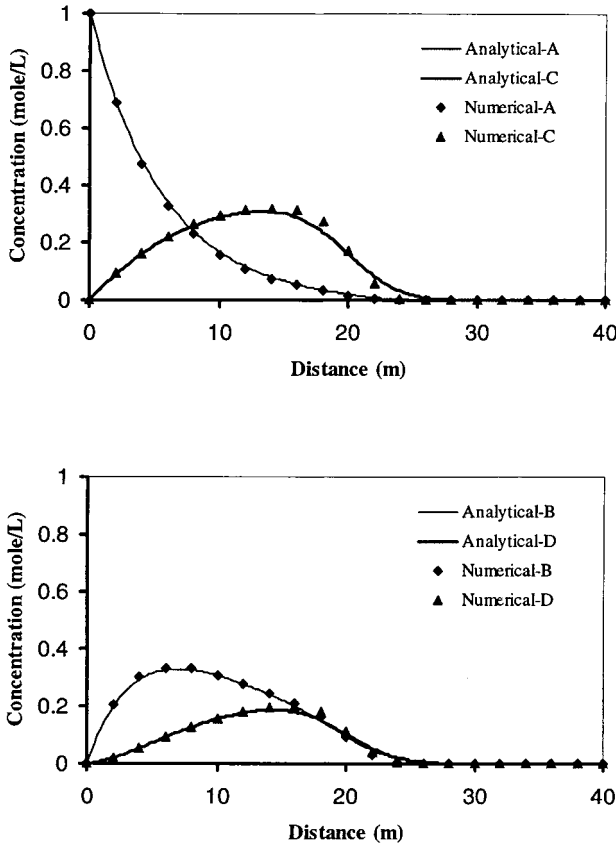


Figure 3. Comparison of the results from the presented solution scheme against numerical solutions obtained using the RT3D code.

envalues: $-k_1$, $-k_2$, $-k_3$, and $-k_4$. Therefore the $\bar{\mathbf{K}}$ matrix for the system can be written as

$$\bar{\mathbf{K}} = \begin{bmatrix} -k_1 & 0 & 0 & 0 \\ 0 & -k_2 & 0 & 0 \\ 0 & 0 & -k_3 & 0 \\ 0 & 0 & 0 & -k_4 \end{bmatrix}. \quad (17)$$

When the eigenvalue is equal to $-k_1$ (i.e., when $\lambda_1 = -k_1$), the eigenvector for the system can be derived as

$$\begin{bmatrix} s_{1,1} \\ s_{2,1} \\ s_{3,1} \\ s_{4,1} \end{bmatrix} = \begin{bmatrix} 1 \\ \frac{-y_2 k_1}{(k_1 - k_2)} \\ \frac{-y_2 y_3 k_1 k_2}{(k_1 - k_2)(k_1 - k_3)} \\ \frac{-y_2 y_3 y_4 k_1 k_2 k_3}{(k_1 - k_2)(k_1 - k_3)(k_1 - k_4)} \end{bmatrix}. \quad (18)$$

Similarly, for $\lambda_2 = -k_2$, $\lambda_3 = -k_3$, and $\lambda_4 = -k_4$ we can derive the eigenvectors as

$$\begin{bmatrix} s_{1,2} \\ s_{2,2} \\ s_{3,2} \\ s_{4,2} \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \\ \frac{-y_3 k_2}{(k_2 - k_3)} \\ \frac{-y_3 y_4 k_2 k_3}{(k_2 - k_3)(k_2 - k_4)} \end{bmatrix},$$

$$\begin{bmatrix} s_{1,3} \\ s_{2,3} \\ s_{3,3} \\ s_{4,3} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 1 \\ \frac{-y_4 k_3}{(k_3 - k_4)} \end{bmatrix}, \quad \begin{bmatrix} s_{1,4} \\ s_{2,4} \\ s_{3,4} \\ s_{4,4} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}. \quad (19)$$

It should be noted that these eigenvectors are not the unique solution to the eigenvalue problem. Any scalar multiple of each of these eigenvectors will also satisfy its respective eigenvalue equation, and hence it is possible to derive an infinite number of \hat{s} vectors. We selected this particular set of eigenvectors to facilitate comparison of our solution with the solution strategy proposed by *Sun et al.* [1999b].

Now, using the properties of similarity transformation, we can assemble the \mathbf{S} matrix for the problem as

$$\mathbf{S} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ \frac{-y_2 k_1}{(k_1 - k_2)} & 1 & 0 & 0 \\ \frac{-y_2 y_3 k_1 k_2}{(k_1 - k_2)(k_1 - k_3)} & \frac{-y_3 k_2}{(k_2 - k_3)} & 1 & 0 \\ \frac{-y_2 y_3 y_4 k_1 k_2 k_3}{(k_1 - k_2)(k_1 - k_3)(k_1 - k_4)} & \frac{-y_3 y_4 k_2 k_3}{(k_2 - k_3)(k_2 - k_4)} & \frac{-y_4 k_3}{(k_3 - k_4)} & 1 \end{bmatrix} \quad (20)$$

Note that the \mathbf{S} matrix assembled above is not a unique possibility even for the selected set of four independent \hat{s} vectors. This is because the columns of the \mathbf{S} matrix can be rearranged by placing the individual \hat{s} vectors in any order. However, note that the column location j of an eigenvector in the \mathbf{S} matrix should always be matched with its eigenvalue by entering the corresponding eigenvalue (the appropriate decay coefficient, in our case) in the location j, j within the $\bar{\mathbf{K}}$ matrix. Again, we selected this particular arrangement of eigenvectors in the \mathbf{S} matrix to facilitate comparison of our solution with the work by *Sun et al.* [1999b].

Matrix \mathbf{S} can be inverted and an analytical expression for \mathbf{S}^{-1} can be written as

$$\mathbf{S}^{-1} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ \frac{y_2 k_1}{(k_1 - k_2)} & 1 & 0 & 0 \\ \frac{y_2 y_3 k_1 k_2}{(k_1 - k_3)(k_2 - k_3)} & \frac{y_3 k_2}{(k_2 - k_3)} & 1 & 0 \\ \frac{y_2 y_3 y_4 k_1 k_2 k_3}{(k_1 - k_4)(k_2 - k_4)(k_3 - k_4)} & \frac{y_3 y_4 k_2 k_3}{(k_3 - k_4)(k_2 - k_4)} & \frac{y_4 k_3}{(k_3 - k_4)} & 1 \end{bmatrix} \quad (21)$$

By observing a repetitive pattern in the entries of matrices (20) and (21), we formulated the following algorithm to assemble \mathbf{S} and \mathbf{S}^{-1} matrices for a general “ n ” component sequential decay system:

$$\begin{aligned} s_{i,j} &= s_{i,j}^{-1} = 0, & j > i \\ s_{i,j} &= s_{i,j}^{-1} = 1, & i = j \end{aligned} \quad (22)$$

$$s_{i,j} = \prod_{m=j}^{i-1} \frac{-y_{m+1} k_m}{k_j - k_{m+1}}, \quad s_{i,j}^{-1} = \prod_{m=j}^{i-1} \frac{y_{m+1} k_m}{k_m - k_i} \quad j < i.$$

These general expressions can be used to assemble the transformation matrices \mathbf{S} and \mathbf{S}^{-1} for solving any number of sequential reactive transport equations. It could be inferred from (20)–(22) that this solution method is feasible only when the

first-order rate constants of the transported species have different numerical values.

It is interesting to note that the entries of \mathbf{S}^{-1} have a format similar to the analytical transformation format proposed by Sun *et al.* [1999b]. Sun *et al.* presented (without any fundamental analysis) the following transformation format for solving sequential reactive transport problems:

$$b_i = c_i + \sum_{j=1}^{i-1} \left[\prod_{m=j}^{i-1} \frac{y_{m+1}k_m}{k_m - k_i} \right] c_j, \quad \forall i = 2, \dots, n. \quad (23)$$

By comparing (22) and (23), one can infer that the Sun *et al.* [1999b] transformation format is a generic equation that can be used to evaluate the nonzero elements of the i th row of the transformation matrix \mathbf{S}^{-1} and to compute the i th row of the matrix product $\mathbf{S}^{-1} \hat{\mathbf{c}}$. The solution steps discussed by Sun *et al.* [1999b] essentially perform the linear transformation described by the equation $\hat{\mathbf{b}} = \mathbf{S}^{-1} \hat{\mathbf{c}}$ and solve the transport problem in the uncoupled "b" domain. However, they do not use the inverse transformation equation $\hat{\mathbf{c}} = \mathbf{S} \hat{\mathbf{b}}$ to transform the concentrations back into the "c" domain; instead, they use a simple successive substitution strategy to directly solve the matrix equation $\hat{\mathbf{b}} = \mathbf{S}^{-1} \hat{\mathbf{c}}$ in an inverse mode. Since their \mathbf{S}^{-1} matrix is guaranteed to be in a lower triangular form, the successive substitution strategy will always be feasible for their restricted case. However, this approach is clearly limited for solving sequential reaction chains. More complex reactions, such as reversible reactions, converging reactions, and multiparent reactions, cannot be solved by their approach. Also, it should be noted that Sun *et al.* [1999b] format is just one of the infinite number of linear transformation formats that could be derived, from various possible \mathbf{S} and \mathbf{S}^{-1} matrices, to solve the sequential reactive transport problem.

The solution steps similar to those discussed above can be used to derive analytical transformation matrices to other simple reaction systems with large number of species or to complex reaction systems with a limited number of species. However, it should be noted that the entries of \mathbf{S} and \mathbf{S}^{-1} matrices will become more complex and unstructured with an increase in the number of species and with increases in the complexity of the reaction system. Therefore, using a numerical routine for evaluating the \mathbf{S} and \mathbf{S}^{-1} matrices and employing the general algorithm shown in Figure 1 seems to be a more pragmatic approach for developing general-purpose, first-order-network coupled reactive transport codes.

6. Conclusions

A general solution method is presented for solving multispecies transport equations coupled with multiparent, serial, parallel, converging, diverging, and/or reversible first-order reactions. The method is flexible for analytically solving any type of coupled, first-order reactive transport system in one, two, or three dimensions under uniform flow conditions. Mathematical steps are presented to show how linear transformation techniques can be used to derive analytical solutions to this class of coupled reactive transport problems. The analysis also shows how the Sun *et al.* [1999b] solution format, which was previously presented without any fundamental analysis, can be derived using linear transformation principles. The major limitation of this approach is that the method cannot be extended

for solving multispecies transport equations with different retardation factors. This is an important shortcoming of the solution strategy. An example problem was solved to illustrate the application of the proposed solution scheme. Results of the presented solution scheme compared well with the results from a numerical solution computed using the numerical reactive transport code RT3D. The proposed analytical methodology is a useful tool for testing the performance of complex multispecies transport codes under first-order reactive transport conditions.

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References

- Aris, R., *Introduction to the Analysis of Chemical Reactors*, pp. 97–101, Prentice-Hall, Englewood Cliffs, N. J., 1965.
- Bear, J., *Hydraulics of Groundwater*, pp. 268–269, McGraw-Hill, Inc., New York, 1979.
- Chilakapati, A., and S. Yabusaki, Nonlinear reactions and nonuniform flows, *Water Resour. Res.*, 35(8), 2427–2438, 1999.
- Chilakapati, A., T. Ginn, and J. Szecsy, An analysis of complex reaction networks in groundwater modeling, *Water Resour. Res.*, 34(7), 1767–1780, 1998.
- Clement, T. P., A modular computer model for simulating reactive multi-species transport in three-dimensional groundwater systems, *Rep. PNNL-SA-28967*, Pac. Northwest Natl. Lab. Richland, Wash., 1997.
- Clement, T. P., Y. Sun, B. S. Hooker, and J. N. Petersen, Modeling multi-species reactive transport in groundwater aquifers, *Groundwater Monit. Remed.*, 18(2), 79–92, 1998.
- Clement, T. P., C. D. Johnson, Y. Sun, G. M. Klecka, and C. Bartlett, Natural attenuation of chlorinated solvent compounds: Model development and field-scale application, *J. Contam. Hydrol.*, 42, 113–140, 2000.
- Culen, C. G., *Linear Algebra and Differential Equations, an Integrated Approach*, p. 180, PWS, Boston, Mass., 1979.
- Domenico, P. A., An analytical model for multidimensional transport of a decaying contaminant species, *J. Hydrol.*, 91, 49–58, 1987.
- Johnson, L. W., and R. D. Riess, *Introduction to Linear Algebra*, pp. 155–160, Addison-Wesley-Longman, Reading, Mass., 1981.
- Khandelwal, A., and A. J. Rabideau, Transport of sequentially decaying reaction products influenced by linear nonequilibrium sorption, *Water Resour. Res.*, 35(6), 1939–1945, 1999.
- Kim, C. L., P. L. Chambre, W. W.-L. Lee, and T. H. Pigherd, Contaminant transport from an array of sources, *Rep. LBL-24200, UC-403, 43-47*, Earth Sci. Div., Lawrence Berkeley Lab., Univ. of Calif., Berkeley, 1988.
- Lunn, M., R. J. Lunn, and R. Mackay, Determining analytic solution of multiple species contaminant transport, with sorption and decay, *J. Hydrol.*, 180, 195–210, 1996.
- Press, W. H., S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in Fortran*, Cambridge Univ. Press, New York, 1992.
- Smith, B. T., *Matrix Eigen-System Routines—EISPACK Guide*, 2nd ed., *Lect. Notes Comput. Sci.*, vol. 6, Springer-Verlag, New York, 1976.
- Sun, Y., and T. P. Clement, A generalized decomposition method for solving coupled multi-species reactive transport problems, *Transp. Porous Media*, 37(3), 327–346, 1999.
- Sun, Y., J. N. Petersen, and T. P. Clement, A new analytical solution for multiple species reactive transport in multiple dimensions, *J. Contam. Hydrol.*, 35(4), 429–440, 1999a.

Sun, Y., J. N. Petersen, T. P. Clement, and R. S. Skeen, Development of analytical solutions for multispecies transport with serial and parallel reactions, *Water Resour. Res.*, 35(1), 185–190, 1999b.

van Genuchten, M. T., Convective-dispersive transport of solutes involved in sequential first-order decay reactions, *Comput. Geosci.*, 11(2), 129–147, 1985.

Wilson, J. L., and P. J. Miller, Two-dimensional plume in uniform groundwater flow, *J. Hydraul. Div. Am. Soc. Civ. Eng.*, 104, 503–514, 1978.

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