

A SEMI-ANALYTICAL SOLUTION FOR MULTI-MONO-VALENT CATION EXCHANGE REACTIVE TRANSPORT IN GROUNDWATER

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ABSTRACT

This paper presents a semi-analytical solution of cation exchange reactive transport for any number of mono-valent cations in steady 1-, 2- or 3-D groundwater flow. Nonlinear cation exchange mass-action-law equations are first linearized by means of a first-order Taylor expansion of log-concentrations around the arithmetic average of boundary and initial concentrations and then substituted back into transport equations. The resulting set of coupled partial differential equations (PDEs) is decoupled by means of a matrix similarity transformation which is applied also to boundary and initial concentrations. Uncoupled PDE's are solved by standard analytical solutions. Concentrations of the original problem are obtained by back-transforming the solution of uncoupled PDEs. The semi-analytical solution compares well with nonlinear numerical solutions computed with a reactive transport code (CORE^{2D}) for a 1-D test case. Deviations of the semi-analytical solution from numerical solutions increase with increasing cation exchange capacity (CEC).

1. INTRODUCTION

Cation exchange in groundwater is one of the dominant surface reactions in natural systems [Appelo and Postma, 1993] as well as in polluted sites [Steeffel et al., 2003]. Mass transfer of cation exchanging pollutants in groundwater is highly nonlinear. This makes difficult to derive analytical solutions for transport equations coupled with cation exchange reactions. However, it is still possible to simplify the problem so that analytical solutions can be derived. Bolt (1979) addressed the solution of nonlinear cation exchange and transport in steady saturated flow and presented graphical and numerical integration methods to calculate cation breakthrough curves. Bond and Phillips (1990) extended this approach to obtain approximate quasi-analytical solutions for transport with nonlinear adsorption including ion exchange, specific adsorption and anion exclusion during transient unsaturated flow. Valocchi (1984) presented an effective K_d approach to calculate cation front velocities and determine front locations for solute transport coupled with multi-ion exchange in aquifers for advectively-dominated problems.

There is a major group of methods for solving multication exchange reactive transport in aquifers which assume that hydrodynamic dispersion is negligible and formulate the system as a Riemann problem. The problem is then solved by the method of characteristics [Rhee et al., 1989] or by resorting to self-similar solutions [Smoller, 1983, Charbeneau, 1988, Thoolen and Hemker, 1994]. Dou and Jin (1996) used the method of characteristics with a special treatment of shock waves to derive a closed-form solution for binary homovalent ion

exchange and transport in an infinite 1-D domain. Jin and Ye (1999) extended this approach and derived an approximate analytical solution for binary monovalent-divalent ion exchange transport. Due to the complexity of exchange isotherms, most of these analytical solutions have addressed mostly simple cases, usually for 1-D transport of two cations and often by neglecting hydrodynamic dispersion.

In this paper, a semi-analytical solution for multi-dimensional transport coupled with any number of cation exchange reactions in steady saturated groundwater flow is presented. The semi-analytical solution is useful to verify reactive transport codes, understand the nonlinearities of cation reactive transport and interpret reactive transport column experiments. The mathematical formulation of the problem is introduced first. Then, the solution procedure to derive the semi-analytical solution is presented. A test case involving three monovalent cations is used to illustrate its derivation and comparing it with the numerical solution computed with a reactive transport code (CORE^{2D}).

2. MATHEMATICAL FORMULATION

Assuming a uniform flow velocity in the x direction, transport equations for a coupled set of exchanging cations in a 3-D domain are given by

$$\frac{\partial C_i}{\partial t} + \frac{\partial W_i}{\partial t} = D_x \frac{\partial^2 C_i}{\partial x^2} + D_y \frac{\partial^2 C_i}{\partial y^2} + D_z \frac{\partial^2 C_i}{\partial z^2} - v \frac{\partial C_i}{\partial x} \quad i = 1, 2, \dots, n \quad (1)$$

where C_i is concentration of the i th dissolved cation, i , [ML⁻³]; W_i is concentration of the i th exchange cation [ML⁻³]; D_x , D_y and D_z are dispersion coefficients in x , y and z directions, respectively, [L²T⁻¹]; v is groundwater velocity, [LT⁻¹] and t is time.

A general expression of mass-action law for mono-valent cation exchange reactions according to the Gaines-Thomas convention is given by [Appelo and Postma, 1993],

$$K_{ij} = \frac{\beta_i \cdot C_j}{\beta_j \cdot C_i} \quad (2)$$

where β_i is equivalent fraction of the i -th exchange cation [-], and K_{ij} is exchange coefficient or selectivity coefficient. W_i in Equation (1) can be calculated from the equivalent fraction, β_i , through:

$$W_i = \beta_i \frac{CEC \rho_d}{100\theta} \quad (3)$$

where CEC is cation exchange capacity (meq/100g), θ is porosity and ρ_d is bulk density (g/cm³). Exchange reactions are usually written in terms of a reference cation S_1 . Then, Equation (3) becomes [Xu et al., 1999],

$$\frac{\beta_1 \cdot C_j}{\beta_j \cdot C_1} = K_{1j} \quad j = 2, \dots, n \quad (4)$$

By definition, equivalent fractions add to one,

$$\sum_{i=1}^{N_w} \beta_i = 1 \quad (5)$$

With appropriate initial and boundary conditions, Equations (1), (3), (4) and (5) define the mathematical formulation of multicomponent reactive transport coupled with cation exchange in groundwater.

3. SOLUTION PROCEDURE

The first step for deriving the semi-analytical solution involves linearizing cation mass-action law equations. Taking logarithms of Equation (4) leads to

$$\ln \beta_1 + \ln C_j = \ln \beta_j + \ln C_1 + \ln K_{1j} \quad j = 2, \dots, n \quad (6)$$

Performing a first-order Taylor expansion of terms $\ln \beta_1$, $\ln C_j$, $\ln \beta_j$ and $\ln C_1$ in Equation (6) around selected reference concentrations, C_i^0 and C_1^0 , one has

$$\frac{\beta_1}{\beta_1^0} + \frac{C_j}{C_j^0} = \frac{\beta_j}{\beta_j^0} + \frac{C_1}{C_1^0} \quad (7)$$

where β_j^0 and C_j^0 are the reference values of equivalent fractions calculated according to Equations (4) and (5) for given C_i^0 and C_1^0 . The semi-analytical solution depends on the choice of reference concentrations. Samper and Yang (2006b) found that the best results are obtained with reference concentrations equal to the arithmetic average of boundary and initial concentrations.

Taking time derivatives of Equations (5) and (7) and combining them into a matrix form, one has:

$$\mathbf{A}\hat{\beta}_t = \mathbf{B}\hat{C}_t \quad (8)$$

where \mathbf{A} and \mathbf{B} are square ($n \times n$) matrices given by:

$$\mathbf{A} = \begin{pmatrix} 1 & 1 & 1 & 1 & \dots & 1 \\ \frac{1}{\beta_1^0} & -\frac{1}{\beta_2^0} & 0 & 0 & \dots & 0 \\ \frac{1}{\beta_1^0} & 0 & -\frac{1}{\beta_3^0} & 0 & \dots & 0 \\ \dots & 0 & \dots & \dots & \dots & \dots \\ \frac{1}{\beta_1^0} & 0 & \dots & 0 & \dots & -\frac{1}{\beta_n^0} \end{pmatrix}_{(n \times n)} \quad \mathbf{B} = \begin{pmatrix} 0 & 0 & 0 & 0 & \dots & 0 \\ \frac{1}{C_1^0} & -\frac{1}{C_2^0} & 0 & 0 & \dots & 0 \\ \frac{1}{C_1^0} & 0 & -\frac{1}{C_3^0} & 0 & \dots & 0 \\ \dots & 0 & \dots & \dots & \dots & \dots \\ \frac{1}{C_1^0} & 0 & \dots & 0 & \dots & -\frac{1}{C_n^0} \end{pmatrix}_{(n \times n)}$$

and $\hat{\beta}_{t(n \times 1)} = \left(\frac{d\beta_1}{dt}, \dots, \frac{d\beta_n}{dt} \right)'$ and $\hat{C}_{t(n \times 1)} = \left(\frac{dC_1}{dt}, \dots, \frac{dC_n}{dt} \right)'$.

Taking time derivatives of W_i in Equation (3) and taking into account Equation (8) results in,

$$\hat{W}_t = CEC^* \mathbf{A}^{-1} \mathbf{B} \cdot \hat{C}_t \quad (9)$$

where \hat{W}_t is a ($1 \times n$) column vector of time derivatives of W_i , and $CEC^* = CEC \frac{\rho_d}{100\theta}$.

Substituting Equation (9) back into Equation (1) leads to the following set of transport equations

$$\mathbf{R}\hat{C}_t = D_x \hat{C}_x^2 + D_y \hat{C}_y^2 + D_z \hat{C}_z^2 - v \hat{C}_x^1 \quad (10)$$

where \hat{C}_x^1 is a ($1 \times n$) vector containing the x -components of the first-order spatial derivatives of cation concentrations. Similarly, \hat{C}_x^2 is a ($1 \times n$) column vector of x - components of second-order spatial derivatives of cation concentrations. A similar notation is used for y and z components. \mathbf{R} is a ($n \times n$) square matrix of retardation coefficients given by

$$\mathbf{R} = \mathbf{I} + \text{CEC}^* \mathbf{A}^{-1} \mathbf{B} \quad (11)$$

where \mathbf{I} is the identity matrix. Since the retardation matrix is not diagonal, the set of PDE's are coupled together and must be solved simultaneously for unknown concentrations.

Sun et al. (1999) and Sun and Clement (1999) used a linear transformation to derive analytical solutions for multispecies transport coupled with first-order sequential chemical reactions. Clement (2001) further proposed a general approach to find out a linear transformation matrix by using a similarity transformation based on the work of Sun et al. (1999). A similar type of similarity transformation is used here to decouple transport equations in (10). It is worth noting that Clement (2001) used the similarity transformation to decouple first-order chemical reaction terms while here it is employed to decouple the retardation matrix arising from cation exchange reactions.

The similarity transformation of the retardation matrix \mathbf{R} consists on finding a linear transformation of (10) so that the transformed set of equations are decoupled and have a diagonal retardation matrix, $\tilde{\mathbf{R}}$. The transformation matrix, \mathbf{S} , is defined except for a constant and satisfies the following expression [Johnson and Riess, 1981]

$$\mathbf{R}\mathbf{S} = \mathbf{S}\tilde{\mathbf{R}} \quad (12)$$

Transformed variables \mathbf{U} are defined by:

$$\hat{\mathbf{U}} = \mathbf{S}^{-1} \hat{\mathbf{C}} \quad (13)$$

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

$$\hat{\mathbf{C}} = \mathbf{S}\hat{\mathbf{U}} \quad (14)$$

Taking time and space derivatives of (14), substituting them into Equation (10) and pre-multiplying (10) by the inverse matrix \mathbf{S}^{-1} results in,

$$\tilde{\mathbf{R}}\hat{\mathbf{U}}_t = D_x \hat{\mathbf{U}}_x^2 + D_y \hat{\mathbf{U}}_y^2 + D_z \hat{\mathbf{U}}_z^2 - v\hat{\mathbf{U}}_x \quad (15)$$

Since $\tilde{\mathbf{R}}$ is a diagonal matrix, this set of partial differential equations for transformed variables can be solved separately using available analytical solutions for 1-, 2- and 3-D transport conditions such as those reported by Wilson and Miller (1978), van Genuchten and Alves (1982) and Huyakorn et al. (1987).

4. TEST CASE

This section illustrates the application of the semi-analytical solution to the transport of dissolved Na^+ , K^+ , and Li^+ which interact with exchanged cations Na-X, K-X, and Li-X in a 1-D domain. Governing transport equations for the three cations are

$$\frac{\partial C_i}{\partial t} + \frac{\partial W_i}{\partial t} = D \frac{\partial^2 C_i}{\partial x^2} - v \frac{\partial C_i}{\partial x} \quad (i=\text{Na}^+, \text{K}^+, \text{Li}^+) \quad (16)$$

where $D = v\alpha_L$ and α_L is longitudinal dispersivity (m).

A water containing a 1 mM Na^+ , 4 mM K^+ and 120 mM Li^+ is injected at the left boundary of a column which is initially filled with a water having initial concentrations of 100 mM for Na^+ , 50 mM for K^+ and 1 mM for Li^+ . Dissolved Li^+ exchanges with exchanged Na^+ and K^+ and causes the release of exchanged Na^+ and K^+ into solution. Other parameter values used in the calculation are listed in Table 1. According to (11), the retardation matrix is given by:

$$\mathbf{R} = \begin{pmatrix} 1 + CEC^* \frac{(\beta_{Na}^0 \beta_{Li}^0 + \beta_{Na}^0 \beta_K^0)}{C_{Na}^0} & -\frac{CEC^* \beta_K^0 \beta_{Na}^0}{C_K^0} & -\frac{CEC^* \beta_{Li}^0 \beta_{Na}^0}{C_{Li}^0} \\ -\frac{CEC^* \beta_{Na}^0 \beta_K^0}{C_{Na}^0} & 1 + CEC^* \frac{(\beta_K^0 \beta_{Na}^0 + \beta_K^0 \beta_{Li}^0)}{C_K^0} & -\frac{CEC^* \beta_{Li}^0 \beta_K^0}{C_{Li}^0} \\ -\frac{CEC^* \beta_{Na}^0 \beta_{Li}^0}{C_{Na}^0} & -\frac{CEC^* \beta_K^0 \beta_{Li}^0}{C_K^0} & 1 + CEC^* \frac{(\beta_{Li}^0 \beta_{Na}^0 + \beta_{Li}^0 \beta_K^0)}{C_{Li}^0} \end{pmatrix}$$

Applying the similarity transformation to the retardation matrix, \mathbf{R} , one gets transformed variables \mathbf{U} which can be obtained by a standard analytical solution such as those reported by van Genuchten and Alves (1982). Concentrations of Na^+ , K^+ , and Li^+ of the original problem are obtained by applying the back-transformation of Equation (14).

Coupled nonlinear cation exchange reactive transport equations have been solved with CORE^{2D} , a finite element code for modelling non-isothermal variably saturated water flow and reactive transport. CORE^{2D} is an extended and improved version of TRANQUI (Xu et al., 1999) that has undergone extensive verification and has been used to model laboratory tests and field case studies [Samper et al., 2003; Molinero et al., 2004; Dai and Samper, 2004, Molinero and Samper, 2006, Dai and Samper, 2006 and Samper and Yang, 2006a].

Breakthrough curves of dissolved Na^+ , K^+ , and Li^+ at a distance of 1 m obtained with the semi-analytical solution are compared with numerical solutions in Figure 1. Results are shown for two values of CEC (0.03 and 0.2 meq/100g). It can be seen that the semi-analytical solution coincides well with the numerical solution for $\text{CEC} = 0.02$ meq/100g. For $\text{CEC} = 0.2$ meq/100g, however, the semi-analytical solutions of K^+ and Li^+ show some mild deviations from the numerical solution.

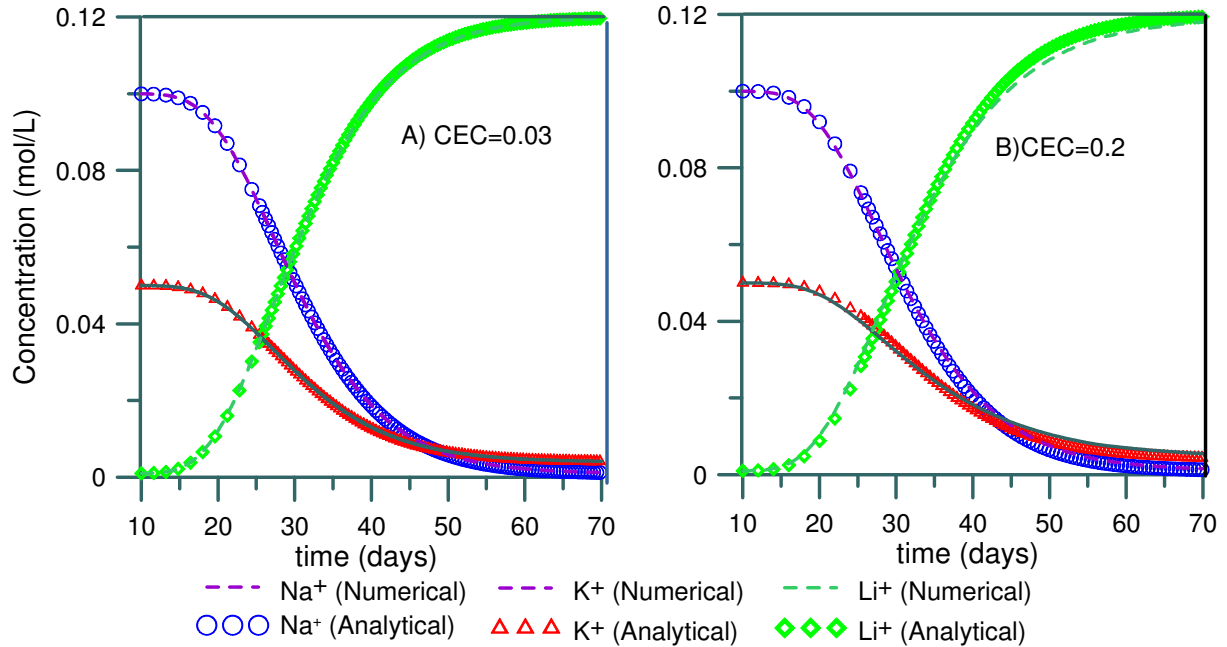


FIGURE 1. Breakthrough curves of dissolved Na^+ , K^+ and Li^+ at a distance of 1 m obtained with semi-analytical and numerical solutions for two values of $\text{CEC} = 0.03$ meq/100g (left) and $\text{CEC} = 0.2$ meq/100g (right).

In order to evaluate the effect of CEC on the accuracy of the semi-analytical solution, several runs were performed for increasing values of CEC from 0.03 to 0.5 meq/100g. Since dissolved concentrations usually vary over several log scales, a log-type error is defined for measuring the deviations of the semi-analytical solution from the numerical solution for dissolved Na^+ , K^+ and Li^+ . The average log-error for the i th cation, $\bar{\varepsilon}_i$, is defined as

$$\bar{\varepsilon}_i = \frac{1}{\sum_{in=1}^{node} \sum_{it=1}^{ntime}} \left| \log \left(\frac{c_a(i, in, it)}{c_n(i, in, it)} \right) \right| \quad (17)$$

while the average error for all n dissolved cations, $\bar{\varepsilon}$, is computed from,

$$\bar{\varepsilon} = \frac{1}{n} \sum_{i=1}^n \bar{\varepsilon}_i \quad (18)$$

where $|\cdot|$ denotes absolute value, $c_a(i, in, it)$ and $c_n(i, in, it)$ are dissolved concentrations of the i th species (1 for Na^+ , 2 for K^+ , and 3 for Li^+) for the in -th node at the it -th time obtained with semi-analytical and numerical solutions, respectively, $node$ is the total number of nodes in the finite element grid and $ntime$ is the total number of time steps. The maximum log-error for the i -th cation, ε_i^M , is computed as

$$\varepsilon_i^M = \text{Max}_{\substack{in=1, node \\ it=1, ntime}} \left\{ \left| \log \frac{c_a(i, in, it)}{c_n(i, in, it)} \right| \right\} \quad (19)$$

TABLE 1. Parameters used for the test case of ternary homovalent cation exchange.

Parameter	Value
Length of the column (m)	2
Darcy velocity (m/day)	0.1
Porosity	0.3
Longitudinal dispersivity (m)	0.05
Selectivity coefficient ($K_{\text{Na/K}}$)	0.2
Selectivity coefficient ($K_{\text{Na/Li}}$)	1.2
Cation exchange Capacity (CEC) (meq/100g)	0.02
Bulk density (g/cm^3)	1.855

Figure 2A shows the plots of $\bar{\varepsilon}_i$ for Na^+ , K^+ and Li^+ and the average error $\bar{\varepsilon}$ as a function of CEC. Figure 2B shows the plots of maximum errors, ε_i^M , for Na^+ , K^+ and Li^+ . One can see in Figure 2 that average errors increase quasi linearly with CEC from less than 0.015 for CEC = 0.03 meq/100g to 0.2, 0.15 and 0.03 (for Na^+ , K^+ and Li^+ , respectively) for CEC = 0.5 meq/100g. Both average and maximum errors of Li^+ are smaller than those of Na^+ and K^+ . Maximum errors for Li^+ are smaller than those of Na^+ and K^+ when CEC ranges from 0.03 to 0.5. It can be concluded that for the conditions of this test case the semi-analytical solution presented here is sufficiently accurate for CEC values up to 0.5 meq/100g. For larger CEC one should resort to reactive transport solutions.

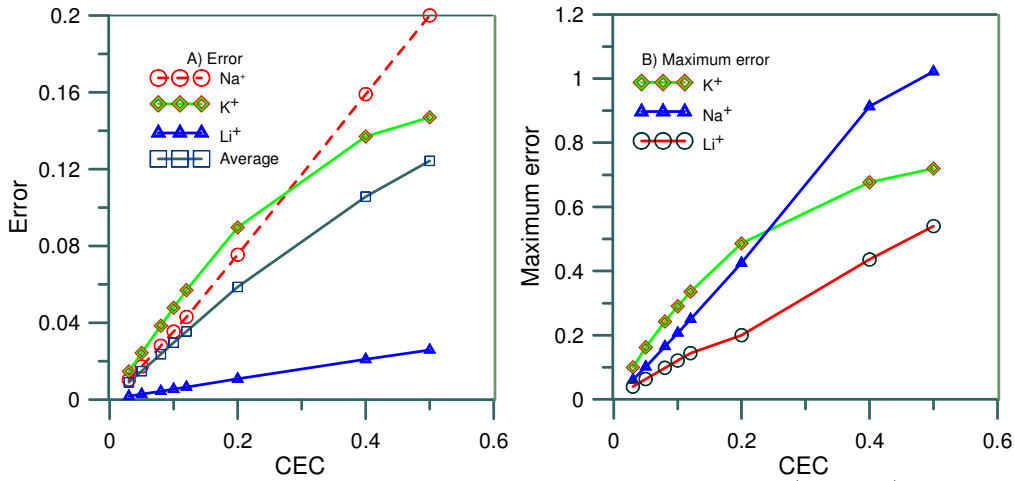


FIGURE 2. Average (left) and maximum (right) log-errors for Na^+ and K^+ versus CEC.

5. CONCLUSIONS

A semi-analytical solution for multi-mono-valent cation exchange reactive transport has been presented which should be useful for verification of reactive transport codes and understanding the nonlinearities of cation reactive transport. The solution is based on a first-order Taylor expansion of the cation exchange mass-action-law equations around some selected reference concentrations. Linearized exchange equations are then substituted into transport equations to obtain a set of coupled partial differential equations (PDEs) which are decoupled by a similarity transformation. Uncoupled PDE's are solved by standard analytical solutions. Concentrations of the original are obtained by back-transforming the solution of uncoupled PDEs.

The semi-analytical solution has been compared with numerical solutions obtained with a reactive transport code (CORE^{2D}). The semi-analytical solution compares well with nonlinear numerical solutions for a 1-D test case involving Na^+ , K^+ , and Li^+ . Deviations of the semi-analytical solutions from numerical solutions are generally small.

Since cation concentrations usually vary over several log scales, a log-type error has been used to measure the deviations of the semi-analytical solution from the numerical solution for the test case. Average errors increase quasi linearly with CEC. Maximum errors for Li^+ are smaller than those of Na^+ and K^+ . The semi-analytical solution departs from the exact solution for too large CEC values.

Although the semi-analytical solution has been tested here for 3 mono-valent cation exchange transport in a 1-D column, it can be applied to any number of homo-valent cations in 2- or 3-D domains. Future studies should explore the use of the semi-analytical solution for the interpretation of column cation exchange experiments.

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