

Water Mixing Approach (WMA) for reactive transport modeling

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Abstract

We describe a formulation to solve reactive transport problems. The basic idea is to represent transport as mixing water instead of individual solute concentrations, hence the Water Mixing Approach (WMA) name. This representation simplifies calculations as it decouples transport from chemical calculations. Transport is first solved in terms of water mixing ratios (λ), which is feasible for any transport solution method. Chemical calculations can then be written as reactive mixing calculations, which may be non-linear but local, so that they do not need to iterate with transport. We have implemented the WMA to a mixed Eulerian-Lagrangian method transport solver with streamline-oriented grid and constant travel time between sequential cells (isochronal grid), which is free of numerical dispersion. We test the WMA on two reactive transport cases. First, an existing analytical solution of binary system case is used compared to test accuracy of the using of mixing ratios. Second, a calcite dissolution case compared the WMA to the Direct Substitution Approach to test both accuracy and computational cost (CPU). Results confirm the high accuracy and efficiency (low CPU cost) due decoupling transport and chemical steps, especially for a refined grid was. Transport through highly heterogeneous media remains a challenge, but the definite separation of mixing processes in WMA opens a new path for reactive transport modelling.

Keywords: Reactive Transport, Mixing, WMA, water mixing ratios,

1. Introduction

The study of geochemical processes in porous media is critical in many engineering fields (e.g., clean-up of contaminated aquifers, geological storage of CO₂, nuclear waste storage, mining or other geoenvironmental problems). In all of these, solute transport mechanisms such as advection and dispersion need to be coupled to chemical reactions (e.g., complexation, adsorption, biodegradation or precipitation), leading to reactive transport (RT). Fully coupled RT is needed to assess the rate of chemical reactions, their location, or the conditions under which they occur (Rezaei *et al.*, 2005). Although analytical solutions exist for particular conditions and problems (Donado *et al.* 2009; Haberman 1998; Cirpka and Valocchi 2007; De Simoni *et al.* 2005), numerical methods are needed in most cases.

Numerical solution of reactive transport involves coupling transport PDEs for each species to algebraic equations representing chemical reactions (basically mass action law for fast reactions and kinetic laws for slow reactions), which leads to a nonlinear set of equations. Nonlinearity often causes RT to become complex and non-trivial and requires iterative solution methods. Both Picard (e.g., the Sequential Iteration Approach, SIA or Operator splitting approach), and Newton-Raphson methods (e.g., the Direct Substitution Approach, DSA or Global implicit) have been used to solve RT problems (reviews of RT are given by Steefel and MacQuarrie, 1996, Steefel, 2019; or Liu *et al.*, 2019). It should be noted, that SIA and DSA become identical when explicit schemes are used. Examples of model codes that use SIA include those of Nardi *et al.* (2014); Parkhurst and Appelo (1999); Parkhurst *et al.* (2010); Samper *et al.* (2003); Šimůnek *et al.* (2008); Xu *et al.* (2011); Yeh and Li (2004). Examples of model codes that use DSA include those of Mayer *et al.* (1999); Mills *et al.* (2005); Pruess (2005); Saaltink *et al.* (2004); Steefel and Yabusaki (1996). See Steefel *et al.* (2015) for a review. Figure 1a and 1b provide the calculation flow algorithm of SIA and DSA, respectively.

Actually, the key to accurate reactive transport is proper simulation of (1) mixing, which control the rate of fast reactions (Rezaei *et al.* 2005; De Simoni *et al.* 2005; Sanchez-Vila *et al.* 2007), and (2) residence times, which control the rate of slow reactions. The latter is well reproduced by most simulation methods. Therefore, the challenge is to develop an approach that reproduces mixing properly.

In this paper, we propose a reactive transport methodology to simplify and effectively decouple transport from chemical calculations by formulating reactive transport as a reactive mixing calculation of waters at every time step. Therefore, we term it Water Mixing Approach (WMA).

2. Governing equations

2.1. The ADE as a Water Mixing Equation

The standard formulation for solute reactive transport relies on representing transport through the Advection Dispersion equation (ADE), which expresses the mass balance of each aqueous species (Saaltink et al. 1998; Yeh and Tripathi 1989) as

$$\phi \frac{\partial c}{\partial t} = \nabla \cdot (\mathbf{D} \nabla c) - \mathbf{q} \cdot \nabla c + b(c_e - c) + f_Q \quad (1)$$

where c [M/L^3] is concentration, ϕ [-] is porosity, t [T] is time, \mathbf{D} [L^2/T] is the hydrodynamic dispersion tensor, \mathbf{q} [$L^3/L^2/T$] is the Darcy flux, b represent sink/sources of water with concentration c_e (when $b > 0$) or directly the resident concentration c (when $b < 0$) and f_Q [$M/L^3/T$] includes the contributions of chemical reactions to the mass balance of the species. This equation applies to aqueous species. The full reactive problem needs to be complemented with the mass balance of immobile species (minerals and sorbed species), the mass action law for equilibrium reactions, and appropriate expressions for kinetic reactions (See, e.g., Bethke 1996, Parkhurst and Appelo, 1999 or Saaltink et al., 1998 for details).

The ADE expresses that the rate at which concentration change (left hand side of Eq. (1)) results from dispersion, advection, chemical reactions, and sinks and sources. Insight on dispersion can be gained from perturbation approaches, typical of stochastic formulations. In these formulations, variables are split as the sum of an (ensemble) mean plus a zero-mean perturbation (i.e., $c = \bar{c} + c'$, $\mathbf{q} = \bar{\mathbf{q}} + \mathbf{q}'$). Assuming that the ADE is valid at some microscopic scale, the “hydromechanical” dispersive flux becomes $\overline{\mathbf{q}'c'}$, and the total (“hydrodynamic”) dispersive flux is

$$\mathbf{J}_D = \overline{\mathbf{q}'c'} - D_m \nabla c \quad (2)$$

where D_m is the molecular diffusion coefficient. Eq. (2) expresses that the solute is spread by molecular diffusion and by velocity fluctuations with respect to the mean. Gelhar and Axness (1983) demonstrated that this dispersive flux can be approximated by a fickian term ($\mathbf{D}\nabla c$) for large scale transport, but the choice of a fickian form for dispersion is much older (Bear, 1972). Dispersion represents that, when the plume advances, the high permeability portions of the porous medium (i.e., where \mathbf{q} is larger than the mean) will likely be invaded by the (upstream) water (i.e., where c is larger than the mean), whereas the low \mathbf{q} portions will remain with downstream water. That is, dispersion represents exchange between the upstream and downstream waters. Since the difference in upstream and downstream concentrations can be approximated by ∇c times a characteristic exchange distance (L_D), the fickian form emerges naturally. However, it might have been equally natural to keep the water exchange formulation, that is:

$$\mathbf{J}_D = \overline{\mathbf{q}'c'} - D_m \nabla c \simeq -\mathbf{D}\nabla c = \overline{\mathbf{q}_D c} \quad (3)$$

where \mathbf{q}_D is the water flux that exchanges around the mean flux (similar to \mathbf{q}' , but accounting also for molecular diffusion) and we have chosen to write c , instead of c' , in the last term to emphasize that it is the whole water parcel (not only the concentration perturbation) what is exchanging around the mean flux. The water exchange instead of net flux of solute is why no concentration gradient appears in Eq. (3) (see Figure 2).

In the following we will adopt a WMA form of the ADE, by assuming (3) to be valid, so that (1) can be written as:

$$\phi \frac{\partial c}{\partial t} = -\nabla \cdot (\overline{\mathbf{q}_D c}) - \mathbf{q} \cdot \nabla c + b(c_e - c) + f_Q \quad (4)$$

Several remarks can be made regarding this equation. First, when $\mathbf{q}_D c$ represents Fickian dispersion term, then Eq. (4) is just another form of the ADE. But other forms of dispersion may be adopted and Eq. (4) would still be valid. We write it here in this way both for generality and, especially, to highlight that mixing can be viewed as occurring in response to water flux fluctuations. The latter is convenient for reactive

transport, but they are identical provided that $D_L = q_{DL}L_{DL}$ and $D_T = q_{DT}L_{DT}$, where subscripts L and T stand for longitudinal and transverse, respectively (in fact, we will assume that D_L and D_T are known to define the water exchange rates). Therefore, Eq. (4) represents a possibly crude approximation of reality because, at the microscopic scale, $\overline{\mathbf{q}'c'}$ spreads solutes but does not produce mixing, but equating mixing and spreading is a feature of the ADE. If all species have the same dispersion coefficient,

Eq. (4) can be extended to transport of a concentrations vector $\vec{c} = \langle c_1, c_2, \dots, c_{ns} \rangle$ where ns is the number of species. In this case, Eq. (4) could be seen as a water transport equation. However, it might be argued that mixing (if viewed as dissipation of concentration gradients) is species dependent in at least two cases: (1) when diffusion is acknowledged to be species dependent, or (2) when advection is slowed down by fast adsorption. In the first case, it is possible to correct Eq. (4) for the species dependent molecular diffusion (and we will show how to do it in Section 2.4). However, species dependent diffusivity implies also a species dependent dispersion (Chiogna et al. 2010), for which a proper formulation is lacking. While the issue may be important for neutral compounds, it is usually disregarded for ionic species on the basis that the resulting electrical imbalance tends to compensate the relative displacements of one species with respect to another (but this remains to be proven). Adsorption is strictly a chemical reaction and, as such, its role is included in the reaction rates term. The fact that the reaction rate is proportional to $\partial c / \partial t$ causes the velocity of concentration fronts to depend on the retardation coefficient, but this effect is properly represented in Eq. (4), although it may complicate numerical solution.

2.2. Generic numerical formulation.

The ADE and WMA can be solved with a broad range of numerical methods (Finite Element Method, Finite Volumes or Finite Differences among others), but all of them lead to equations of the form (e.g., Huyakorn 1983):

$$\phi_i V_i \frac{c_i^{k+1} - c_i^k}{\Delta t} = \sum_{j \neq i}^{N_{conn}} F_{ij} (c_j - c_i) + b_i V_i (c_{ei} - c_i) + V_i f_{Qi} \quad (5)$$

where k identifies the time step and typically, V_i represents the volume associated to numerical target (i.e., nodes, cell or elements) i , Δt is the time increment, N_{conn} is the number of all targets j connected to i (i.e.: $F_{ij} \neq 0$). Note that the first term on the right hand side of Eq. (5) represents the contributions associated to water exchanges (including both advective and dispersive exchanges) from targets. The second term represents mass input from inflowing water. Note also that we have left purposefully undefined the time at which concentrations are evaluated in the right hand side of Eq. (5). In traditional numerical formulations, this time can be k , $k + 1$, or any time in between, which leads to explicit, fully implicit or time centered schemes, respectively.

Regardless of the time integration scheme, transport is linear, so that concentrations at time step $k + 1$ can be written as a linear combination of those at time step k , plus the possibly non-linear reactions term, which reads:

$$c_i^{k+1} = \sum_j^{N_{conn}+1} \lambda_{ij} c_j^k + \frac{f_{Qi}}{\phi_i} \Delta t \quad (6)$$

where the sum now includes not only targets connected to i , but also target i and external waters. Note that $\sum_j \lambda_{ij} = 1$, to ensure that when all c_j^k are equal and in the absence of reactions, c_i^{k+1} is equal to the same value. Therefore, Eq. (6) can be viewed as a reactive mixing equation (e.g., Pelizard et al., 2017) and it is natural to call λ_{ij} a mixing ratio, although it represents not only mixing but also advection (it is simply the fraction of water in target i that started in target j at the beginning of the time step).

While this equation can represent any transport formulation, its terms are easiest to obtain for explicit integration schemes (otherwise inversion of the full system matrix or subblocks is required). In such case, Eq. (6) can be obtained by dividing Eq. (5) by the volume of parcel i (water content associated to the numerical target i , i.e., $\phi_i V_i$) and multiplying by the time step Δt . Therefore, $\lambda_{ij} = \Delta t F_{ij} / \phi_i V_i$ for connected parcels or $\lambda_{ij} = \Delta t b_i / \phi_i$ for external waters. Note that mixing ratio is expressed as a fraction of the parcel volume i . The latter differs from the use of mixing ratios of end members proposed by (De Simoni et al. 2007; Cirpka and Valocchi 2007; Ginn et al. 2017).

Some observations can now be made about Eq. (6). First, c can be extended to a vector of only concentrations of aqueous species with the result that it can be regarded

as a definition of a water zone. Thus, Eq. (6) indicates that solute transport can be reproduced as a consequence of mixing between connected waters and/or external sources waters. In other words, Eq. (6) could be understood as a fluid mass balance that takes into account water diffusion (Harris and Woolf 1980; Spyrou 2009), which has no effect on water flux phenomenon but can reproduce the solute diffusion. This is important because it reduces the number of transport equations from ns (the number of aqueous species) to 1:

$$W_i^{k+1} = \sum_j^{N_{conn}+1} \lambda_{ij} W_j^k \quad (7)$$

where W_i is the water parcel definition (or water solution) of cell i . Moreover, the equation is very simple. Now concentrations are considered just attributes of W (like Temperature, viscosity or density). This way, chemistry is separated from transport because transport is defined entirely by the water mixing ratio term λ . Thus, the WMA only iterates at chemical step (unlike DSA or SIA) because concentration becomes solely a chemical variable (see Figure 1). Chemical effects are produced by f_{Qi} which is calculated as described in section 2.3.

The use of water as a transport of solute has already been applied by (Konikow, 2010; Winston, Konikow and Hornberger, 2018), although it was not formulated as an equation.

2.3. Chemical Calculations

The evaluation of the chemical sink/source term, f_{Qi} , or directly, the computation of concentrations can be viewed as the mass balance resulting from reactive mixing of waters connected to parcel i , with mixing ratios λ_{ij} , given by

$$\begin{bmatrix} \mathbf{c}_{ai}^{k+1} \\ \mathbf{c}_{imi}^{k+1} \end{bmatrix} = \begin{bmatrix} \sum_j^{N_{conn}+1} \lambda_{ij} \mathbf{c}_{aj}^k \\ \mathbf{c}_{imi}^k \end{bmatrix} + \mathbf{S}_{ei}^t \mathbf{r}_{ei} \frac{\Delta t}{\phi_i} + \mathbf{S}_{ki}^t \mathbf{r}_{ki} \frac{\Delta t}{\phi_i} + \begin{bmatrix} \mathbf{f}_i^c \\ \mathbf{0} \end{bmatrix} \quad (8)$$

where the top row represents the mass balance of aqueous (mobile) species (vector of concentrations \mathbf{c}_{ai} at parcel i) and the bottom row represents the mass balance of immobile species (vector of concentrations \mathbf{c}_{imi}), \mathbf{S}_{ei} and \mathbf{S}_{ki} are the stoichiometric matrices for equilibrium and kinetic reactions, which depends on i because the number and types of reactions may change depending on the minerals and sorption surfaces available (Rubin, 1983), \mathbf{r}_{ei} and \mathbf{r}_{ki} are the vectors of equilibrium and kinetic reaction rates, respectively, and \mathbf{f}_i^c is the vector of correction terms for species dependent dispersion. These equations need to be complemented with the mass action law for equilibrium reactions and with kinetic rate laws for kinetic reactions.

Note that, except for the separation between mobile and immobile species and the inclusion of the correction term, \mathbf{f}_i^c , Eq. (8) is a conventional set of reactive mixing equations (similar to, e.g., Eq. (5.57) of Parkhurst and Appelo, 1999, or Eq. (8) of Pelizardi et al. 2017). Numerous methods are available to solve this type of equations (Fang et al. 2003; Friedly and Rubin 1992; Kräutle and Knabner 2005, 2007; Molins et al. 2004; Saaltink et al. 1998; De Simoni et al. 2005; Yeh and Tripathi 1989). Here, we multiply the concentration vector by a full-ranked components matrix \mathbf{U} (Steeffel, MacQuarrie 1996; Lichtner 1985) to eliminate the rates of equilibrium reactions and by a matrix \mathbf{E} (Saaltink et al. 1998) to eliminate constant activity species. Saaltink et al. 1998 discussed six of such formulations to reduce the number of chemical equations. Any of the six formulations would be valid for WMA. We use their fifth formulation.

$$\begin{bmatrix} \mathbf{E}_i \mathbf{U}_{ai} \mathbf{c}_{ai}^{k+1} \\ \mathbf{E}_i \mathbf{U}_{si} \mathbf{c}_{si}^{k+1} \end{bmatrix} = \begin{bmatrix} \sum_j^{N_{conn}+1} \lambda_{ij} \mathbf{u}_{aj}^k \\ \mathbf{u}_{si}^k \end{bmatrix} + \sum_j \mathbf{E}_i \mathbf{U}_i \mathbf{S}_{kin}^t \mathbf{r}_{kin}(\mathbf{c}_j^k) \frac{\Delta t}{\phi_i} + \begin{bmatrix} \mathbf{E}_i \mathbf{U}_{ai} \mathbf{f}_i^c \\ \mathbf{0} \end{bmatrix} \quad (9)$$

where \mathbf{U}_a and \mathbf{U}_s are submatrices of components matrix \mathbf{U} referring to aqueous and sorbed species, respectively, and where \mathbf{u}_a and \mathbf{u}_s are the aqueous and sorbed component concentrations ($\mathbf{u}_a = \mathbf{U}_a \mathbf{c}_a$, $\mathbf{u}_s = \mathbf{U}_s \mathbf{c}_s$). Note that if there are no kinetic and no adsorption reactions, \mathbf{r}_{kin} and \mathbf{u}_s disappear and component \mathbf{u}_a may be found by solving the system as a conservative solute problem. Concentrations of the next time step ($\mathbf{c}_{a,i}^{k+1}$ and $\mathbf{c}_{s,i}^{k+1}$) can be solved from Eq.(9) and the mass action laws for the equilibrium reactions. Note that the right-hand side of Eq.(9) is calculated entirely from the concentrations of the previous time step. However, other time schemes can also be used. Calculation of $\mathbf{c}_{a,i}^{k+1}$ and $\mathbf{c}_{s,i}^{k+1}$ constitutes the only non-linear part of the proposed

method, and is therefore the costliest part of the calculations with respect to CPU time. However, Eq.(9) can be solved for each parcel independently, thereby reducing the size of the non-linear system to the number of chemical components. The concentration of the minerals can also be calculated by formulating a mass balance similar to Eq.(9) but without eliminating the minerals. Solving Eq. (9) is a standard chemical speciation calculation and any speciation code may be used.

2.4. Isochronal formulation for WMA.

For the sake of generality, section 2.1 formulates ADE as water mixing terms (i.e. WMA) in Eulerian form. Then, a general discretization valid for any numerical method was presented in section 2.2 . However, standard ADE models tend to overpredict solute mixing (Ginn et al. 1995; Kitanidis 1988, 1994; MacQuarrie and Sudicky 1990; Molz and Widdowson 1988) in part because modellers adopting Eulerian transport formulations are forced to either use large dispersion coefficients (which affects mixing ratios in Eq. (6)) or to accept numerical dispersion. The latter can be explained because Eq. (6) includes advection, so that the “mixing ratios” for parcels downstream of i will tend to be negative, which is appropriate to represent advection, but not for mixing calculations (pointing that mixing is a dissipative process, while advection is not). These problems can be overcome by adopting Eulerian-Lagrangian formulations (e.g., Bell and Binning, 2004 ; Cirpka et al., 1999b; Batlle et al., 2002; Ramasomanana et al., 2012; Zhang et al., 2007), which allows modelling advection dominated problems. In these formulations, the time variation of concentration in a flowing parcel of water is written with the material derivative $Dc/Dt = \partial c/\partial t + (\mathbf{q}/\phi) \cdot \nabla c$. Using this definition in Eq. (4) leads to

$$\phi \frac{Dc}{Dt} = -\nabla \cdot (\overline{\mathbf{q}_D c}) + r(c_e - c) + f_Q \quad (10)$$

Written this way, the equation expresses that flowing water concentration changes only due to mixing and reactions, thus highlighting that advection does not produce mixing and therefore does not produce change in the concentrations of flowing water. The material derivative can be approximated as

$$\frac{Dc}{Dt} = \frac{c_i^{k+1} - c_{i-}^k}{\Delta t} \quad (11)$$

where $i-$ refers to the location in the previous time step of the center of the water parcel that ended in parcel i at time $k+1$. Note that Eqs. (5), (6) and (7) may still be valid, except that (1) now the sum is extended over the concentrations that were at locations $i-$ at the end of the previous time step, and (2) only dispersive processes are included within F_{ij} , which ensures that λ_{ij} are positive (a sufficient condition of stability for all conventional numerical methods).

To facilitate numerical evaluation of the material derivative and water mixing fluxes, we adopt a streamline oriented grid (Cirpka et al 1999a; Frind 1982; Crane and Blunt 1999; Thiele et al. 1997; Di Donato et al. 2003; Yabusaki et al. 1998; Herrera et al. 2010). This choice reduces significantly numerical dispersion (Cirpka et al. 1999a) and facilitates the use of finite volumes methods. Still, some smoothing may remain because concentrations at locations $i-$ need to be interpolated from the surrounding parcels.

To eliminate interpolation errors, we define isochronal grids by ensuring that location $i-$ must coincide with a cell center (see Figure 3). That is, a downstream position j exists such that

$$x_j = x_{i-} = x_i - \mathbf{v}\Delta t \quad (12)$$

where \mathbf{v} is the velocity (\mathbf{q}/ϕ) upstream of cell i .

Eq. (12) implies that the initial mesh must be recalculated if either time step simulation or flow (velocity) change. Appendix A shows the building procedure of the proposed isochronal grid. This grid also facilitates the computation of the mixing ratios λ_{ij} . Transport terms are calculated from concentrations of the previous time step in explicit schemes. Explicit schemes are fast, but they are subject to stability criteria that require dispersion coefficients to be small. Therefore, mixing ratios equal zero except for the following cases:

$$\lambda_{ij} = \frac{D_L w_{ij} \Delta t}{\phi_i V_i L_{ij}} \text{ if } i \text{ and } j \text{ are adjacent along a streamline} \quad (13a)$$

$$\lambda_{ij} = \frac{D_T w_{ij} \Delta t}{\phi_i V_i L_{ij}} \text{ if } i \text{ and } j \text{ belong to adjacent streamlines} \quad (13b)$$

$$\lambda_{ij} = \frac{r_i \Delta t}{\phi_i} \text{ if } j \text{ represents an external inflow} \quad (13c)$$

$$\lambda_{ii} = 1 - \sum_{j \neq i}^{N_{adj}} \lambda_{ij} \quad (13d)$$

where w_{ij} is the width of the interface between cells i and j , L_{ij} is the distance between cell centers in (13a) or the mean distance between streamlines in (13b), and D_L and D_T are the longitudinal and transverse, respectively, dispersion coefficients. Note that, for λ_{ii} to be positive, Eq. (13d) requires $\sum_{j \neq i} \lambda_{ij} < 1$, which is a stability condition for any explicit method. Otherwise, the parcel volume entering the cell would be larger than that in the cell.

The obtained formulation can be viewed as a generalization of the mixing-cells approach of Campana (1975), which was extended to reactive transport by Appelo and Willemssen (1987), and is now widely used in 1-D as part of PHREEQC (Parkhurst and Appelo 1999). However, one can use it in 2D problems (see Eq. (13b)).

It must be stressed that these mixing ratios are identical for all species provided that the dispersion coefficients are. We obtain the following expression

$$c_i^{k+1} = \sum_{j=-}^{N_{adj}+1} \lambda_{ij} c_{j-}^k + \frac{f_{Qi}}{\phi_i} \Delta t \quad (14)$$

where N_{adj} is the number of all parcels j adjacent to i . If dispersion coefficients are species dependent, the transport equation can be corrected as follows

$$c_i^{k+1} = \sum_{j=-}^{N_{adj}+1} \lambda_{ij} c_{j-}^k + \frac{f_{Qi}}{\phi_i} \Delta t + f_i^c \quad (15)$$

Where $f_i^c = \sum_{j=-} \lambda_{ij}^c c_{j-}^k$ is a species dependent correction, with λ_{ij}^c given by Eq. (13), except that D 's in (13a) and (13b) are substituted by $(D - D^c)$, where D^c is the dispersion coefficient of each species. As discussed in section 2.1, this correction should be small for ionic species.

3. Applications

We test here the accuracy and efficiency of the WMA by comparison to both analytical solutions (section 3.1) and computational results from the literature (section 3.2). While the WMA could be implemented in any transport simulator, we test it on the formulation presented in section 2.4 in all cases. An explicit scheme is used. We employed the chemical library CHEPROO in both WMA and DSA models. CHEPROO is an object oriented code for geochemical calculations (Bea *et al.*, 2009). Soler-Sagarra *et al.* (2016) also tested the WMA in multi-porosity cases and reaction localizations.

3.1. Half injection domain

This test aims at verifying that the WMA performs well in cases of transverse dispersion and equilibrium reactions, which are particularly relevant for the amount of mixing and reaction rate (see e.g., Werth *et al.* 2006; De Simoni *et al.* 2005). We consider the steady-state analytical solution of De Simoni *et al.* (2007) for reactive transport, based on the analytical solution of Haberman (1998) for conservative transport. Flow occurs in a 2D homogeneous domain with velocity aligned along the x axis. Two end member waters enter the domain at the inflow boundary ($x = 0$), creating a transverse mixing zone. Longitudinal dispersion is neglected. We consider a binary chemical system consisting of two species, Ca^{2+} and SO_4^{2-} , in equilibrium with gypsum. The physical problem is defined in Table 1. The analytical solution for aqueous component concentration, considering the end members with u values of 1 and 0, is the follow

$$u_a(x, y) = \frac{1}{2} \left(1 - \operatorname{erf} \left[\frac{\eta}{2} \right] \right) \quad (16)$$

Where $\eta = \sqrt{Pe} y/x$ is a similarity variable, representing a normalized transverse coordinate with dependency of x and y space coordinates and Peclet number $Pe = v \cdot x / D_T$. v is the velocity. $erff[\cdot]$ is the error function. The analytical expression of reaction rate is giving as

$$r(x, y) = \phi \frac{v}{x} \frac{\partial^2 c_{Ca^{2+}}}{\partial u^2} \left(\frac{du}{d\eta} \right)^2 \quad (17)$$

Where $du/d\eta = -1/(2\sqrt{\pi}) \exp[-\eta^2/4]$ and $\partial^2 c_{Ca^{2+}}/\partial u^2 = 2K/(u^2 + 4K)^{3/2}$. K is the equilibrium constant. Although the analytical solution is steady state, WMA is solved as a transient problem.

Figure 4 shows the cross sections along the y axis of (a) reaction rates and (b) u component at three different x values. Analytical and numerical solutions appear to be very similar. Nevertheless, errors are slightly larger close to the injection boundary where concentration gradients are highest. This may be attributed to the poor reproduction of concentration gradient at this stage, which may violates the criterion of 5 elements across a front suggested by Kinzelbach (1986). Close to the injection boundary, the size of the transverse front is too small with respect to element size.

Because no concentration gradient is defined in mixing term of Eq. (4) neither in Eq. (6), the WMA formulation supplies a complementary explanation. The conservative form of Eq. (14) tells us that the error comes from either the mixing ratios λ_{ij} or the previous step concentration distribution c_{j-}^k . It is easy to check that λ is constant at any time step because all the terms of Eq. (13b) are also constants. That is, only a small portion of solute near the interface does actually exchange. Therefore, approximating it by the mean parcel concentration is poor close to the injection boundary, when concentration varies sharply within the cell. In short, a proper discretization is needed for an accurate solution. The discretization is sufficient when concentrations are smooth. Despite the previous discussion, the results are very acceptable even near the injection boundary.

3.2. The CAL case

Accuracy and efficiency of WMA for reactive transport performance are tested in this section by comparison with the DSA method. DSA method has been preferred because it is more robust than SIA. We tests the chemical system of Saaltink et al. (2001) termed CAL, which consists of the injection of calcite subsaturated water in a domain with initial saturated water and the consequent dissolution of calcite. Both, equilibrium and kinetic cases are tested. Transport and chemical details are shown in Table 2.

The transport part of the DSA method is performed by TRACONF code (Carrera et al. 1993). Both compared codes use the same chemical library, CHEPROO (Bea *et al.*, 2009). Therefore, the differences between the two methods are due to the treatment of transport. TRACONF transport formulation has two main differences from the formulation defined in section 2.4. First, time integration of TRACONF transport is calculated with implicit scheme which involves concentrations at the next time step. Although this implies the use of full system matrix, it is free of time instabilities, unlike faster explicit schemes. Second, an Eulerian formulation (Eq. (1)) is applied instead of mixed Eulerian-Lagrangian formulation (Eq. (10)). Eulerian solution approaches need to meet spatial stability criteria. To avoid complications with stability, the stability criteria are met in all tested models.

First, we compare the CPU time as a function of the number of numerical targets. We perform a 2D simulation (see Table 2). A calculation proposed by Saaltink et al. (2001) is used to predict the CPU time for more refined grids. We assumed that the CPU time consumed by DSA is the sum of that of the chemical calculations, the LU decomposition and the construction of the Jacobian matrix expressed by subscripts *chem*, *dec* and *jac*, respectively. Then the CPU^{DSA} time can be calculated as

$$CPU^{DSA} = CPU_{chem}^{DSA} + CPU_{dec}^{DSA} + CPU_{jac}^{DSA} \quad (18)$$

$$CPU_{chem}^{DSA} = k_{chem}^{DSA} N_{nod} \quad (19)$$

$$CPU_{jac}^{DSA} = k_{jac}^{DSA} N_{nod} N_{con} \quad (20)$$

$$CPU_{dec}^{DSA} = k_{dec}^{DSA} (N_{ban})^2 N_{nod} = k_{dec}^{DSA} m (N_{nod})^2 \quad (21)$$

Where N_{nod} is the number of nodes and N_{ban} is the semi-bandwidth. As we work with rectangular grids (because the medium is homogeneous), N_{ban} is proportional to the square root of N_{nod} times m (m being the ratio between the number of rows and columns). k are constants that only depend on the test case. N_{con} is the maximum number of nodes connected to a particular node including itself (which equals 7 for regular grids of triangular finite elements).

Since we use an explicit scheme for the WMA transport part, the module does not need to solve a system of equations. Almost all CPU time is consumed by the calculation of the chemistry. However, unlike DSA, the spatial discretization affects the time discretization because of the isochronal mesh (see Figure 3). To calculate the CPU time we assumed the number of chemical systems to be solved to be proportional to the number of nodes and the number of time steps. Therefore, the consumption of CPU time can be expressed as:

$$CPU^{WMA} = CPU_{chem}^{WMA} = k_{chem}^{WMA} N_{nod} N_{\Delta t} \quad (22)$$

Where $N_{\Delta t}$ is the number of time steps, which is proportional to the number of columns (Figure 3). This, together with the definition of m , leads to:

$$CPU^{WMA} = k_{chem}^{WMA} (N_{nod})^{1.5} \quad (23)$$

The results are plotted in Figure 5. As can be observed, the measured CPU time is consistent with the calculated CPU time for DSA cases. Kinetic case is slightly costlier though equal convergence criteria are employed. Regarding WMA, calculations using equation (23) do not fit well the measured CPU time. The measurements fit better an exponent of 1.2 instead of 1.5. This can be attributed to the fact that less iterations are employed to solve chemical systems with finer grids. In both cases the differences between WMA and DSA become important when large numbers of nodes are employed. It may therefore be concluded that the WMA outperforms the DSA in both equilibrium and kinetic problems.

Second, the absence of numerical dispersion as evidenced in section 2.4 should be confirmed. To this end, 1D simulations were performed (see Table 2) using the previous WMA and DSA codes. Three different time steps were used for both methods (3 months, 1.5 month and 22 days). Because of the mesh definition (see Figure 3), the WMA needs 20, 40 and 80 parcels, respectively whereas the DSA mesh is composed by 101 nodes in all models. Results are plotted in Figure 6. Note that results of the DSA using an implicit scheme depend on the time step indicating numerical dispersion. On the other hand, the WMA isochronal method presents no numerical dispersion even when the isochronal grid employs a smaller number of nodes.

DSA is also performed and plotted with Crank-Nicholson time integration in Figure 6a. Crank-Nicholson provides a second order error, unlike the first order error of explicit and implicit scheme. Theoretically, this should be without numerical dispersion. Indeed, it gives almost identical results to the WMA.

4. Conclusions

We have presented a new reactive transport formulation and modeling method based on water mixing which we term the Water Mixing Approach (WMA). The basic idea behind the approach is to restrict the coupling between chemistry and transport only to the terms that matter: residence time (relevant for kinetic reactions) and mixing (relevant for fast reactions). These are strictly transport concepts. The resulting reactive transport problem is restricted to the computation of a sequence of reactive mixing calculations, which is simpler and more efficient than traditional reactive transport methods. Effectively, the method implies modelling the transport of water volumes instead of components or species. This decouples transport from chemistry.

Two cases have tested the satisfactory accuracy and computational efficiency of WMA. The approach can be employed in any existing transport approach, although the proper definition and computation of mixing ratios is an important issue. This is why the WMA method has been tested using a streamline oriented isochronal grid, which allows for numerical simulations free of numerical dispersion even for coarse grids. In particular, mixing ratios definition should be especially relevant for transport

formulations in heterogeneous media. In this article we have discussed only cases with uniform flow. Nevertheless, the results suggest that the WMA will also perform well for 2D or 3D heterogeneous cases with non-uniform flow. This is shown by the fact that the WMA becomes increasingly more competitive to the Eulerian methods of DSA for grids of higher dimension and larger number of targets.

Appendix A: Example of streamline oriented isochronal mesh building procedure

The procedure to build the isochronal grid consists of the following steps (Figure A 1:):

1. Solve the flow equation using any available method to compute the flux field. Here we used the finite elements code TRACONF (Carrera et al. 1993).
2. Compute $2N+1$ streamlines, N being the number of flowtubes. Again, any method may be appropriate. Here we used the method of Cordes and Kinzelbach (1992). The one of Pollock (1988) would have been appropriate for finite differences.
3. Define “isochronal” points (Figure A1b), starting at the inflow points of even streamlines and separated a distance $\Delta s = \Delta t \cdot q/\phi$ along stream lines.
4. Finally, build the cells by any of two options: (a) by joining points with the same travel time from the inflow, which is best for regular geometry boundaries; or (b) by joining points with the same head (Figure A 1: c and Figure A1d).

Note that, using the isochronal grid, advection is perfectly reproduced by the water parcels moving from cell to cell during each time step.

Acknowledgments

Data used for producing the figures can be downloaded from [digital.csic.es](http://digital.csic.es/handle/10261/218840) ([https://digital.csic.es/handle/10261/218840](http://digital.csic.es/handle/10261/218840)).

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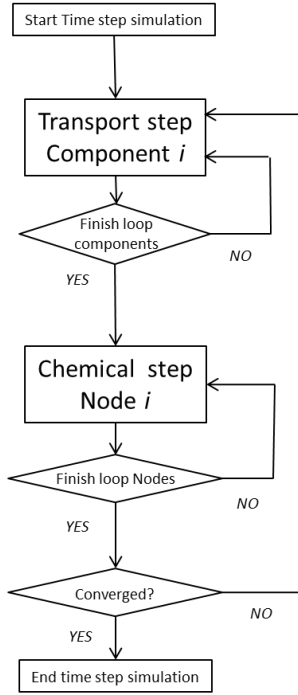
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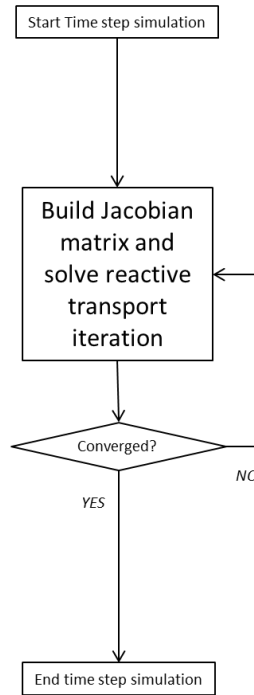
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Figures and Tables captions

a) SIA



b) DSA



c) WMA for reactive transport

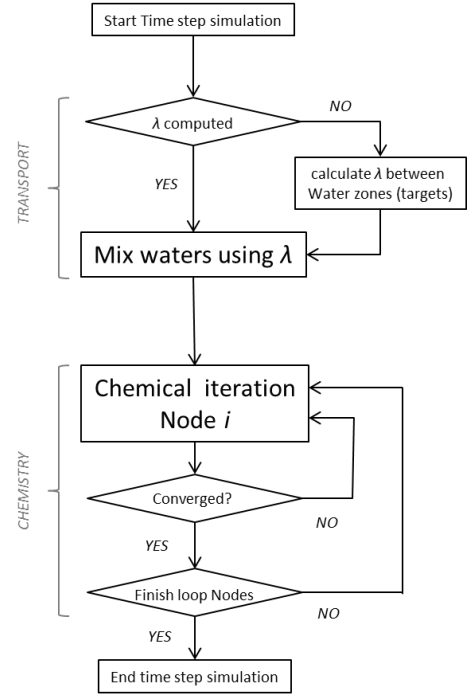
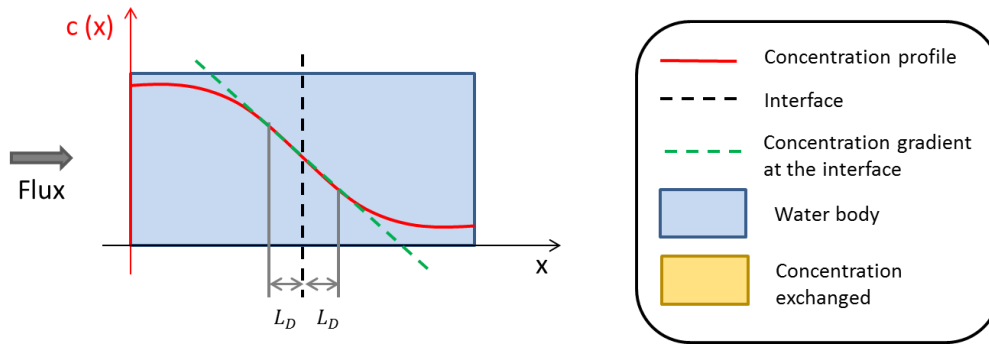


Figure 1: Algorithm flow to solve reactive transport time step simulation using: a) SIA, b) DSA and c) applied WMA formulation to reactive transport



$$\text{ADE} \quad F_c [\text{MOL}/t] = D \nabla c = D \frac{(c_j - c_i)}{L_D}$$

$$\text{WMA} \quad \overline{q_D c} = F_w c_j - F_w c_i = \frac{D}{L_D} c_j - \frac{D}{L_D} c_i$$

$$F_w [V_w/t]$$

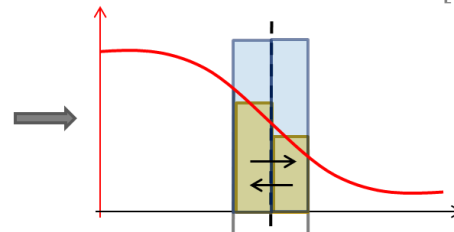
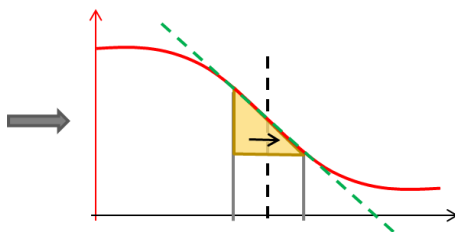


Figure 2: Graphical scheme of dispersion process in ADE and WMA formulations. L_D
 $[M]$ is the length scale of the dispersion process

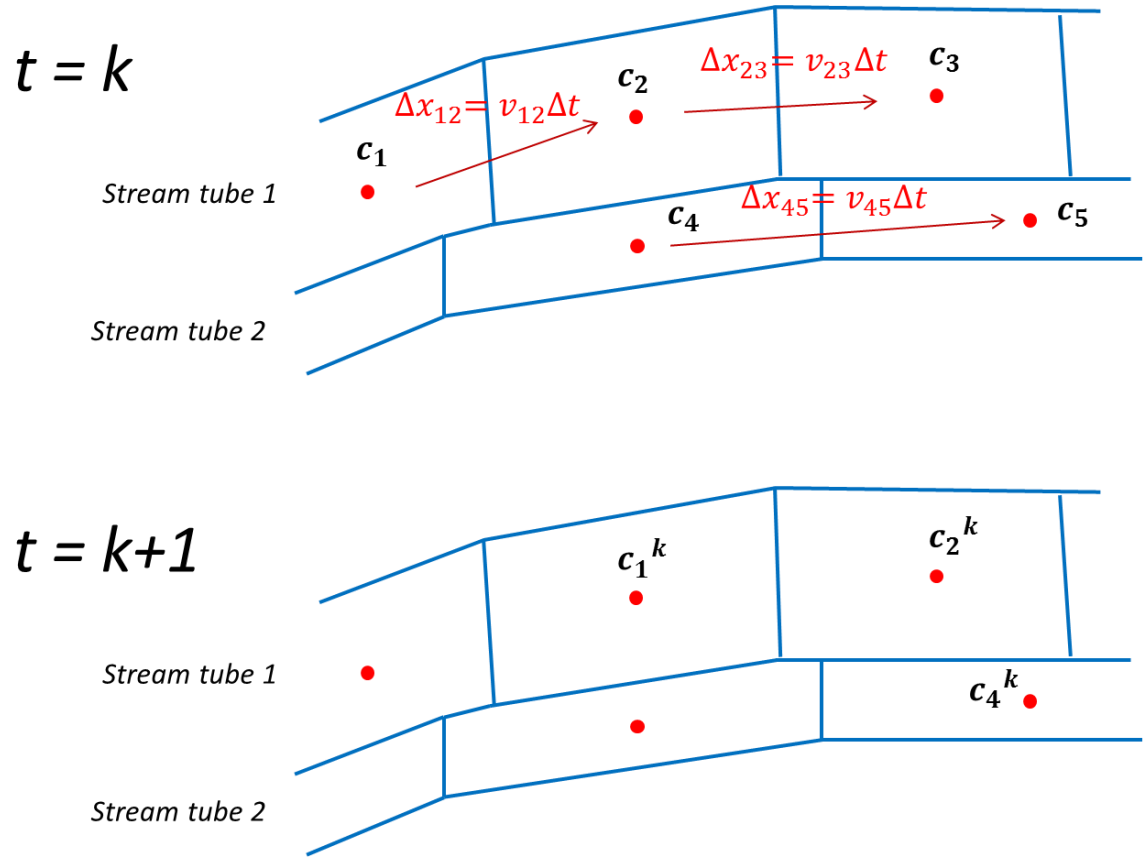


Figure 3: Advection within a dual stream-tube in the proposed isochronal grid

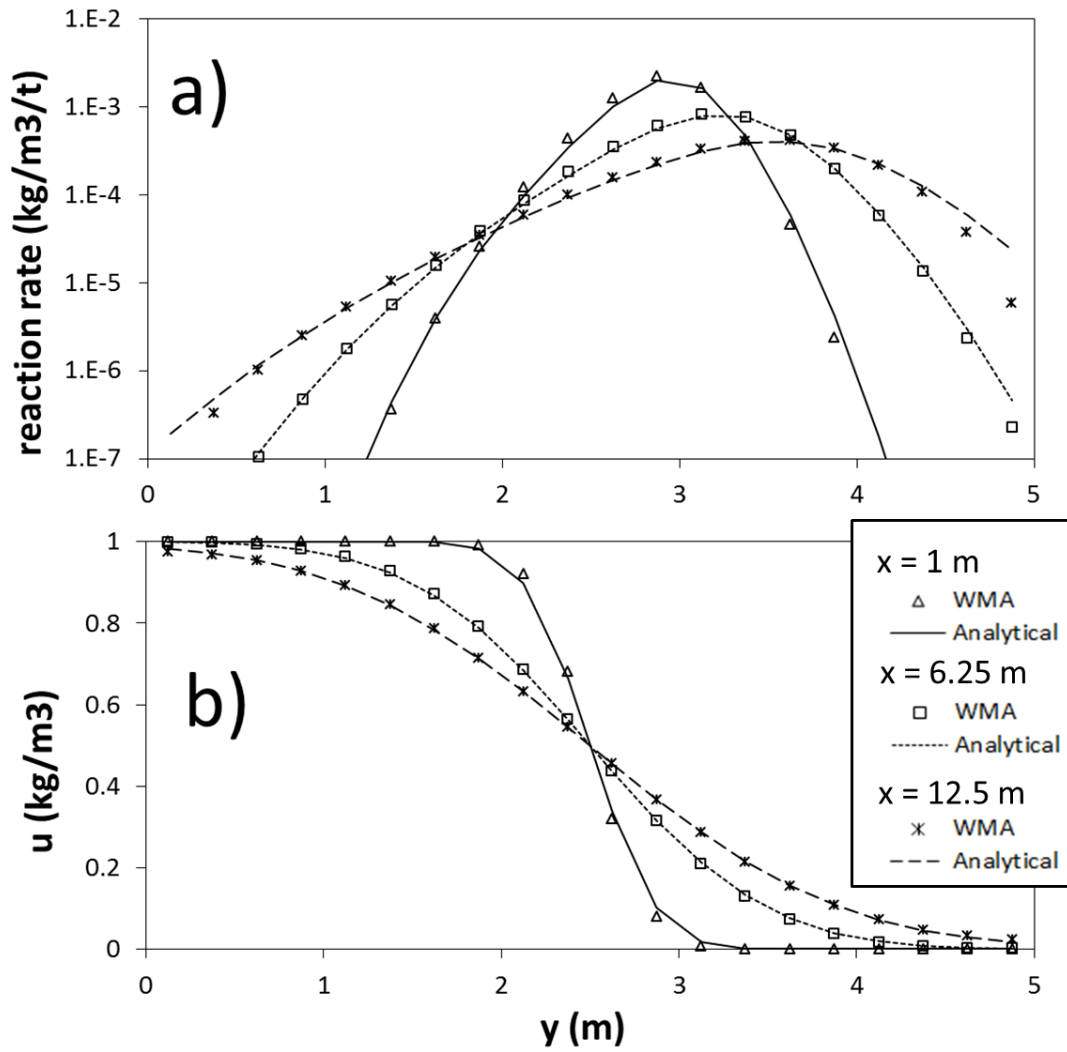


Figure 4: Profiles at different x positions of reaction rate and component concentration of numerical and analytical solutions for the half injection domain.

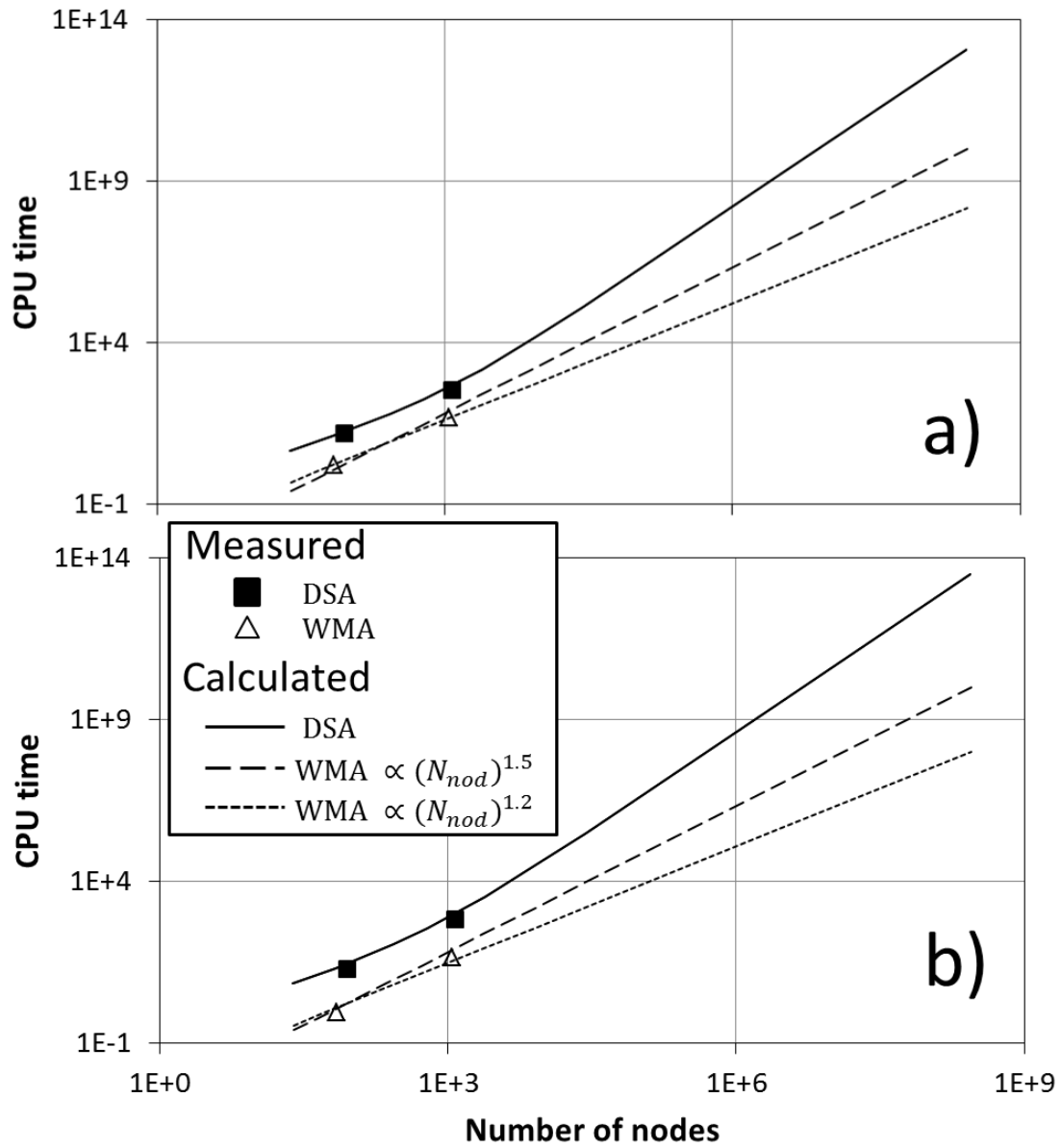


Figure 5: Measured and calculated CPU times as a function of the total number of nodes for both WMA and DSA for (a) equilibrium CAL case and (b) kinetic CAL case.

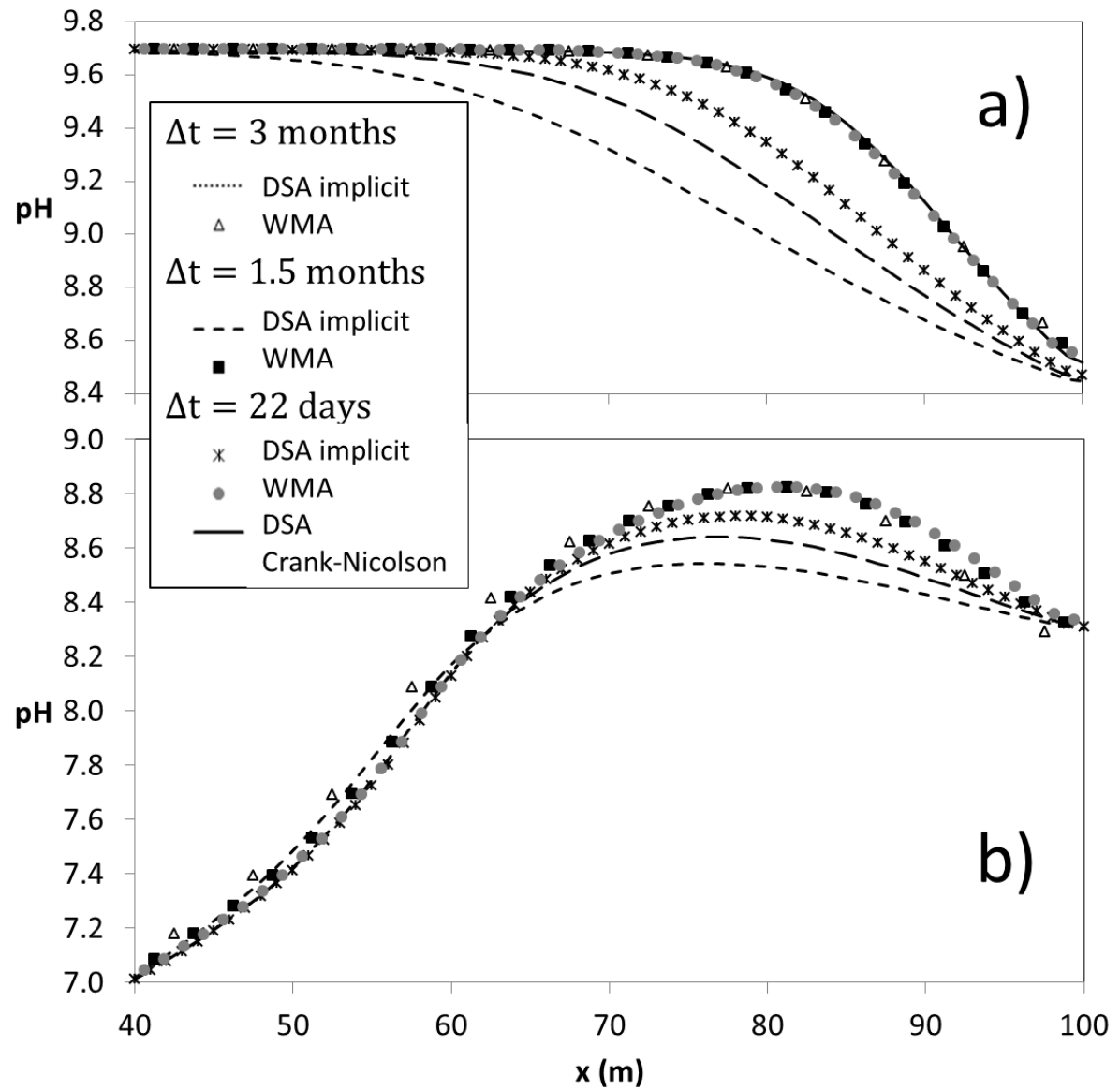
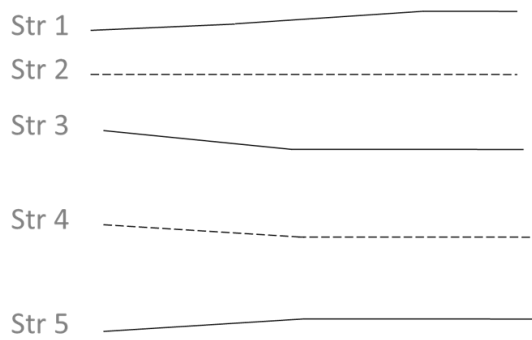
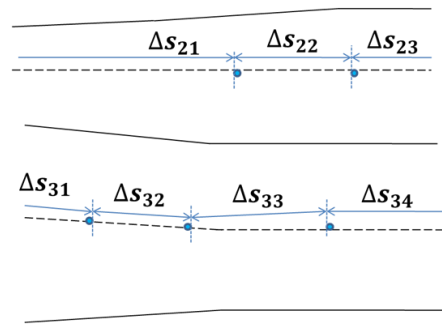


Figure 6: Spatial distribution of pH at 1 pore volume (5 years) for WMA using isochronal mesh, DSA in implicit scheme and DSA in Crank-Nicolson scheme using 3 different time steps for (a) equilibrium CAL case and (b) kinetic CAL case.

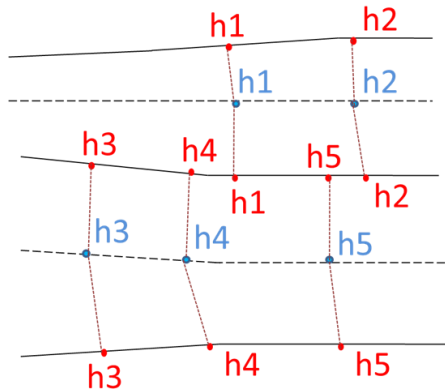
a) Compute streamlines



b) Isochronal steps: $\Delta s = v(s)\Delta t$



c) Compute cell ends



d) Compute cells

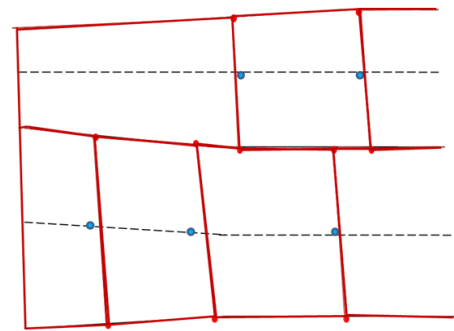


Figure A 1: Construction methodology of an isochronal grid

Table 1: Solute transport parameters of half injection domain

Transport		Chemistry			
q (m/d)	0.142857	K = 10 ⁻² (Temperature 25 °C)			
Δx (m)	0.25	Injection water 1 (kg/m ³)		Injection water 2 (kg/m ³)	
Δy (m)	0.25	$c_{Ca^{2+}}$	$9.902 \cdot 10^{-3}$	$c_{Ca^{2+}}$	0.1
ϕ	0.3	$c_{SO_4^{2-}}$	1.009902	$c_{SO_4^{2-}}$	0.1
Δt (d)	0.525	u_a	1	u_a	0
α_t (m)	0.02				
P_e	12.5				

691 Table 2: Physical and chemical parameters of the CAL case in both equilibrium and
692 kinetic reactions. Equilibrium constant is taken from the program EQ3NR (Wolery,
693 1992)

CAL case				
Transport		Chemistry		
q (m/yr)	2	Mineral	Calcite	Rate Constant (mol·m ⁻² s ⁻¹) 4.64·10 ⁻⁷
φ	0.1	Initial conc. of primary species (log mol l ⁻¹)		Initial conc. of primary species (log mol l ⁻¹)
1D problem		H ⁺	-7.978	H ⁺ -5.496
L (m)	100	HCO ₃ ⁻	-3.018	HCO ₃ ⁻ -5.421
α (m)	0.6	Ca ²⁺	-3.019	Ca ²⁺ -4.398
2D problem		Kinetic case		Initial reactive surface (m ⁻¹) 6.8·10 ⁻⁵
L _x (m)	280			
L _y (m)	100			
α _x (m)	1.2			
α _y (m)	1.2			

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