Modeling reactive transport using exact solutions for first-order reaction networks

Yunwei Sun · Thomas A. Buscheck · Yue Hao

Abstract Operator splitting is often used for solving advection-dispersion-reaction (ADR) equations. Each operator can be solved separately using an algorithm appropriate to its mathematical behavior. Although a lot of research has been done in operator splitting for solving ADR equations, numerical approaches for the reaction operator are computationally expensive. To meet the convergence criteria of ODE (ordinary differential equation) or DAE (differential algebraic equation) solvers, a transport time step has to be subdivided into a large number of reaction time steps. Additional computation effort is also required to reduce the splitting error. In this paper, we develop exact solutions of various first-order reaction networks for the reaction operator and couple those solutions with numerical solutions of the transport operator. The reactions are treated as local phenomena and simulated using exact solutions that we develop, while advection and dispersion are treated as global processes and simulated numerically. The proposed method avoids the numerical error from the reaction operator and requires a single-step calculation to solve the reaction operator. Compared to conventional operator-splitting methods, the proposed method offers both computational efficiency and simulation accuracy.

Keywords Reactive transport · First-order reaction · Operator splitting · Numerical modeling · Analytical solution

1 Introduction

Equations of multispecies reactive transport in porous media are described as (Bear 1979)

Y. Sun (✉) · T. A. Buscheck · Y. Hao
Lawrence Livermore National Laboratory,
808, L-631, Livermore,
CA 94550, USA
e-mail: sun4@llnl.gov

$$R_i \frac{\partial c_i}{\partial t} = \nabla \cdot (\nabla \cdot \mathbf{D}c_i - \mathbf{v}c_i) + R_i f_i(\mathbf{c}), \quad \forall i = 1, 2, \ldots, n \tag{1}$$

where c_i [ML^{-3}] is the concentration of ith species; t is time [T]; $\mathbf{v}$ [LT^{-1}] is the vector of velocity; $\mathbf{D}$ [L^{2}T^{-1}] is the tensor of dispersion coefficients; f_i is the gain or loss of ith species due to reactions; R_i is the retardation factor of ith species; and n is the total number of species. Divided by R_i, Eq. 1 can be written as

$$\frac{\partial c_i}{\partial t} = \nabla \cdot (\nabla \cdot \mathbf{D}_i c_i - \mathbf{v}_i c_i) + f_i(\mathbf{c}), \quad \forall i = 1, 2, \ldots, n \tag{2}$$

where each species has its specific velocity vector and dispersion tensor,

$$\mathbf{v}_i = \frac{\mathbf{v}}{R_i}, \quad \mathbf{D}_i = \frac{\mathbf{D}}{R_i}.$$

If all reactions are assumed to be first-order, Eq. 2 can be expressed in the matrix format:

$$\frac{\partial \mathbf{c}}{\partial t} = \mathcal{L} + \mathbf{A}\mathbf{c}, \quad \mathcal{L} = \begin{bmatrix} \nabla \cdot (\nabla \cdot \mathbf{D}_1 c_1 - \mathbf{v}_1 c_1) \\ \nabla \cdot (\nabla \cdot \mathbf{D}_2 c_2 - \mathbf{v}_2 c_2) \\ \cdots \\ \nabla \cdot (\nabla \cdot \mathbf{D}_i c_i - \mathbf{v}_i c_i) \\ \cdots \\ \nabla \cdot (\nabla \cdot \mathbf{D}_n c_n - \mathbf{v}_n c_n) \end{bmatrix}. \tag{3}$$

In Eq. 3, $\mathbf{A}$ is the first-order reaction matrix.

Equation 3 can be solved either analytically or numerically according to the complexity of the modeled system. Besides analytical approaches, three predominant approaches, including globally implicit (GIA), sequentially iterative (SIA), and sequentially non-iterative (SNIA, also called operator splitting, OS) algorithms, are used to solve the coupled reactive transport systems (Yeh and Tripathi 1989; Robinson et al. 2000; Prommer et al. 2003; Hammond et al. 2004; Chen and MacQuarrie 2005). The use of an implicit numerical method for the time integration may lead to excessive algebraic manipulations because the dimension of the system matrices is typically determined by the product of the number of variables, the number of species, and the number of grid blocks. Operator-splitting methods reduce the dimension of matrices. Advection, dispersion, source/sink mixing, and reactions can be solved separately using various numerical algorithms (Zheng and Wang 1999; Miller and Rabideau 1993; Steefel and MacQuarrie 1996; Clement et al. 1996, 1998; Yabusaki et al. 1998; Schäfer et al. 1998).

Although operator-splitting methods are easy to implement and require less computational capability, they introduce operator-splitting error into the simulated results (Valocchi and Malmstead 1992; Lu et al. 1996; Barry et al. 1996a, 1996b, 2000; Cheng et al. 2003; Hammond et al. 2004). Several investigators have analyzed the splitting error to advection-dispersion-reaction simulations (Valocchi and Malmstead 1992; Kaluarachchi and Morshed 1995; Morshed and Kaluarachchi 1995; Barry et al. 1996a, 1996b, 2000; Lanser and Verwer 1999; Carrayrou et al. 2004). To avoid or reduce the splitting error, several techniques have been developed (e.g., Lanser and Verwer 1999; Simpson et al. 2005), but they come with an additional computation effort. There is always a tradeoff between computational efficiency (both labor and resources) and the accuracy of simulated systems.

The reaction term, described by a set of ordinary differential equations, is usually simulated by using ODE solvers, such as the fourth-order Runge–Kutta method (Clement et al. 1998). When the first-order reaction rates of neighboring species differ by a large magnitude, the reaction system may require small time steps because the fast reacting species lead to a

stiff system. Consequently, the ODEs of the reaction system cannot be solved by using conventional ODE solvers (Sportisse 2000). For large simulation times (for example, 10^6 years for the Yucca Mountain Project), the simulation of reactive transport with stiff reactions becomes computationally expensive and even prohibitive. Often, stiff ODE solvers must be used.

Schulz and Reardon (1983) used an analytical solution of the transport operator for solving ADR equations and Valocchi and Malmstead (1992) were the first to use an exact solution of a single-species first-order reaction in their OS procedure to examine the OS error from the transport operator. Geiser (2001) introduced an exact solution of sequential first-order reactions (Sun et al. 1999a) into an operator-splitting procedure. The use of exact solutions in OS procedures requires only a single-step calculation of a closed-form solution, eliminating the numerical error from ODE solvers. Thus, both the computational efficiency and the accuracy of simulated results can be enhanced. However, the OS procedure of Geiser (2001) is limited to a typical case of a sequential and unimolecular reaction chain.

In this paper, we propose a generalized OS scheme to cover more general and complex reaction networks, such as sequential, parallel, convergent, and reversible reactions using previously published analytical solutions (e.g., Sun et al. 1999b; Lu et al. 2003; Sun et al. 2004). Recently, singular-value decomposition (SVD) has been used for solving linear reaction systems (Clement 2001; Samper-Calvete and Yang 2006). Instead of using the typical transform of Sun et al. (1999a) (Geiser 2001), we conducted singular-value decomposition analytically for generalized reaction matrices and developed a solution library of a wide range of reaction networks. The total system of reaction equations is analytically diagonalized (transformed) into a new coordinate system in which there is no coupling between the different coordinate directions (species concentrations) and the system is resolved into a set of *n* independent scalar equations with the same mathematical format. Then, closed-form solutions of reaction systems are obtained for these independent scalar equations. The application can be extended from radionuclide decay to more general purposes, such as biodegradation reaction networks, denitrification, etc.

2 Solution methodology

The advection-dispersion-reaction system (3) is separated as transport and reaction equations. The transport equation is solved using numerical methods, such as finite difference and finite element, and the reaction equation is solved using exact solutions. The mass balance equation, Eq. 3, can be expressed by transport and reaction operators:

$$\frac{\partial \mathbf{c}}{\partial t} = \mathcal{L}(\mathbf{c}) + \mathcal{R}(\mathbf{c}), \tag{4}$$

where

$$\mathcal{L}_i = -\nabla \cdot (\mathbf{v}_i c_i - \nabla \cdot \mathbf{D}_i c_i), \quad i = 1, 2, \ldots, n \tag{5}$$

$$\mathcal{R} = \mathbf{A}\mathbf{c}. \tag{6}$$

In the transport operator, Eq. 5, advection and dispersion are species-independent and spatially dependent. The velocity and dispersion coefficient are normalized by the retardation factor of the species. Therefore, the transport operator for each species can be solved without considering other species concentrations. The reaction operator is spatially independent; however, it is a function of other species concentrations at a given node. Consequently, reaction equations can be solved only by discretizing the time domain.

To use a finite difference method in order to solve the transport operator, Eq. 5, the spatial and time domains need to be discretized. *Peclet* number and *Courant* number are used to determine transport time steps and spatial intervals:

$$P_e = \frac{v \Delta x}{D_L} \leq 1, \quad C_r = \frac{v \Delta t}{\Delta x} \leq 1$$

where D_L [L^{2}T^{-1}] is the longitudinal dispersion coefficient. Then,

$$\Delta t \leq \frac{D_L}{v^2}.$$

Each transport time step, $t_i \leq t \leq t_{i+1}$, is conventionally subdivided into a large number of reaction time steps to meet the convergence criteria of ODE solvers. However, if the first-order reaction matrix, $\mathbf{A}$, is analytically diagonalizable, closed-form solutions can be used to represent the reaction operator,

$$\mathbf{c} = \mathcal{F}(\mathbf{c}^t, \Delta t) \tag{7}$$

where $\mathbf{c}^t$ is the concentration vector at time, t_{i+1}, calculated from the transport operator and $\mathcal{F}$ denotes a closed-form solution.

The focus of this method is to use an analytical solution, $\mathcal{F}$, to a given reaction matrix, $\mathbf{A}$, in the operator-splitting scheme. If $\mathbf{A}$ is diagonalizable either analytically or numerically,

$$\mathbf{A} = \mathbf{S}\mathbf{\Lambda}\mathbf{S}^{-1}, \tag{8}$$

where $\mathbf{\Lambda}$ is an $n \times n$ diagonal matrix containing the eigenvalues of $\mathbf{A}$, and $\mathbf{S}$ is a matrix whose columns are linearly independent eigenvectors of $\mathbf{A}$. Substituting Eq. 8 into Eq. 6 yields

$$\frac{d\mathbf{c}}{dt} = \mathbf{S}\mathbf{\Lambda}\mathbf{S}^{-1}\mathbf{c}. \tag{9}$$

Multiplying by $\mathbf{S}^{-1}$, Eq. 9 becomes

$$\frac{d\mathbf{a}}{dt} = \mathbf{\Lambda}\mathbf{a}, \quad \mathbf{a} = \mathbf{S}^{-1}\mathbf{c}. \tag{10}$$

Each ODE in Eq. 10 is independent of other PDEs. Thus, we can write,

$$\frac{da_i}{dt} = \lambda_i a_i, \quad i = 1, 2, \ldots, n, \tag{11}$$

and

$$a_i^r = a_i^o \exp(\lambda_i t), \quad i = 1, 2, \ldots, n. \tag{12}$$

Then, the solution in terms of $\mathbf{c}$ is obtained:

$$\mathbf{c}^r = \mathbf{S}\mathbf{a}^r \tag{13}$$

with $\mathbf{c}^r$ and $\mathbf{a}^r$ denoting the concentration vectors calculated from the reaction operator.

3 Analytical solutions of reaction networks

Reaction networks can be decomposed and categorized as sequential, reversible, parallel, and convergent subsystems as shown in Fig. 1. All reactions are assumed to be first order in this work. Although the first-order reaction rates can be spatially and temporally dependent

Fig. 1 Reaction patterns.
(**a**) basic reaction; (**b**) sequential
reactions; (**c**) reversible reactions;
(**d**) parallel reactions; and
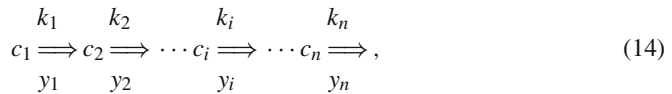(**e**) convergent reactions
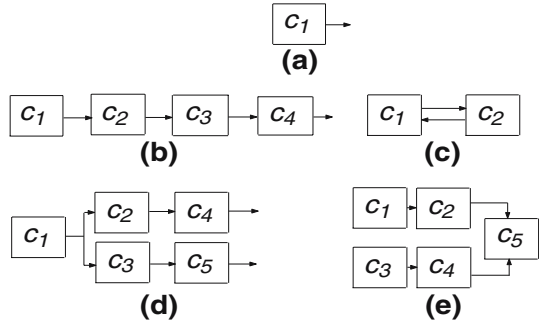
at a given node and during a time interval, the study domain of the reaction operator is treated as a batch reactor.

Among those reaction patterns, a single-species first-order reaction is the basic pattern. The emphasis of this paper is to decompose those coupled reactions into the basic reaction, a single-species first-order reaction, for which Eq. 12 can be used as its closed-form solution. Complex reaction networks can be decomposed to those basic reaction patterns. Therefore, a solution library of previously developed analytical solutions can be coupled by transport codes for simulating the reaction operator. In addition to the method that Sun et al. (1999a) used for deriving analytical solutions of sequential and unimolecular reaction chains, singular-value decomposition (SVD) is commonly used to derive closed-form solutions (Sun and Clement 1999; Clement 2001; Samper-Calvete and Yang 2006). In this section, we demonstrate how to apply SVD to derive analytical solutions for (but not limited to) the sequential and parallel/convergent reaction patterns.

3.1 Sequential reactions

The sequential reactions can be expressed as

$$
c_1 \overset{k_1}{\underset{y_1}{\Longrightarrow}} c_2 \overset{k_2}{\underset{y_2}{\Longrightarrow}} \cdots c_i \overset{k_i}{\underset{y_i}{\Longrightarrow}} \cdots c_n \overset{k_n}{\underset{y_n}{\Longrightarrow}},
\tag{14}
$$

where y_i is the yield coefficient of ith reaction and $y = 1$ is for unimolecular reactions. The yield coefficient is defined as the amount of a daughter species produced per unit of a reactant (parent species) consumed. The reaction matrix is written as:

$$
\mathbf{A} =
\begin{bmatrix}
-k_1 & 0 & \cdot & & \cdots & 0 \\
\frac{R_1}{R_2} y_1 k_1 & -k_2 & \cdot & & \cdot & 0 \\
\vdots & \vdots & \ddots & & \vdots & \vdots \\
0 & \cdots & \frac{R_{i-1}}{R_i} y_{i-1} k_{i-1} & -k_i & & \cdots \\
\vdots & \vdots & \ddots & & \vdots & \vdots \\
\cdots & \cdots & \cdots & & \frac{R_{n-1}}{R_n} y_{n-1} k_{n-1} & -k_n
\end{bmatrix}.
\tag{15}
$$

The first decoupling method of n-species sequential reactions was developed for unimolecular reactions ($y_i = 1$, $R_i = 1$, $i = 1, \ldots, n$, Sun et al. 1999a), in which one unit of a reactant reacts to produce one unit of a product. The method was modified for sequential reactions with yield coefficients ($y_i \neq 1$, $R_i = 1$, $i = 1, \ldots, n$, Sun et al. 1999b). Geiser

(2001) extended the method of Sun et al. (1999a) with distinct retardation factors in his operator-splitting approach ($y_i = 1$, $R_i \neq 1$, $i = 1, \ldots, n$). Considering both yield coefficients and retardation factors, the transform is derived as (see Appendix A)

$$a_i = c_i + \sum_{j=1}^{i-1} \frac{R_j}{R_i} \prod_{l=j}^{i-1} \frac{y_l k_l}{k_l - k_i} c_j, \tag{16}$$

$$c_i = a_i + \sum_{j=1}^{i-1} \frac{R_j}{R_i} \prod_{l=j+1}^{i} \frac{y_{l-1} k_{l-1}}{k_l - k_j} a_j. \tag{17}$$

The transform matrices can be expressed as (for example, when $n = 5$)

$$\mathbf{S} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ \frac{R_1}{R_2} \frac{y_1 k_1}{k_2 - k_1} & 1 & 0 & 0 & 0 \\ \frac{R_1}{R_3} \prod_{l=2}^{3} \frac{y_{l-1} k_{l-1}}{k_l - k_1} & \frac{R_2}{R_3} \frac{y_2 k_2}{k_3 - k_2} & 1 & 0 & 0 \\ \frac{R_1}{R_4} \prod_{l=2}^{4} \frac{y_{l-1} k_{l-1}}{k_l - k_1} & \frac{R_2}{R_4} \prod_{l=3}^{4} \frac{y_{l-1} k_{l-1}}{k_l - k_2} & \frac{R_3}{R_4} \frac{y_3 k_3}{k_4 - k_3} & 1 & 0 \\ \frac{R_1}{R_5} \prod_{l=2}^{5} \frac{y_{l-1} k_{l-1}}{k_l - k_1} & \frac{R_2}{R_5} \prod_{l=3}^{5} \frac{y_{l-1} k_{l-1}}{k_l - k_2} & \frac{R_3}{R_5} \prod_{l=4}^{5} \frac{y_{l-1} k_{l-1}}{k_l - k_3} & \frac{R_4}{R_5} \frac{y_4 k_4}{k_5 - k_4} & 1 \end{bmatrix} \tag{18}$$

$$\mathbf{S}^{-1} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ \frac{R_1}{R_2} \frac{y_1 k_1}{k_1 - k_2} & 1 & 0 & 0 & 0 \\ \frac{R_1}{R_3} \prod_{l=1}^{2} \frac{y_l k_l}{k_l - k_3} & \frac{R_2}{R_3} \frac{y_2 k_2}{k_2 - k_3} & 1 & 0 & 0 \\ \frac{R_1}{R_4} \prod_{l=1}^{3} \frac{y_l k_l}{k_l - k_4} & \frac{R_2}{R_4} \prod_{l=2}^{3} \frac{y_l k_l}{k_l - k_4} & \frac{R_3}{R_4} \frac{y_3 k_3}{k_3 - k_4} & 1 & 0 \\ \frac{R_1}{R_5} \prod_{l=1}^{4} \frac{y_l k_l}{k_l - k_5} & \frac{R_2}{R_5} \prod_{l=2}^{4} \frac{y_l k_l}{k_l - k_5} & \frac{R_3}{R_5} \prod_{l=3}^{4} \frac{y_l k_l}{k_l - k_5} & \frac{R_4}{R_5} \frac{y_4 k_4}{k_4 - k_5} & 1 \end{bmatrix} \tag{19}$$

$$\mathbf{\Lambda} = \mathrm{diag}(-\mathbf{k}) = \mathrm{diag}\left([-k_1 - k_2 \cdots - k_i \cdots - k_n]\right). \tag{20}$$

The proof of Eq. 16 is provided in Appendix A. Therefore, using Eq. 12, species concentrations are updated by the reaction operator as

$$c_i^r = a_i^t \exp\left(-k_i \Delta t\right) + \sum_{j=1}^{i-1} \frac{R_j}{R_i} \prod_{l=j+1}^{i} \frac{y_{l-1} k_{l-1}}{k_l - k_j} a_j^t \exp\left(-k_j \Delta t\right). \tag{21}$$

where

$$a_i^t = c_i^t + \sum_{j=1}^{i-1} \frac{R_j}{R_i} \prod_{l=j}^{i-1} \frac{y_l k_l}{k_l - k_i} c_j^t \tag{22}$$

is the transformed concentration calculated by the transport operator. The superscripts t and r represent concentrations calculated by transport and reaction operators, respectively.

Figure 2 shows both coupled and decoupled concentration profiles. In the decoupled domain, the concentration of each species is independent of other species concentrations and can be expressed as an exponential decaying function (12). Therefore, the transformed concentration profiles can be calculated separately using species-specific first-order decay rates.
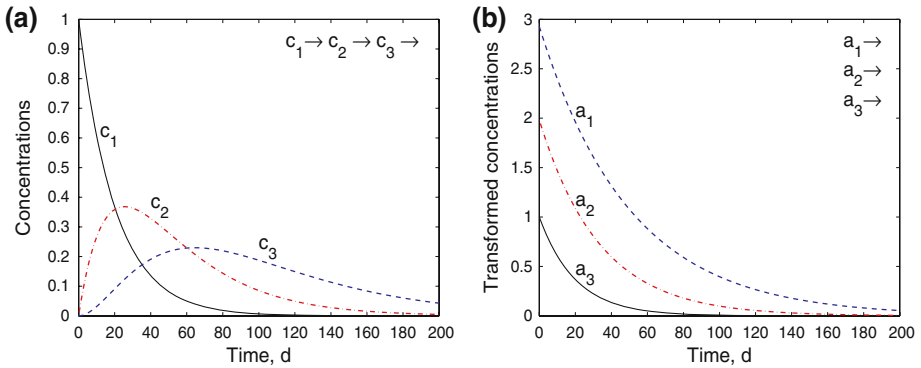
Fig. 2 Concentration profiles in both concentration domain and transformed domain

3.2 Parallel and convergent reaction networks

A typical parallel and convergent reaction network is given by biodegradation of chlorinated solvents when *cis*-DCE, 1,1-DCE, and *trans*-DCE are considered as different species (Lu et al. 2003). However, Lu et al. (2003) is limited to the same retardation assumption. In this subsection, we extend their solution of convergent reactions to those reaction systems with species-specific retardation factors. Shown in Fig. 3, three DCEs simultaneously react to produce the same daughter product, vinyl chloride (VC), and the reaction matrix is expressed as:

$$
\mathbf{A} = \begin{bmatrix}
-k_1 & 0 & 0 & 0 & 0 \\
\frac{R_1}{R_2}\alpha_1 y_1 k_1 & -k_2 & 0 & 0 & 0 \\
\frac{R_1}{R_3}\alpha_2 y_1 k_1 & 0 & -k_3 & 0 & 0 \\
\frac{R_1}{R_4}\alpha_3 y_1 k_1 & 0 & 0 & -k_4 & 0 \\
0 & \frac{R_2}{R_5} y_2 k_2 & \frac{R_3}{R_5} y_2 k_3 & \frac{R_4}{R_5} y_2 k_4 & -k_5
\end{bmatrix},
\tag{23}
$$

where α_i, $i = 1, 2, 3$ are product distribution factors for the reduction of species 1. Conducting singular-value decomposition analytically, the transform matrices are derived as

$$
\mathbf{S} = \begin{bmatrix}
1 & 0 & 0 & 0 & 0 \\
\frac{R_1}{R_2}\frac{\alpha_1 y_1 k_1}{k_2 - k_1} & 1 & 0 & 0 & 0 \\
\frac{R_1}{R_3}\frac{\alpha_2 y_1 k_1}{k_3 - k_1} & 0 & 1 & 0 & 0 \\
\frac{R_1}{R_4}\frac{\alpha_3 y_1 k_1}{k_4 - k_1} & 0 & 0 & 1 & 0 \\
\frac{R_1}{R_5}\frac{y_1 y_2 k_1}{k_5 - k_1}\left(\frac{\alpha_1 k_2}{k_2 - k_1} + \frac{\alpha_2 k_3}{k_3 - k_1} + \frac{\alpha_3 k_4}{k_4 - k_1}\right) & \frac{R_2}{R_5}\frac{y_2 k_2}{k_5 - k_2} & \frac{R_3}{R_5}\frac{y_2 k_3}{k_5 - k_3} & \frac{R_4}{R_5}\frac{y_2 k_4}{k_5 - k_4} & 1
\end{bmatrix}
\tag{24}
$$

$$
\mathbf{S}^{-1} = \begin{bmatrix}
1 & 0 & 0 & 0 & 0 \\
-\frac{R_1}{R_2}\frac{\alpha_1 y_1 k_1}{k_2 - k_1} & 1 & 0 & 0 & 0 \\
-\frac{R_1}{R_3}\frac{\alpha_2 y_1 k_1}{k_3 - k_1} & 0 & 1 & 0 & 0 \\
-\frac{R_1}{R_4}\frac{\alpha_3 y_1 k_1}{k_4 - k_1} & 0 & 0 & 1 & 0 \\
\frac{R_1}{R_5}\frac{y_1 y_2 k_1}{k_5 - k_1}\left(\frac{\alpha_1 k_2}{k_5 - k_2} + \frac{\alpha_2 k_3}{k_5 - k_3} + \frac{\alpha_3 k_4}{k_5 - k_4}\right) & -\frac{R_2}{R_5}\frac{y_2 k_2}{k_5 - k_2} & -\frac{R_3}{R_5}\frac{y_2 k_3}{k_5 - k_3} & -\frac{R_4}{R_5}\frac{y_2 k_4}{k_5 - k_4} & 1
\end{bmatrix},
$$

$$
\tag{25}
$$

Fig. 3 An example of parallel and convergent reactions (Lu et al. 2003)
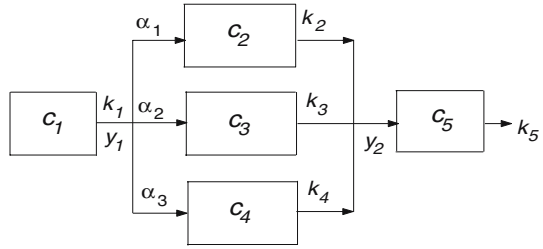
when $R_1 = R_2 = \cdots = R_n$, Eqs. 24 and 25 are identical to Eqs. 10 and 11 in Lu et al. (2003). Correspondingly,

$$\boldsymbol{\Lambda} = \text{diag}(-\mathbf{k}) = \text{diag}\left([-k_1 - k_2 - k_3 - k_4 - k_5]\right). \tag{26}$$

Then, the closed-form solution of the reaction network (Fig. 3) is

$$\mathbf{c}^r = \mathbf{S}\mathbf{a}^r \tag{27}$$

where

$$a_i^r = a_i^t \exp\left(-k_i \Delta t\right), \quad i = 1, 2, \ldots, 5.$$

and

$$\mathbf{a}^t = \mathbf{S}^{-1}\mathbf{c}^t.$$

Note that $\mathbf{S}$ and $\mathbf{S}^{-1}$ differ from Eqs. 10 and 11 of Lu et al. (2003) by species-specific retardation factors.

4 Implementation and applications

As a demonstration of the proposed method, we illustrate with simple examples that are traceable analytically or numerically from previously published literature. Although we are not limiting ourselves to a one-dimensional description, in order to simplify the presentation of the mathematical model and the methodology, only a one-dimensional case is discussed.

4.1 Implementation

The basic concept of RT3D code (Clement et al. 1998) is implemented in the MATLAB (MathWorks 2000) environment. Advection and dispersion are solved using the finite difference method with temporal and spatial weighting (Ataie-Ashtiani and Hosseini 2005). A predefined flow field is implemented as input data. Therefore, this MATLAB version of RT3D keeps the same assumption as the original version that reactions do not alter the flow field. Instead of using LSODE (the Livermore Solver for Ordinary Differential Equations, Radhakrishnan and Hindmarsh 1993) for solving the reaction ODEs, we list four methods for solving the reaction operator as shown in Table 1.

In contrast to the transport operator, the reaction operator is often solved as a local batch-reactor problem in an operator-splitting framework, conventionally solved using ODE and DAE solvers, respectively, for kinetic and equilibrium systems. For the first-order kinetic reaction networks, the explicit Runge–Kutta is often used (Clement et al. 1998). In order to avoid the stiffness of first-order reactions, exact solutions are calculated in the transformed

Table 1 Solution methods

Method	Advection–dispersion	Reaction	Note
0	Finite difference	Exact	Exponential function
1	Finite difference	ode45[a]	Explicit Runge–Kutta
2	Finite difference	ode23s[a]	Implicit Runge–Kutta
3	Finite difference	Numerical SVD	LAPACK[b]

[a] MATLAB ODE solver (MathWorks 2000)
[b] Linear Algebra PACKage (Press et al. 1996)

Fig. 4 Solution flow chart for analytical solutions of first-order reaction systems
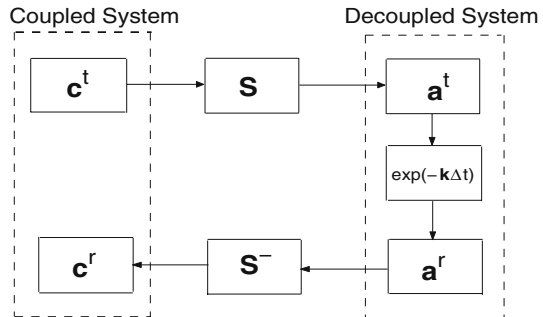
domain. As shown in Fig. 4, for each transport time step, concentrations are first updated by solving the transport operator (temporal and spatial weighting finite difference) and then transformed into a decoupled system as the initial conditions for the reaction operator. The transformed concentrations are modified using the exponentially decaying function (12). Finally, the modified concentrations are transformed back into the concentration-domain (13).

A closed-form library of $\mathbf{S}$ and $\mathbf{S}^{-1}$ matrices was developed for various reaction networks. Once a reaction network is selected from the library list, the corresponding $\mathbf{S}$ and $\mathbf{S}^{-1}$ matrices are loaded into the simulation for the concentration transformation between coupled and decoupled systems. If the selected reaction network is not available in the library, method 3 (see Table 1) is used. In method 3, a numerical SVD (singular-value decomposition, Clement 2001) is activated instead of the analytical transformation for decoupling the reaction system.

4.2 Transport in a homogeneous domain

To verify the proposed method, a transport system with five-species sequential reactions was simulated in a one-dimensional column of 50 m in length. The column was discretized into 50 evenly spaced elements. Transport and reaction parameters are summarized in Table 2. Initial conditions for all species were assumed to be zero and a constant boundary condition ($c_1^o = 1$ and $c_i^o = 0$, $i \geq 2$) was set at the inlet of the column.

Explicit Runge–Kutta methods are often used for non-stiff reaction systems. In order to demonstrate the OS procedure with exact solutions for the reaction operator, let us select ode45 of MATLAB (MathWorks 2000) as the reference ODE solver. The default relative and absolute tolerances are 10^{-3} and 10^{-6}, respectively. Concentration profiles calculated by methods 0 and 1 (see Table 1) are compared in Fig. 5. Method 0 is 74.62 times faster than method 1. It is expected that analytical solutions of the reaction operator requires only single

Table 2 System parameters

Parameter	Value	Parameter	Value	Parameter	Value
v	$0.2\,\mathrm{m\,d^{-1}}$	D	$0.18\,\mathrm{m^2\,d^{-1}}$	t	$200\,\mathrm{d}$
y_1	0.7927	k_1	$0.05\,\mathrm{d^{-1}}$	R_1	1.0
y_2	0.7385	k_2	$0.03\,\mathrm{d^{-1}}$	R_2	1.5
y_3	0.6458	k_3	$0.02\,\mathrm{d^{-1}}$	R_3	2.0
y_4	0.4516	k_4	$0.015\,\mathrm{d^{-1}}$	R_4	2.5
		k_5	$0.01\,\mathrm{d^{-1}}$	R_5	3.0

Fig. 5 Comparison of concentration profiles calculated using MATLAB solver ode45 (solid lines) and exact solutions (circles) for reactions. Reaction and transport parameters in Table 2 are used
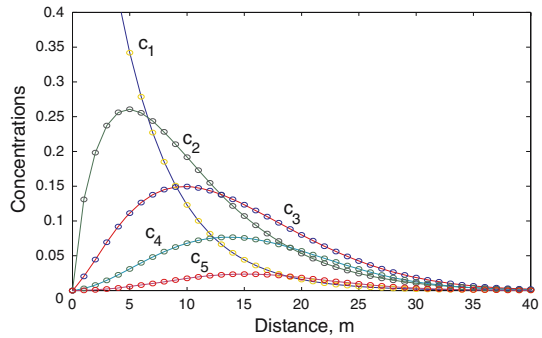
time step while numerical ODE solvers which need multiple time steps to meet convergence requirements.

When all retardation factors are assumed to be the same, the exact solution of the five-species sequentially reactive transport is available in a semi-infinite domain with Dirichlet boundary conditions (Sun et al. 1999a). This case is considered here to compare the operator splitting (OS) solution that uses the exact solution of the reaction operator with the exact solution of the entire reactive transport system. Concentration profiles after 200 days from these three methods are compared in Fig. 6. Although the solutions using the analytical reaction term and ODE solver are both reasonably close to the exact solution, the CPU time for the OS solution using the exact solution of reactions is 59.79 faster than the OS solution using the ode45 solver.

### 4.3 Transport in a heterogeneous domain

To demonstrate the application of the proposed method to more realistic cases, a synthetic flow field is generated in a heterogeneous domain. As shown in Fig. 7, velocity is a function of x-coordinate (dashed line). Dispersion coefficient is calculated as $D = 0.9v$. The mean values of both velocity and dispersion coefficient are assigned the values shown in Table 2. Other system parameters remain unchanged.

The concentration profiles of five-species sequential reactions (Fig. 1b) and of five-species parallel/convergent reactions (Fig. 3), respectively, are provided in Figs. 7 and 8. The solution of concentration profiles of the sequentially reactive species, calculated using the exact solutions of reactions, can be considered identical to those calculated using the MATLAB solver ode45 (MathWorks 2000) although the method derived here requires 1.54% CPU time. As shown in Fig. 3, the fifth species is coupled by three parent species. Geiser (2001) fails to produce a solution because of the limitation of sequential reactions. The solution of Lu et al. (2003) for the parallel/convergent reactions is limited to the same retardation assumption and
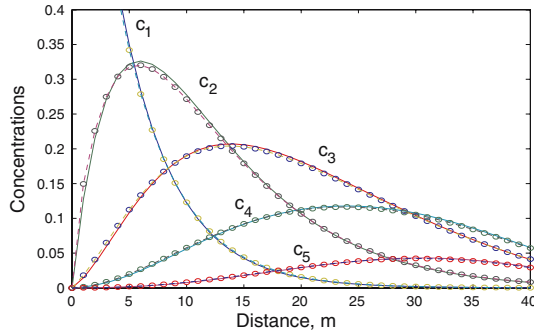
Fig. 6 Concentration profiles calculated using the exact solution of Sun et al. (1999a), method 0 (see Table 1) with an exact solution for the reaction operator, and method 1 using MATLAB ode45 (MathWorks 2000). Solid lines, circles, dashed lines, represent the exact solution, OS solution with an exact solution of reaction operator, and OS solution using MATLAB ode45. Note that the same retardation factors ($R_i = 1, \forall i = 1, \ldots, 5$) are applied in order to use the analytical solution of Sun et al. (1999a) for comparison

Fig. 7 Comparison of concentration profiles calculated using MATLAB solver ode45 (solid lines) and exact solutions (circles) of reactions for the sequential reactions (Fig. 1b)
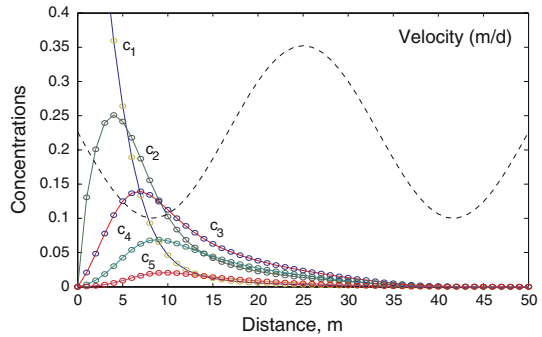
Fig. 8 Concentration profiles after 200 days for the parallel/convergent reactions shown in Fig. 3. $\alpha_1 = 0.7$, $\alpha_2 = 0.2$, and $\alpha_3 = 0.1$
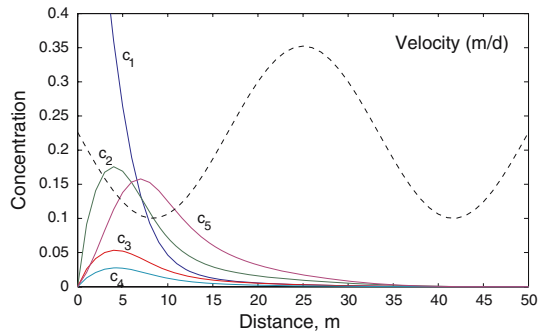

uniform flow conditions. Compared to both solutions of Geiser (2001) and Lu et al. (2003), Fig. 8 demonstrates the applicability of the method developed here to complex reaction networks in heterogeneous domains.

4.4 Stiff reactions

Incorporation of first-order reactions in a transport system can result in *stiffness* of the governing equations. As a consequence of stiffness, the explicit time integration of the reaction

Table 3 Radionuclide transport example

Species	^{234}Th$\rightarrow$	^{234}U$\rightarrow$	^{230}Th$\rightarrow$	^{226}Ra$\rightarrow$
Half-life (yr)	24.1/365.25	2.44×10^5	7.7×10^4	1.6×10^3
Reaction rate (d^{-1})	2.88×10^{-2}	7.78×10^{-9}	2.46×10^{-8}	1.19×10^{-6}
Source	Geiser (2001)	Harada et al. (1980)	Harada	Harada
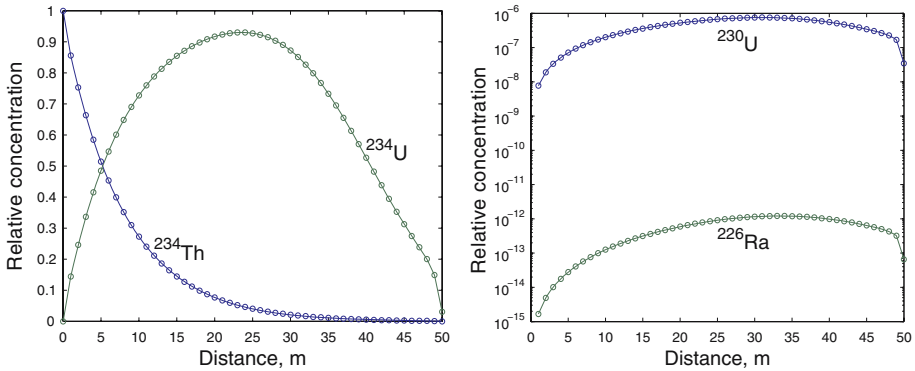
Fig. 9 Concentration profiles of ^{234}Th, ^{234}U, ^{230}Th, and ^{226}Ra after 200 days. The solid lines and circles represent solutions using the stiff ODE solver (ode23s) and the analytical solutions of reactions, respectively

terms is severely restricted. The system is said to be *stiff* when two neighboring species have widely varied reaction rates. Then, explicit time integration of the reaction operator fails to yield a converged solution while fully implicit time integration of the reaction term together with the implicit time scheme of transport equations requires much larger computer memory. By avoiding use of the implicit integration, the OS procedure with an analytical reaction operator provides considerable advantages.

A typical example of stiff reactions was given by Geiser (2001) who considered a two-species decay chain from ^{234}Th (Thorium) to ^{234}U (Uranium). As shown in Table 3, ^{234}Th and ^{234}U have very different reaction time scales. The stability condition requires reaction time step $\Delta t < 10^{-6}$ while the influence of $k_2 c_2$ can only be seen after $10^3 \sim 10^9$ time steps. In this way, the explicit scheme will accumulate round-off errors and fails to provide an accurate solution. For this reason, ode45 fails to get a converged result. Instead, we used ode23s (method 2 in Table 1), an implicit Runge–Kutta technique, to solve the reaction operator. Initial concentrations of all species were assumed to be zero. The boundary concentration for ^{234}Th and the other species was set as one and zeros, respectively. The concentration profiles of four radionuclides after 200 days are calculated and compared in Fig. 9. This example indicates that the method proposed (method 0 in Table 1) can provide the same result as what ode23s does with 1/82 CPU time.

5 Conclusions

A new solution method is proposed to solve reactive transport systems with first-order reaction networks. Incorporation of exact solutions for the reaction operator can eliminate the error from ODE solvers and significantly increase simulation speed. The new operator-splitting

approach has been validated by comparison against an exact solution and a conventional OS solution. The examples of reactive transport in this paper indicate that the proposed approach offers both simulation accuracy and computational efficiency compared to conventional OS methods. As a caveat, the approach developed in this paper is limited to the availability of analytical solutions for reactions. Thus, additional development of analytical solutions for more complex reactions in batch reactors will prove beneficial with modeling reactive transport using this method. To obtain analytical or semi-analytical solutions for non-linear reactions, a further effort of linearization techniques is needed.

Appendix A: a proof of transformation of Eq. 16

Since the transformation is defined as

$$a_i = c_i + \sum_{j=1}^{i-1} \frac{R_j}{R_i} \prod_{l=j}^{i-1} \frac{y_l k_l}{k_l - k_i} c_j, \tag{28}$$

the first-order derivative of a_i for the reaction terms can be expressed as follows:

$$\partial_t a_i = \partial_t c_i + \sum_{j=1}^{i-1} \frac{R_j}{R_i} \prod_{l=j}^{i-1} \frac{y_l k_l}{k_l - k_i} \partial_t c_j, \tag{29}$$

where

$$\partial_t c_i = \frac{R_{i-1}}{R_i} y_{i-1} k_{i-1} c_{i-1} - k_i c_i. \tag{30}$$

Then,

$$\partial_t a_i = \underbrace{\frac{R_{i-1}}{R_i} y_{i-1} k_{i-1} c_{i-1} - \overbrace{k_i c_i}^{A_2}}_{A_1} + \sum_{j=1}^{i-1} \frac{R_j}{R_i} \prod_{l=j}^{i-1} \frac{y_l k_l}{k_l - k_i} \left[\overbrace{\frac{R_{j-1}}{R_j} y_{j-1} k_{j-1} c_{j-1}}^{A_3} - \underbrace{k_j c_j}_{A_4} \right]. \tag{31}$$

Combining terms with common factor c_s (term A_3 when $j = s+1$ and term A_4 when $j = s$),

$$\frac{R_{s+1}}{R_i} \prod_{l=s+1}^{i-1} \frac{y_l k_l}{k_l - k_i} \frac{R_s}{R_{s+1}} y_s k_s c_s, \quad j = s+1 \tag{32}$$

$$-\frac{R_s}{R_i} \prod_{l=s}^{i-1} \frac{y_l k_l}{k_l - k_i} k_s c_s, \quad j = s, \tag{33}$$

the sum is

$$\frac{R_{s+1}}{R_i} \prod_{l=s+1}^{i-1} \frac{y_l k_l}{k_l - k_i} \frac{R_s}{R_{s+1}} y_s k_s c_s - \frac{R_s}{R_i} \prod_{l=s}^{i-1} \frac{y_l k_l}{k_l - k_i} k_s c_s$$

$$= \frac{R_s}{R_i} k_s c_s \left[\prod_{l=s}^{i-1} \frac{y_l k_l}{k_l - k_i} \right] \left(y_s \frac{k_s - k_i}{y_s k_s} - 1 \right) = -k_i \frac{R_s}{R_i} \prod_{l=s}^{i-1} \frac{y_l k_l}{k_l - k_i} c_s. \tag{34}$$

Similarly, term A_4 when $j = i - 1$ can be combined with term A_1,

$$- \frac{R_{i-1}}{R_i} \frac{y_{i-1} k_{i-1}}{k_{i-1} - k_i} k_{i-1} c_{i-1} + \frac{R_{i-1}}{R_i} y_{i-1} k_{i-1} c_{i-1} = -k_i \frac{R_{i-1}}{R_i} \frac{y_{i-1} k_{i-1}}{k_{i-1} - k_i} c_{i-1}. \tag{35}$$

Therefore, Eq. 31 can be written as:

$$\partial_t a_i = -k_i \left[c_i + \sum_{j=1}^{i-1} \frac{R_j}{R_i} \prod_{l=j}^{i-1} \frac{y_l k_l}{k_l - k_i} c_j \right] = -k_i a_i. \tag{36}$$

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