

CONTINUOUS AND DISCRETE ADJOINT STATE FORMULATIONS OF CONSERVATIVE AND REACTIVE SOLUTE TRANSPORT IN POROUS MEDIA

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RESUMEN. El método del estado adjunto (AS) es comúnmente utilizado para calcular las derivadas locales de la función objetivo del problema inverso de la estimación automática de los parámetros de modelos numéricos de flujo y transporte de solutos y para calcular las sensibilidades de los resultados de los modelos a variaciones de sus parámetros. El método AS se puede aplicar: (a) Al problema original (método continuo) o (b) A la versión discretizada del problema original (método discreto). El método AS continuo consiste en obtener las ecuaciones del estado adjunto a partir de las ecuaciones en derivadas parciales del problema original y, posteriormente, resolver numéricamente dichas ecuaciones. El método AS discreto consiste en obtener las ecuaciones del estado adjunto directamente a partir de las ecuaciones discretizadas del problema original. Este trabajo presenta la formulación del estado adjunto continuo y discreto para el transporte de solutos conservativos y reactivos en medios porosos. Se incluye la descripción de los dos métodos, el análisis de sus propiedades y la comparación de ambas versiones así como su aplicación a sistemas multicomponente de solutos conservativos y sistemas reactivos con reacciones de disolución/precipitación de minerales y de intercambio catiónico.

ABSTRACT. The adjoint state (AS) method is commonly used for calculating local derivatives of objective functions in the solution of the inverse problem of parameter estimation and computing model sensitivities for water flow and solute transport. The AS method can be applied to: (a) The continuous version of the original problem (continuous AS method) and (b) The discretized form of the original problem (discrete AS method). The continuous AS method consists on deriving the AS equations from the partial differential equations (PDEs) of the original problem and then solving numerically the resulting PDEs of the AS. The discrete adjoint state method consists on obtaining the discretized AS equations directly from the discretized equations of the original problem. Here we present the formulation of both the continuous and discrete AS for conservative solute transport in porous media. The methods are described and the properties of both continuous and discrete AS formulations are analysed and compared. We also present the AS equations for multicomponent reactive systems with mineral dissolution/precipitation and cation exchange reactions.

1.- Introduction

The adjoint state (AS) method is commonly used for calculating the gradient of the objective function in the solution of the inverse problem of parameter estimation (Carrera and Neuman, 1986; Samper and Neuman, 1986, 1989). Evaluating the adjoint state requires a single calculation similar to that of the original problem, regardless the number of parameters, and the method can be applied to the continuous version of the original problem or to the discretized form. Most of the reported applications rely upon discrete approaches.

A comparison of the continuous and discrete adjoint states for solving the inverse problem of groundwater flow in heterogeneous dual porosity systems is presented by Delay et al. (2017). They reported that both discrete and continuous AS led to similar results when sufficiently refined grids are used.

The AS method has been applied recently to model the steady-state sequentially coupled radionuclide transport in porous media (Hayek et al., 2019, 2020). To the best of our knowledge, the AS method has not been applied yet for modelling reactive solute transport.

We present first the mathematical and numerical formulation of conservative solute transport for a single species. Then, the continuous and discrete adjoint state equations are described. Afterwards, a comparison of the continuous and discrete adjoint state methods are presented. Section 6 presents the AS equations for multicomponent solute transport. AS equations of multicomponent reactive transport systems are described in Sections 7 and 8.

2.- Formulation of conservative solute transport

2.1. Solute transport equation and boundary conditions

The partial differential equation (PDE) of conservative solute transport is given by:

$$\begin{aligned} \nabla \cdot (\phi \mathbf{D} \nabla c - \mathbf{q} c) + q_r c_r - q_d c - \lambda_d \phi c + \phi g \\ = \frac{\partial}{\partial t} \phi c \quad \text{in } \mathbf{R}^n \times \mathbf{T} \end{aligned} \quad (13)$$

where ϕ is porosity, \mathbf{D} is the dispersion/diffusion tensor, c is the solute concentration, ∇c is the solute concentration gradient, \mathbf{q} is the Darcy velocity, q_r and q_d are water source/sink terms, respectively, c_r is the

concentration of the water inflow, λ_d is the decay constant, g is the solute mass source term, R is the space domain, t is time and T is the time domain (see the list of terms in Appendix E). The Darcy velocity is given by Darcy's law:

$$\mathbf{q} = -\mathbf{K}\nabla\mathbf{h} \quad (14)$$

where \mathbf{K} is the hydraulic conductivity tensor and $\nabla\mathbf{h}$ is the gradient of the hydraulic head. The boundary and initial conditions of the solute transport in Eq. (1) are given by:

$$(\emptyset\mathbf{D}\nabla\mathbf{c} - \mathbf{qc}) \mathbf{n} = -\beta_{bc}(c - C) + G - \mathbf{qnc} \quad \text{in } \Gamma_1 \times T \quad (15)$$

$$(\emptyset\mathbf{D}\nabla\mathbf{c} - \mathbf{qc}) \mathbf{n} = -\beta_{bc}(c - C) + G - \mathbf{qnc} \quad \text{in } \Gamma_2 \times T \quad (16)$$

$$c = c_0 \quad \text{for } t = t_0 \quad \text{in } R \quad (17)$$

where Γ_1 denotes the inflow and no-flow boundaries, Γ_2 denotes the outflow boundaries, \mathbf{n} is a unit vector normal to the boundary pointing outwards, C is the external concentration along the boundary, G is the prescribed solute mass flux along the boundary, β_{bc} is a parameter controlling the type of solute transport boundary and c_0 is the steady-state concentration.

2.2. Finite element numerical formulation

The numerical solution of Eqs. (1)-(5) with the finite element method (FEM) is based on the following approximation:

$$c(\mathbf{x}, t) \approx c^N(\mathbf{x}, t) = \sum_{i=1}^N c_i(t) \xi_i(\mathbf{x}) \quad (18)$$

where N is the total number of nodes in the grid, c_i is the nodal solute concentration and $\xi_i(\mathbf{x})$ is the i -th basis function used for the spatial interpolation. Using the Galerkin finite element method for space discretization and the finite differences method for time discretization, the resulting finite element equations for solute transport are given by:

$$(\bar{\mathbf{F}} \cdot \theta_1 + \bar{\mathbf{E}}/\Delta t^k) \cdot \bar{\mathbf{c}}^k - [-\bar{\mathbf{F}} \cdot (1 - \theta_1) + \bar{\mathbf{E}}/\Delta t^k] \cdot \bar{\mathbf{c}}^{k-1} - \bar{\mathbf{r}}^{k-1} = 0 \quad (19)$$

where $\bar{\mathbf{F}}$ is a $N \times N$ conductance matrix, $\bar{\mathbf{E}}$ is a $N \times N$ storage matrix, θ_1 is a time discretization parameter which takes values between 0 and 1, $\bar{\mathbf{c}}^k$ is the vector of nodal concentrations at time t^k , $\Delta t^k = t^k - t^{k-1}$ and K is the total number of time intervals where concentrations are calculated, so that $k = 1, 2, \dots, K$. The expressions of matrices $\bar{\mathbf{F}}$ and $\bar{\mathbf{E}}$ and the vector $\bar{\mathbf{r}}$ are given by:

$$F_{ij} = \int_R \left[\emptyset \nabla \xi_j \mathbf{D} \nabla \xi_i - \mathbf{q} \cdot \nabla \xi_i \xi_j + (q_d + \lambda_d \emptyset) \xi_i \xi_j \right] dR + \int_{\Gamma} \beta_{bc} \xi_i \xi_j d\Gamma + \int_{\Gamma_2} \mathbf{q} \cdot \mathbf{n} \xi_i \xi_j d\Gamma \quad (20)$$

$$E_{ij} = \int_R \emptyset \xi_i \xi_j dR \quad (21)$$

$$r_i = \int_R (q_r c_r + \emptyset g) \xi_i dR + \int_{\Gamma} (\beta_{bc} C + G) \xi_i d\Gamma - \int_{\Gamma_1} \mathbf{q} \cdot \mathbf{n} C \xi_i d\Gamma \quad (22)$$

2.3. Objective function

Solving the inverse problem of solute transport requires to minimize an objective function, Ω . The integral form of the objective function has the following expression:

$$\Omega = \int_R J_1(c_0) dR + \iint_{R,T} [J_2(c) + J_3(\bar{\mathbf{y}})] dRdt \quad (23)$$

where J_1, J_2, J_3 are known functions and $\bar{\mathbf{y}}$ is a vector of model parameters. The parameters for conservative solute transport include $\emptyset, \mathbf{D}, q_r, q_d, c_r, g, \mathbf{K}, \beta_{bc}, C$ and G .

The discrete form of the objective function is given by:

$$\Omega^N = J_1^N(\mathbf{c}_0) + J_2^N(\mathbf{c}_0, \mathbf{c}^k) + J_3^N(\bar{\mathbf{y}}) \quad (24)$$

In order to minimize Ω , its gradient can be obtained in terms of the adjoint state variables, which in turn are obtained from the original problem. The AS equations can be derived from the continuous and discretized versions of the original problem.

3.- Continuous adjoint state

The continuous adjoint state method consists on deriving the AS equations from the PDEs of the original problem and then solving numerically the resulting PDEs of the AS. The continuous adjoint state method involves the following steps:

- Define the adjoint state variable for solute concentration, τ . The model parameters γ_s are collected in a vector $\bar{\mathbf{y}}$.
- Define the objective function in terms of the variables and model parameters, such as that in Eq. (11).
- Take derivatives of the solute transport PDEs

and associated initial and boundary conditions in Eqs. (1)-(5) with respect to parameter γ_s . The derivatives are denoted with a superscript ', i.e., \mathbf{r}' denotes the derivative of \mathbf{r} with respect to γ_s .

- Multiply the resulting derivative equations by the adjoint state τ and integrate in RxT.
- Apply Green's first identity and divergence theorem to substitute the divergence terms by lower-order derivatives. The resulting boundary integrals are evaluated by their respective boundary equations obtained after steps 3 and 4.
- Eliminate the terms involving $\nabla \mathbf{c}'$ by applying Green's first identity and divergence theorem.
- Lump together in F_c^1 all the terms containing derivatives of solute concentration with respect to the parameter γ_s . The rest of the terms are lumped into a term denoted F^1 . The resulting expression is given by:

$$F^1 + F_c^1 = 0 \quad (25)$$

- Take derivatives of the objective function Ω with respect to γ_s and add it to Eq. (13). The gradient of the objective function becomes:

$$\frac{d\Omega}{d\gamma_s} = F + F_c \quad (26)$$

where F and F_c have the following expressions:

$$F = F^1 + \iint_{R,T} \frac{\partial J_3}{\partial \gamma_s} dRdt \quad (27)$$

$$F_c = F_c^1 + \iint_{R,T} \frac{\partial J_2}{\partial c} c' dRdt \quad (28)$$

- Select τ so that F_c cancels out. This leads to a PDE for the adjoint state variable, τ , with its corresponding final and boundary conditions.
- Derive the expressions of the derivatives of the objective function with respect to model parameters, which involve the original and the adjoint state variables.

The PDE of the transient adjoint state variable and its associated "final" and boundary conditions are given by:

$$\nabla \cdot (\emptyset \mathbf{D} \nabla \tau + \mathbf{q} \nabla \tau) - \tau \cdot (q_d + \lambda_d \emptyset) + \frac{\partial J_2}{\partial c} = -\frac{\partial \tau \emptyset}{\partial t} \text{ in RxT} \quad (29)$$

$$\emptyset \mathbf{D} \nabla \tau \cdot \mathbf{n} = -\beta_{bc} \tau \text{ in } \Gamma_1 \times T \quad (30)$$

$$(\emptyset \mathbf{D} \nabla \tau + \mathbf{q} \tau) \cdot \mathbf{n} = -\beta_{bc} \tau \text{ in } \Gamma_2 \times T \quad (31)$$

$$\tau(x, t_f) = 0 \text{ in R} \quad (32)$$

where t_f is the final time. The expressions of $\frac{d\Omega}{d\gamma_s}$ for selected parameters are listed in Appendix A.

Numerical methods are used to solve the adjoint PDE. By using discretization methods similar to those of the original problem (Galerkin finite elements for spatial discretization and finite differences for time discretization), the finite element equations of the adjoint state variable are given by:

$$(\bar{\mathbf{F}}\theta_1 - \bar{\mathbf{E}}/\Delta t^k) \bar{\boldsymbol{\tau}}^{k-1} + [\bar{\mathbf{F}}(1 - \theta_1) + \bar{\mathbf{E}}/\Delta t^k] \bar{\boldsymbol{\tau}}^k = \bar{\mathbf{r}}_{\boldsymbol{\tau}}^k \quad (33)$$

where $\bar{\mathbf{F}}$ is the N x N conductance matrix, $\bar{\mathbf{E}}$ is the N x N symmetric storage matrix, θ_1 is a time discretization parameter ($0 < \theta_1 < 1$), $\bar{\boldsymbol{\tau}}^k$ is the vector of nodal adjoint state concentrations at time t^k and K is the total number of time intervals where concentrations are calculated. Matrices $\bar{\mathbf{F}}$ and $\bar{\mathbf{E}}$ are the same matrices defined in the original problem in Eqs.(8) and (9) and vector $\bar{\mathbf{r}}_{\boldsymbol{\tau}}^k$ is given by:

$$r_{\boldsymbol{\tau}}^k = \int_R \frac{\partial J_2}{\partial c} \xi_i dR \Big|_k \quad (34)$$

The analysis of the continuous version of the adjoint state equations indicates that the adjoint state τ satisfies a PDE similar to that of c. However, the "adjoint solute" corresponding to τ moves upstream, unlike the solute with concentration c. Therefore, τ must be solved backwards in time from the final to the initial time. Furthermore, the PDE of the adjoint state is intrinsically linear, unlike the equations of the original problem which may be non-linear for non-linear chemical sinks and sources.

4.- Discrete adjoint state

The discrete adjoint state method consists on obtaining the finite element equations of the adjoint states directly from the discretized equations of the original problem. The discrete method involves the following steps:

- Define the adjoint state vector $\bar{\boldsymbol{\tau}}^k$ ($k = 1, 2, \dots, K$) of nodal concentrations at time t^k .
- Define the objective function in terms of model parameters and outputs.
- Take derivatives of the discretized equations of the original problem, Eq. (7), with respect to the parameter γ_s .
- Premultiply the equations by the transposed adjoint state vector $\bar{\boldsymbol{\tau}}^{k-1}$ and sum for all the K time intervals.
- Lump together all the terms in the left-hand side and add them to the derivative of the objective function.

The finite element equations of the discrete adjoint state are given by:

$$\begin{aligned} & (\bar{\mathbf{F}} \cdot \theta_1 + \bar{\mathbf{E}}/\Delta t^k)^T \cdot \bar{\boldsymbol{\tau}}^{k-1} \\ & - [-\bar{\mathbf{F}} \cdot (1 - \theta_1) \\ & + \bar{\mathbf{E}}/\Delta t^k]^T \cdot \bar{\boldsymbol{\tau}}^k = \zeta^k \end{aligned} \quad (35)$$

where the matrices $\bar{\mathbf{F}}$ and $\bar{\mathbf{E}}$ are the same matrices defined in the original problem and vector ζ^k is given by:

$$\zeta_i^k = \frac{\partial J_2^N}{\partial c_i^k} \quad (36)$$

The resulting general expression of the derivative of the objective function becomes:

$$\begin{aligned} \frac{\partial \Omega^N}{\partial \gamma_s} &= \sum_{k=1}^K -(\bar{\boldsymbol{\tau}}^{k-1})^T \cdot \\ & \left\{ \left(\bar{\mathbf{F}}' \theta + \frac{\bar{\mathbf{E}}'}{\Delta t^k} \right) \bar{\mathbf{c}}^k - \left[-\bar{\mathbf{F}}'(1 - \theta) + \frac{\bar{\mathbf{E}}'}{\Delta t^k} \right] \bar{\mathbf{c}}^{k-1} \right. \\ & \quad \left. - \bar{\mathbf{r}}'^{k-1} \right\} + \\ & + \iint_{R,T} \frac{\partial J_3}{\partial \gamma_s} dRdt \end{aligned} \quad (37)$$

5.- Comparison of the continuous and discrete adjoint methods for solute transport

The discrete and continuous adjoint state methods lead to linear equations. Moreover, in both cases the adjoint state equations must be solved backwards in time, starting at the final conditions where $\tau = 0$.

Although the discrete and continuous adjoint state methods lead in general to different algebraic equations, their solutions are consistent because both methods reflect different ways of discretizing the same partial differential equations. The continuous method is versatile because it allows using a numerical method and a discretization scheme for the adjoint states independent of those of the forward problem.

The discrete AS method must be developed and coded specifically for the code of the forward problem. Therefore, it is an intrusive method. The discrete AS method offers the advantage of ensuring a numerical accuracy of adjoint state similar to that of the forward problem.

6.- Multicomponent conservative transport

Here we present the continuous AS equations for conservative transport of N species. The mathematical formulation of the original problem for N species is given by the following PDEs, boundary and initial conditions:

$$\mathbf{L}(\bar{\mathbf{c}}) + \phi \bar{\mathbf{g}} = \frac{\partial \phi \bar{\mathbf{c}}}{\partial t} \quad (38)$$

$$(\phi \mathbf{D} \nabla \bar{\mathbf{c}} - \mathbf{q} \bar{\mathbf{c}}) \cdot \mathbf{n}|_{\Gamma} = -\beta_{bc}(\bar{\mathbf{c}} - \bar{\mathbf{C}}) + \bar{\mathbf{G}} \quad (39)$$

$$\bar{\mathbf{c}}(\mathbf{x}, t_0) = \bar{\mathbf{c}}_0 \quad (40)$$

where the variables and parameters are those already presented in Section 2. For the i-th species, $L(c_i)$ is a transport operator given by:

$$L(c_i) := \nabla \cdot (\phi \mathbf{D} \nabla c_i - \mathbf{q} c_i) - \lambda_{d,i} \phi c_i \quad (41)$$

The objective function in this case is given in terms of the N solute concentrations $\bar{\mathbf{c}}$ and the model parameters:

$$\Omega = \iint_{R,T} J_2(\bar{\mathbf{c}}) dRdt + \iint_{R,T} J_3(\bar{\boldsymbol{\tau}}) dRdt \quad (42)$$

The adjoint state variables τ associated to the original problem are collected in a column vector of N components, $\bar{\boldsymbol{\tau}}$, which satisfy the following equations:

$$\mathbf{L}(\bar{\boldsymbol{\tau}}) + \frac{\partial J_2}{\partial \bar{\mathbf{c}}} = -\phi \frac{\partial \bar{\boldsymbol{\tau}}}{\partial t} \quad (43)$$

$$(\phi \mathbf{D} \nabla \bar{\boldsymbol{\tau}} + \mathbf{q} \bar{\boldsymbol{\tau}}) \cdot \mathbf{n}|_{\Gamma} = -\beta_{bc} \bar{\boldsymbol{\tau}} \quad (44)$$

$$\bar{\boldsymbol{\tau}}(\mathbf{x}, t_f) = \bar{\mathbf{0}} \quad (45)$$

The expressions of the derivative of the objective function for selected parameters are listed in Appendix B.

Eqs. (31)-(33) show that adjoint states $\bar{\boldsymbol{\tau}}$ satisfy similar equations as in the original problem, with an extra source term which depends on the derivatives of the objective function. Moreover, the AS equations must be solved backwards in time.

7.- Reactive system with kinetically-controlled minerals

This section presents the continuous AS equations for reactive solute transport involving N primary aqueous species and N_p kinetically-controlled mineral phases with precipitation/dissolution rates r_p . The mathematical formulation of the original problem is given by:

$$\mathbf{L}(\bar{\mathbf{c}}) + \bar{\mathbf{S}}_p \bar{\mathbf{r}}_p = \frac{\partial \phi \bar{\mathbf{c}}}{\partial t} \quad (46)$$

$$(\phi \mathbf{D} \nabla \bar{\mathbf{c}} - \mathbf{q} \bar{\mathbf{c}}) \cdot \mathbf{n}|_{\Gamma} = -\beta_{bc}(\bar{\mathbf{c}} - \bar{\mathbf{C}}) + \bar{\mathbf{G}} \quad (47)$$

$$\bar{\mathbf{c}}(\mathbf{x}, t_0) = \bar{\mathbf{c}}_0 \quad (48)$$

where $\bar{\mathbf{c}}$ is the vector of N primary species concentrations and $\bar{\mathbf{S}}_p$ is a $N \times N_p$ rectangular matrix of stoichiometric coefficients given by:

$$\bar{\mathbf{S}}_p = \begin{pmatrix} v_{c1}^{p1} & v_{c1}^{p2} & \dots & v_{c1}^{Np} \\ v_{c2}^{p1} & v_{c2}^{p2} & \dots & v_{c2}^{Np} \\ \vdots & \vdots & \ddots & \vdots \\ v_{cN}^{p1} & v_{cN}^{p2} & \dots & v_{cN}^{Np} \end{pmatrix}_{NxNp} \quad (49)$$

$\bar{\mathbf{r}}_p$ is a column vector of N_p precipitation/dissolution kinetic rates given by:

$$\bar{\mathbf{r}}_p = \begin{pmatrix} r_{p1}(c_1, \dots, c_N) \\ \vdots \\ r_{Np}(c_1, \dots, c_N) \end{pmatrix}_{Np \times 1} \quad (50)$$

where v_{cj}^{pi} is the stoichiometric coefficient of the j -th primary species involved in the chemical reaction of the i -th mineral phase. The terms r_{pi} refers to the kinetic rate of the i -th mineral phase, which in general depends on the concentrations of the primary species.

The term $\bar{\mathbf{S}}_p \bar{\mathbf{r}}_p$ in Eq. (34) is a sink/source term of the concentrations of primary species associated to the kinetic precipitation/dissolution of the mineral phases with concentrations $\bar{\mathbf{P}}$:

$$\bar{\mathbf{S}}_p \bar{\mathbf{r}}_p = -\frac{\partial \phi \bar{\mathbf{P}}}{\partial t} \quad (51)$$

The objective function in this case is given in terms of the N primary species concentrations $\bar{\mathbf{c}}$ and the model parameters $\bar{\mathbf{Y}}$:

$$\Omega = \iint_{R,T} J_2(\bar{\mathbf{c}}) dRdt + \iint_{R,T} J_3(\bar{\mathbf{Y}}) dRdt \quad (52)$$

The adjoint states associated to the original problem are defined by the column vector of N components, $\bar{\boldsymbol{\tau}}$. The adjoint state equations for a reactive system with N_p kinetically-controlled mineral phases are given by:

$$\mathbf{L}(\bar{\boldsymbol{\tau}}) + \bar{\mathbf{R}}^T \bar{\mathbf{S}}_p^T \bar{\boldsymbol{\tau}} + \frac{\partial J_2}{\partial \bar{\mathbf{c}}} = -\phi \frac{\partial \bar{\boldsymbol{\tau}}}{\partial t} \quad (53)$$

$$(\phi \mathbf{D} \nabla \bar{\boldsymbol{\tau}} + \mathbf{q} \bar{\boldsymbol{\tau}}) \cdot \mathbf{n}|_{\Gamma} = -\beta_{bc} \bar{\boldsymbol{\tau}} \quad (54)$$

$$\bar{\boldsymbol{\tau}}(\mathbf{x}, t_f) = \bar{\mathbf{0}} \quad (55)$$

where $\bar{\mathbf{R}}$ is a $N_p \times N$ matrix associated to the first-order derivatives of the precipitation/dissolution kinetic rates with respect to the primary species concentrations:

$$\bar{\mathbf{R}} = \begin{pmatrix} \frac{\partial r_{p1}}{\partial c_1} & \frac{\partial r_{p1}}{\partial c_2} & \dots & \frac{\partial r_{p1}}{\partial c_N} \\ \frac{\partial r_{p2}}{\partial c_1} & \frac{\partial r_{p2}}{\partial c_2} & \dots & \frac{\partial r_{p2}}{\partial c_N} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial r_{Np}}{\partial c_1} & \frac{\partial r_{Np}}{\partial c_2} & \dots & \frac{\partial r_{Np}}{\partial c_N} \end{pmatrix}_{Np \times N} \quad (56)$$

The expressions of the derivatives of the objective function for selected parameters are listed in Appendix C.

Eqs. (41)-(43) show that adjoint states $\bar{\boldsymbol{\tau}}$ of a reactive system with kinetically-controlled mineral phases satisfy similar equations as those of the original problem, with additional sink/source terms which depend on the derivatives of the objective function. Moreover, there is a source term in $\bar{\boldsymbol{\tau}}$ which is associated to the chemical reactions. It should be noticed that contrary to the PDE's of the original problem which in general are nonlinear, the PDE's of the adjoint state variables are linear.

8.- Reactive system with cation exchange reactions

This section presents the continuous AS equations for multicomponent cation exchange reactive transport. The solute transport PDEs for a set of exchanging cations is given by:

$$L(\bar{\mathbf{c}}) = \phi \frac{\partial \bar{\mathbf{c}}}{\partial t} + \lambda \bar{\mathbf{D}}_z \frac{\partial \bar{\boldsymbol{\beta}}}{\partial t} \quad (57)$$

$$L(c_N) = \phi \frac{\partial c_N}{\partial t} + \lambda \frac{\partial \beta_N}{\partial t} \quad (58)$$

where $\bar{\mathbf{c}}$ is the column vector of $N-1$ concentrations of dissolved cation, $\bar{\boldsymbol{\beta}}$ is the column vector of $(N-1)$ equivalent fractions of the exchanged cations, $\bar{\mathbf{D}}_z$ is a $(N-1) \times (N-1)$ diagonal matrix of entries z_i^{-1} , where z_i is the charge of the i -th cation, c_N is the dissolved concentration of the reference cation (usually Na^+), β_N is the equivalent fraction of the reference cation and λ is a constant given by:

$$\lambda = \frac{\text{CEC} \rho_d}{100} \quad (59)$$

where CEC is the cation exchange capacity (meq/100g) and ρ_d is bulk density. Initial and boundary conditions are given by:

$$(\phi \mathbf{D} \nabla \bar{\mathbf{c}} - \mathbf{q} \bar{\mathbf{c}}) \cdot \mathbf{n}|_{\Gamma} = -\beta_{bc} (\bar{\mathbf{c}} - \bar{\mathbf{C}}) + \bar{\mathbf{G}} \quad (60)$$

$$\bar{\mathbf{c}}(\mathbf{x}, t_0) = \bar{\mathbf{c}}_0 \quad (61)$$

Cation exchange reactions take place when dissolved cations exchange with cations at the interlayer positions. These reactions can be assumed to take place at chemical equilibrium. According to the Gaines-Thomas

convention, the mass-action-law of cation exchange reactions is given by the following expression in terms of equivalent fractions β_i :

$$K_{ij} = \frac{\beta_i^{1/z_i} \cdot c_j^{1/z_j}}{\beta_j^{1/z_j} \cdot c_i^{1/z_i}} \quad (62)$$

where K_{ij} is the exchange or selectivity coefficient. By definition, equivalent fractions add to one:

$$\sum_{i=1}^N \beta_i = 1 \quad (63)$$

Exchange reactions are usually expressed in terms of a reference cation. Considering N as the reference cation, Eq. (50) becomes:

$$K_{Nj} = \frac{\beta_N^{1/z_N} \cdot c_j^{1/z_j}}{\beta_j^{1/z_j} \cdot c_N^{1/z_N}} \quad j = 1, \dots, N-1 \quad (64)$$

Using matrix notation and taking logarithms in Eq. (52) leads to:

$$\ln \bar{\mathbf{K}} = \bar{\mathbf{D}}_z (\ln \bar{\mathbf{c}} - \ln \bar{\boldsymbol{\beta}}) + \bar{\mathbf{1}} (\ln \beta_N - \ln c_N) \quad (65)$$

$$\bar{\mathbf{1}}^T \bar{\boldsymbol{\beta}} + \beta_N = 1 \quad (66)$$

Eqs. (45), (46), (53), (54) and initial and boundary conditions in Eqs. (48), (49) define the mathematical formulation of cation exchange reactive transport for deriving the adjoint state equations. By following the steps of the continuous AS method, the adjoint states associated to the original problem are defined in Table 1. The objective function in terms of the variables and model parameters is given by:

$$\Omega = \iint_{R,T} [J_2(\bar{\mathbf{c}}, c_N) + J_3(\bar{\mathbf{y}}) + J_4(\bar{\boldsymbol{\beta}}, \beta_N)] dRdt \quad (67)$$

Table 1. Adjoint states of a reactive system with cation exchange reactions.

Equations of the original problem	Associated adjoint states	Vector dimensions
Eq. (45)	$\bar{\boldsymbol{\tau}}$	(N-1) x 1 column vector
Eq. (46)	τ_N	Scalar
Eq. (53)	$\bar{\boldsymbol{\varepsilon}}$	(N-1) x 1 column vector
Eq. (54)	σ	Scalar

Once the AS method is applied, the adjoint state equations for a reactive system with cation exchange involving N cations are given by:

$$L(\bar{\boldsymbol{\tau}}) - \bar{\mathbf{D}}_c \bar{\mathbf{D}}_z \bar{\boldsymbol{\varepsilon}} + \frac{\partial J_2}{\partial \bar{\mathbf{c}}} = -\phi \frac{\partial \bar{\boldsymbol{\tau}}}{\partial t} \quad (68)$$

$$\bar{\mathbf{D}}_\beta \bar{\mathbf{D}}_z \bar{\boldsymbol{\varepsilon}} + \frac{\partial J_4}{\partial \bar{\boldsymbol{\beta}}} + \sigma \bar{\mathbf{1}} = -\lambda \bar{\mathbf{D}}_z \frac{\partial \bar{\boldsymbol{\tau}}}{\partial t} \quad (69)$$

$$L(\tau_N) + \frac{1}{c_N} \bar{\mathbf{1}}^T \bar{\boldsymbol{\varepsilon}} + \frac{\partial J_2}{\partial c_N} = -\phi \frac{\partial \tau_N}{\partial t} \quad (70)$$

$$-\frac{1}{\beta_N} \bar{\mathbf{1}}^T \bar{\boldsymbol{\varepsilon}} + \frac{\partial J_4}{\partial \beta_N} + \sigma = -\lambda \frac{\partial \tau_N}{\partial t} \quad (71)$$

where $\bar{\mathbf{D}}_c, \bar{\mathbf{D}}_z, \bar{\mathbf{D}}_\beta$ are (N-1)x(N-1) diagonal matrices with entries $D_{c,ii} = c_i^{-1}$, $D_{z,ii} = z_i^{-1}$ and $D_{\beta,ii} = \beta_i^{-1}$.

The system of equations (56)-(59) can be simplified by elimination. The resulting adjoint state equations are given by:

$$\sigma = -\frac{c_N}{\beta_N} \left[L(\tau_N) + \left(\phi + \lambda \frac{\beta_N}{c_N} \right) \frac{\partial \tau_N}{\partial t} + \frac{\beta_N}{c_N} \frac{\partial J_4}{\partial \beta_N} + \frac{\partial J_2}{\partial c_N} \right] \quad (72)$$

$$L(\bar{\boldsymbol{\tau}}^*) + \bar{\mathbf{A}}^{-1} \bar{\mathbf{s}}^* = \bar{\mathbf{A}}^{-1} \bar{\mathbf{B}} \frac{\partial \bar{\boldsymbol{\tau}}^*}{\partial t} \quad (73)$$

where the superscript * indicates that vectors and matrices are N dimensional. Matrices $\bar{\mathbf{A}}^{-1}$ and $\bar{\mathbf{B}}$ and vector $\bar{\mathbf{s}}^*$ are given by:

$$\bar{\mathbf{A}}^{-1} = \begin{pmatrix} & & & w_1 \\ & & & \vdots \\ & & & w_{N-1} \\ \frac{c_1 z_1}{c_N} & \dots & -\frac{c_{N-1} z_{N-1}}{c_N} & w_N \end{pmatrix} \quad (74)$$

$$\bar{\mathbf{s}}^* = \begin{pmatrix} s_1 \\ \vdots \\ s_{N-1} \\ \sum_{i=1}^N c_i z_i \frac{\partial J_2}{\partial c_i} \end{pmatrix} \quad (75)$$

$$\bar{\mathbf{B}} = \begin{pmatrix} & & -\frac{c_N \beta_1}{\beta_N c_1} R_{NN} \\ & & \vdots \\ & & -\frac{c_N \beta_{N-1}}{\beta_N c_{N-1}} R_{NN} \\ -\phi c_1 z_1 & \dots & -\phi c_{N-1} z_{N-1} & -\phi c_N \end{pmatrix} \quad (76)$$

where $\bar{\mathbf{I}}$ is the (N-1)x(N-1) identity matrix, $\bar{\mathbf{R}}$ is a diagonal matrix with entries $R_{ii} = \phi + \lambda \frac{\beta_i}{c_i}$ and w_i , and s_j are given by:

$$w_i = \frac{\beta_j}{c_j \sum_{i=1}^N \beta_i z_i}; \quad i = 1, \dots, N \quad (77)$$

$$s_j = \frac{\partial J_2}{\partial c_j} + \frac{\beta_j}{c_j} \cdot \frac{\partial J_4}{\partial \beta_j} + \frac{\beta_j}{c_j} \frac{c_N}{\beta_N} \cdot \left(\frac{\beta_N}{c_N} \frac{\partial J_4}{\partial \beta_N} + \frac{\partial J_2}{\partial c_N} \right); \quad (78)$$

$$j = 1, \dots, N - 1$$

The adjoint states $\bar{\tau}^*$ in Eq. (61) satisfy a linear system of PDE's which can be solved once the variables of the original problem are known. Once $\bar{\tau}^*$ are known, then σ is calculated according to Eq. (60) and finally $\bar{\epsilon}$ is computed according to Eq. (57). It should be noticed that contrary to the PDE's of the original problem which are highly nonlinear, the PDE's of the adjoint state variables are linear.

The expressions of the derivatives of the objective function for selected parameters are listed in Appendix D.

9.- Conclusions

We have presented the formulation of both the continuous and discrete AS method for conservative and reactive solute transport in porous media. The properties of the continuous and discrete AS formulations have been analysed and compared. The formulation has been extended to multicomponent solute transport systems involving: 1) Purely conservative species; 2) Reactive species participating in kinetic mineral dissolution/precipitation reactions; and 3) Reactive species participating in cation exchange reactions. Contrary to the PDE's of multicomponent reactive solute transport for mineral phases and cation exchange reactions, which are highly nonlinear, the PDE's of the adjoint state variables are always linear.

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10.- References

- Carrera, J., and S.P Neuman 1986. Estimation of aquifer parameters under transient and steady-state conditions. 2. Uniqueness, stability and solution algorithms. *Water Resour. Res.* 22 (2), 211–227.
- Delay, F, H Badri, M Fahs, and P Ackerer 2017. A comparison of discrete versus continuous adjoint states to invert groundwater flow in heterogeneous dual porosity systems, *Ad. Water Resour. Res.* 110: 1–18.
- Hayek, M., RamaRao, B.S., and Lavenue, M. 2019. An adjoint sensitivity model for steady-state sequentially coupled radionuclide transport in porous media. *Water Resources Research*, 55, 8800–8820. <https://doi.org/10.1029/2019WR025686>
- Hayek, M., RamaRao, B.S., and Lavenue, M. 2020. An adjoint sensitivity model for transient sequentially coupled radionuclide transport in porous media. *Water Resources Research*, 56 (7),

e2020WR027274. <https://doi.org/10.1029/2020WR027274>.

- Samper, F.J., and S.P. Neuman 1986. Adjoint state equations for advective-dispersive transport, In: VI International Conference on Finite Elements in *Water Resources*, Lisbon, 423-437.
- Samper, F.J., and S.P. Neuman 1989. Estimation of Spatial Covariance Structures by Adjoint State Maximum Likelihood Cross-validation: 1. Theory, *Wat Resour Res*,25(3):351-362.

Appendix A

This appendix presents the expressions of the derivatives of the objective function with respect to some parameters for the continuous AS method. The parameters are the porosity ϕ , the dispersion/diffusion tensor D and the boundary parameters β_{bc} , G and C .

$$\frac{\partial \Omega}{\partial \phi} = - \iint_{R,T} \nabla \tau \cdot D \nabla c \, dRdt - \iint_{R,T} \tau \left(\lambda c - g + \frac{\partial c}{\partial t} \right) dRdt + \iint_{R,T} \frac{\partial J_3}{\partial \phi} dRdt \quad (A1)$$

$$\frac{\partial \Omega}{\partial D} = - \iint_{R,T} \nabla \tau \otimes \phi \nabla c \, dRdt + \iint_{R,T} \frac{\partial J_3}{\partial D} dRdt \quad (A2)$$

$$\frac{\partial \Omega}{\partial \beta_{bc}} = \iint_{\Gamma,T} [-\tau(c - C)] d\Gamma dt + \iint_{R,T} \frac{\partial J_3}{\partial \beta_{bc}} dRdt \quad (A3)$$

$$\frac{\partial \Omega}{\partial G} = \iint_{\Gamma,T} \tau d\Gamma dt + \iint_{R,T} \frac{\partial J_3}{\partial G} dRdt \quad (A4)$$

$$\frac{\partial \Omega}{\partial C} = \iint_{\Gamma_1,T} \tau(\beta_{bc} - \mathbf{q} \cdot \mathbf{n}) d\Gamma dt + \iint_{\Gamma_2,T} \tau \beta_{bc} d\Gamma dt + \iint_{R,T} \frac{\partial J_3}{\partial C} dRdt \quad (A5)$$

where \otimes denotes the tensorial product.

Appendix B

This appendix lists the expressions of the derivatives of the objective function for the continuous AS method of a multicomponent conservative solute transport system. The derivatives, which correspond to the porosity ϕ , the dispersion/diffusion tensor D , the solute mass source term g_i and the boundary parameters β_{bc} , G_i and C_i , are given by:

$$\frac{\partial \Omega}{\partial \phi} = - \sum_{i=1}^N \iint_{R,T} \nabla \tau_i \cdot D \nabla c_i dRdt - \quad (B1)$$

$$\begin{aligned}
 & - \sum_{i=1}^N \iint_{R,T} \tau_i \left(\lambda_{d,i} c_i - g_i + \frac{\partial c_i}{\partial t} \right) dRdt + \\
 & \quad + \iint_{R,T} \frac{\partial J_3}{\partial \phi} dRdt \\
 \frac{\partial \Omega}{\partial \mathbf{D}} = & - \sum_{i=1}^N \iint_{R,T} \nabla \tau_i \otimes \phi \nabla c_i dRdt \\
 & \quad + \iint_{R,T} \frac{\partial J_3}{\partial \mathbf{D}} dRdt
 \end{aligned} \tag{B2}$$

$$\frac{\partial \Omega}{\partial g_i} = \iint_{R,T} \phi \tau_i dRdt + \iint_{R,T} \frac{\partial J_3}{\partial g_i} dRdt \tag{B3}$$

$$\begin{aligned}
 \frac{\partial \Omega}{\partial \beta_{bc}} = & \iint_{\Gamma,T} -\tau_i (c_i - C_i) d\Gamma dt \\
 & \quad + \iint_{R,T} \frac{\partial J_3}{\partial \beta_{bc}} dRdt
 \end{aligned} \tag{B4}$$

$$\frac{\partial \Omega}{\partial C_i} = \iint_{\Gamma,T} \tau_i \beta_{bc} d\Gamma dt + \iint_{R,T} \frac{\partial J_3}{\partial C_i} dRdt \tag{B5}$$

$$\frac{\partial \Omega}{\partial G_i} = \iint_{\Gamma,T} \tau_i d\Gamma dt + \iint_{R,T} \frac{\partial J_3}{\partial G_i} dRdt \tag{B6}$$

Appendix C

This appendix lists the expressions of the derivatives of the objective function for the continuous AS method of a reactive system with N_p kinetically-controlled mineral phases. The derivatives correspond to porosity ϕ and the dispersion tensor \mathbf{D} and are given by:

$$\begin{aligned}
 \frac{\partial \Omega}{\partial \phi} = & - \sum_{i=1}^N \iint_{R,T} \nabla \tau_i \cdot \mathbf{D} \nabla c_i dRdt - \\
 & - \sum_{i=1}^N \iint_{R,T} \tau_i \left(\lambda_{d,i} c_i + \frac{\partial c_i}{\partial t} \right) dRdt + \\
 & \quad + \iint_{R,T} \frac{\partial J_3}{\partial \phi} dRdt
 \end{aligned} \tag{C1}$$

$$\begin{aligned}
 \frac{\partial \Omega}{\partial \mathbf{D}} = & - \sum_{i=1}^N \iint_{R,T} \nabla \tau_i \otimes \phi \nabla c_i dRdt \\
 & \quad + \iint_{R,T} \frac{\partial J_3}{\partial \mathbf{D}} dRdt
 \end{aligned} \tag{C2}$$

Appendix D

This appendix lists the expressions of the derivatives of the objective function for the continuous AS method of a reactive system with cation exchange reactions. The

derivatives correspond to porosity ϕ , dispersion tensor \mathbf{D} , cation exchange capacity, CEC, and exchange coefficient K_{Nj} and are given by:

$$\begin{aligned}
 \frac{\partial \Omega}{\partial CEC} = & - \frac{\rho_d}{100} \sum_{i=1}^N \iint_{R,T} \frac{\tau_i}{z_i} \frac{\partial \beta_i}{\partial t} dRdt \\
 & \quad + \iint_{R,T} \frac{\partial J_3}{\partial CEC} dRdt
 \end{aligned} \tag{D1}$$

$$\begin{aligned}
 \frac{\partial \Omega}{\partial \phi} = & - \iint_{R,T} \nabla \bar{\tau}^T \cdot \mathbf{D} \nabla \bar{c} dRdt \\
 & - \iint_{R,T} \bar{\tau}^T \left(\lambda_d \bar{c} + \frac{\partial \bar{c}}{\partial t} \right) dRdt \\
 & - \iint_{R,T} \nabla \tau_N \cdot \mathbf{D} \nabla c_N dRdt \\
 & - \iint_{R,T} \tau_N \left(\lambda_d c_N + \frac{\partial c_N}{\partial t} \right) dRdt \\
 & \quad + \iint_{R,T} \frac{\partial J_3}{\partial \phi} dRdt
 \end{aligned} \tag{D2}$$

$$\begin{aligned}
 \frac{\partial \Omega}{\partial \mathbf{D}} = & - \iint_{R,T} \nabla \bar{\tau}^T \otimes \phi \nabla \bar{c} dRdt \\
 & - \iint_{R,T} \nabla \tau_N \otimes \phi \nabla c_N dRdt \\
 & \quad + \iint_{R,T} \frac{\partial J_3}{\partial \mathbf{D}} dRdt
 \end{aligned} \tag{D3}$$

$$\frac{\partial \Omega}{\partial K_{Nj}} = \iint_{R,T} \frac{\varepsilon_j}{K_{Nj}} dRdt + \iint_{R,T} \frac{\partial J_3}{\partial K_{Nj}} dRdt \tag{D4}$$

where $\nabla \bar{\tau}^T \cdot \mathbf{D} \nabla \bar{c}$ is given by:

$$\nabla \bar{\tau}^T \cdot \mathbf{D} \nabla \bar{c} = (\nabla \tau_1 \quad \dots \quad \nabla \tau_{N-1}) \begin{pmatrix} \mathbf{D} \nabla c_1 \\ \vdots \\ \mathbf{D} \nabla c_{N-1} \end{pmatrix} \tag{D5}$$

Appendix E

Table E1. List of terms (variables and parameters).

Variable / Parameter	
$\bar{\beta}$	Vector of equivalent fractions of the exchange cations
β_{bc}	Parameter controlling the type of boundary condition
β_N	Equivalent fraction of the reference cation
Γ	Boundary of the spatial domain
$\bar{\gamma}$	Vector of model parameters
Δt^k	Length of time intervals in finite element numerical formulation
$\nabla(\cdot)$	Gradient operator
$\nabla \cdot (\cdot)$	Divergence operator
$\bar{\varepsilon}$	Adjoint states associated to mass-action-law of cation exchange
θ_1	Time discretization parameter

λ	$\lambda = \text{CEC } \rho_d / 100$	h	Hydraulic head
λ_d	Decay constant	\mathbf{K}	Hydraulic conductivity
ξ_i	Basis functions in finite element numerical formulation	K_{ij}	Exchange coefficient or selectivity coefficient
ρ_d	Bulk density	$L()$	Solute transport operator
ζ	Independent term in the discrete adjoint state equations	\mathbf{n}	Unit vector normal to the boundary
σ	Adjoint state associated to equivalent fractions in cation exchange	\mathbf{q}	Darcy's velocity
$\bar{\tau}$	Adjoint states associated to transport PDEs	R	Space domain
τ_N	Adjoint state associated to reference transport PDEs of the reference cation in cation exchange	$\bar{\mathbf{R}}$	Matrix of first derivatives of the precipitation/dissolution rates with respect to primary species' concentrations
ν_c^p	Stoichiometric coefficient of the species c involved in precipitation/dissolution of mineral p	$\bar{\mathbf{r}}$	Independent term in the finite element numerical formulation of the original problem
ϕ	Porosity	$\bar{\mathbf{r}}_\tau$	Independent term in the continuous AS discretized equations
Ω	Objective function	$\bar{\mathbf{r}}_p$	Vector of precipitation/dissolution rates
C	External concentration along the boundary	$\bar{\mathbf{S}}_p$	Matrix of stoichiometric coefficients in precipitation/dissolution reactions
$c(x,t)$	Solute concentration	T	Time domain
CEC	Cation exchange capacity	t_f	Final time
\mathbf{D}	Dispersion/diffusion tensor	z_i	Charges of the exchange cations
$\bar{\mathbf{E}}$	Storage matrix in the finite element numerical formulation	z_N	Charge of the reference cation
$\bar{\mathbf{F}}$	Conductance matrix in the finite element numerical formulation		
G	Prescribed solute mass flux along the boundary		
g	Solute mass source		
