An analytical solution for bi-component reactive transport in a heterogeneous column

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ABSTRACT: The spatial variations of hydraulic parameters have a singular role in the mechanisms of water mixing in aquifers. Additionally, mixing controls reactions of non-conservative species. An analytical solution of reaction rates to describe mixing in a physically heterogeneous porous media for a system involving two aqueous species in chemical equilibrium with a mineral is presented. Heterogeneity is accounted for by including in the transport equations of the species an effective dynamics term mathematically equivalent to multiple rate mass transfer (MRMT) within a mobile and a number of immobile volumes. Chemical equilibrium is assumed in all those volumes. An example in a 1-D column is presented. A fixed-step function was selected for the inlet water. Heterogeneity in hydraulic conductivity results in tailing in the breakthrough curves corresponding to the two species, which transmits to enhanced dispersion and tailing in the reaction rate.

KEYWORDS : *Physical heterogeneity, Reactive Transport, Groundwater Modeling, Reaction Rate.*

1. Motivation

The variability of hydraulic properties in heterogeneous media produces significant features that cannot be adequately represented by models based in the advection-dispersion equation. As an alternative, approaches based on semi-phenomenological effective dynamic models have been proposed, such as multi-rate mass transfer (MRMT) [Carrera, et al., 1998], continuous time random walk (CTRW) [Margolin, et al., 2003], or fractional advection dispersion equations (FADE) [Cushman, et al., 2002]. These entire methodologies share the concept that large-scale transport can be modeled as if it took place in a homogenous media, provided an additional term is included in the equation to account for some memory about the heterogeneities the solute particles have sampled along their path. Mathematically, this involves multiplying one of the terms in the transport equation written in *Laplace* space by some memory function. The shape of this function and the term which should be multiplied give rise to different methods. Most of the works so far on effective dynamics account for either a conservative or a sorptive solute. In this work, the methodology for the case of two reactive solutes that are in instantaneous chemical equilibrium with a mineral is extended. In such a case, transport of the two species would result in local disequilibria that would result in either precipitation or dissolution. The proposed methodology is based on an extension of a recent work by *De Simoni et al.* [2005] which demonstrate that, whenever the transport of conservative specie is solvable analytically, so is a multi-component reactive transport problem. The objective of this work is to derive a general expression for the spatial and temporal distribution of the reaction (precipitation) rate in heterogeneous media in a binary problem. Then, the results obtained are illustrated by means of an example that of a 1-D column with constant input concentration selected such that reaction takes place along the full size of the column.

2. Problem statement

Two aqueous species, B_1 and B_2, are considered in instantaneous chemical equilibrium with a constant activity specie M_3, such as a mineral, $B_1 + B_2 \rightleftarrows M_3$. The mass balance equations for the mobile and immobile concentrations in a 1-D column are:

$$\phi_m \theta_m \frac{\partial c_{m_i}(x,t)}{\partial t} + \phi_{im}\theta_{im}\Gamma_i(x,t) = \phi_m\left\{-v_x\partial_x c_{m_i}(x,t) + D\partial_x^2 c_{m_i}(x,t)\right\} - r_m$$

$$\phi_{im}\frac{\partial c_{im_i}(x,t)}{\partial t} = \phi_{im}\alpha\left[c_{m_i} - c_{im_i}\right] - r_{im}$$

$$i = 1,2 \quad (1)$$

where c_{m_i} and c_{im_i} are concentrations, ϕ_m and ϕ_{im} porosities, and θ_m and θ_{im} retardation factors in the mobile and immobile domains, respectively. r is the reaction rate expressed as a sink/source term to account for precipitation/dissolution. Finally Γ is the term accounting for multiple rate mass transfer, defined as $\Gamma(x,t) = \int_0^\infty f(\alpha)\frac{\partial c_{im}(x,\alpha,t)}{\partial t}d\alpha = \int_0^\infty \frac{\partial c_m(x,t')}{\partial t'}g(t-t')dt'$ by *Haggerty and Gorelick* [1998]. A MRMT model is fully defined by providing the distribution of $f(\alpha)$, where α [T^{-1}] is the corresponding mass transfer coefficient and f can be seen as a probability density function describing the percentage of sites that transfer mass at a given rate. The memory function, $g(t)$ is given by $g(t) = \int_0^\infty \alpha f(\alpha)e^{-\alpha t}d\alpha$. In order to close the system in terms of number of equations, two mass action law equations, corresponding to the mobile and the immobile concentrations, respectively are needed.

$$\log c_{m_1} + \log c_{m_2} = \log K \text{ and } \log c_{im_1} + \log c_{im_2} = \log K \tag{2}$$

K is the equilibrium constant, related to solubility of the solid phase, and which is a function of the temperature, pressure and chemical activity. In this work, it follow that all activity coefficients equal to 1. This is a valid simplification whenever the characteristic advective time is much larger than that corresponding to reactions (i.e., large *Damkhöler* number).

3. Solution

3.1. Solution for mobile concentration

Following the methodology of *De Simoni et al.* [2005], the geochemical system can be fully defined in terms of a single conservative component for the each domain,

$$u_m = c_{m_1} - c_{m_2} \text{ and } u_{im} = c_{im_1} - c_{im_2}. \tag{3}$$

It is then possible to write a single transport equation of the mobile conservative component by substracting the two equations for the mobile species in (1). A similar operation can be done with the equations corresponding to the immobile species. Denoting the length of the column by L, and velocity of the water by v_x, with $t_{adv} = \frac{L}{v_x}, P_e = \frac{v_x L}{D}, \varphi = \frac{\phi_{im}}{\phi_m}, \beta_{tot} = \frac{\theta_{im}}{\theta_m}, T = \frac{t}{\theta_m t_{adv}}, X = \frac{x}{L}, \omega = \theta_m t_{adv}\alpha, U = \frac{u_m}{u_m^0}, Z = \frac{u_{im}}{u_m^0}$, the final equations are :

$$\frac{\partial U}{\partial T} + \varphi\beta_{tot}\int_0^\infty f(\omega)\frac{\partial Z}{\partial T}d\omega = \frac{1}{P_e}\frac{\partial^2 U}{\partial X^2} - \frac{\partial U}{\partial X} \text{ and } \frac{\partial Z}{\partial T} = \omega(U - Z) \tag{4}$$

The proposed methodology is applied to a problem where an analytical solution to the conservative solute transport problem exists. It follow that the water in the column is initially in equilibrium with the mineral that forms the column. At a given time (t=0) a solution also equilibrated with the mineral but with a different chemical composition that the initial water is injected in the inlet. Flow is steady-state and uniform. The initial and boundary conditions represented by the step-function input are described mathematically as follows:

$$u_m\left(x,t=0\right)=0, x\geq 0; u_m\left(x=0,t\right)=u_m^0, t\geq 0; u_m\left(x=\infty,t\right)=0, t\geq 0 \tag{5}$$

The solution of (4) is obtained in *Laplace* space and numerically back-transformed.

$$\overline{U}\left(X,S\right)=\frac{1}{S}\exp\left[\frac{P_e}{2}X\right]\exp\left\{-\frac{P_e}{2}X\sqrt{1+\frac{4}{P_e}S\left[1+\varphi\beta_{tot}\overline{g}\left(S\right)\right]}\right\} \tag{6}$$

3.2. Reaction rate

Recalling (1) in dimensionless terms, and combining with (4), the total reaction rate ($r_{tot}=r_m+r_{im}$) for the step-function injection is calculated with the following expressions:

$$\frac{t_{adv}}{\phi_m u_m^0}r_m^{21}=R_m^{21}=\varphi\beta_{tot}\left[\frac{\partial C_2}{\partial U}\left(\frac{\partial U}{\partial T}*g\right)-\left(\frac{\partial C_2}{\partial U}\frac{\partial U}{\partial T}\right)*g-R_{im}^{21}*g+R_{im}^{21}\right]+\frac{1}{P_e}\frac{\partial^2 C_2}{\partial U^2}\left(\frac{\partial U}{\partial X}\right)^2$$

$$\frac{\theta_m t_{adv}}{\phi_{im}u_m^0}r_{im}^{21}=R_{im}^{21}=\left[\omega\left(C_2-Y_2\right)-\frac{\partial Y_2}{\partial T}\right] \tag{7}$$

4. Discussion

The main results are summarized in Fig. 1 for the case where $f\left(\omega\right)$ is a delta function, i.e. where ω is a single value and not a distribution. To illustrate the influence of heterogeneity in the reaction rate, some values of the dimensionless parameters have been chosen. First of all, the *Damkholer* number ω, was analyzed in three sceneries: (i) In equilibrium conditions: $\omega\gg 1.0$, (ii) when the rate of mass transfer is the same of the rate of advection, $\omega=1.0$ and (iii) when mass transfer is rate limited, $\omega\ll 1.0$. In the second term, the Peclet number was studied in a highly dispersive system ($P_e=1.0$). Finally, the total capacity factor $\varphi\beta_{tot}$ was defined. The ratio among porosities has a constant value of $\frac{5}{7}$ since Sanchez-Vila and Carrera [2004] shown that this value has an important role in the determination of temporal moments of breakthrough curves with matrix diffusion presence. The ratio between retardation factors was analyzed for a larger retardation in the immobile domain ($\beta_{tot}=5.0$). The temporal distribution of the dimensionless reaction rate was analyzed in a fixed location (in the middle of the column, $x=0.5L$) for the proposed cases. In the Fig. 1, parts *a, b* and *c* an equilibrium system ($\omega\gg 1.0$) is shown. In the parts *d, e* and *f*, a system with $\omega=1.0$ is presented, and in the parts *g, h* and *i*, the rate limited system ($\omega\ll 1.0$) is stated.
In the first row (*a, d* and *g*) of the chart, the dimensionless mobile (U) and immobile (Z) temporal distribution of concentration are represented. In the second row (*b, e* and *h*), the dimensionless spatial (gradient) and temporal derivates are presented. Finally, in the third row (*c, f* and *i*), dimensionless reaction rate and its components are illustrated. It has two components: immobile and mobile. Mobile reaction rate is subdivided in two parts:

heterogeneous $\left\{ \varphi \beta_{tot} \left[\frac{\partial C_2}{\partial U} \left(\frac{\partial U}{\partial T} * g \right) - \left(\frac{\partial C_2}{\partial U} \frac{\partial U}{\partial T} \right) * g - R_{im}^{'21} * g + R_{im}^{'21} \right] \right\}$ and homogeneous $\left\{ \frac{1}{P_e} \frac{\partial^2 C_2}{\partial U^2} \left(\frac{\partial U}{\partial X} \right)^2 \right\}$. The

dimensionless homogeneous reaction rate is equivalent to the founded expression by *De Simoni et al.* [2005] for homogeneous porous media. It can be observed that accounting for heterogeneity in a mixing-driven dissolution/precipitation reaction has important effects. The main one is that when the system is dominated by mass transfer rates; reaction rate is very different to that of a homogeneous system. If the mass transfer rate is small compared to advective rate, reaction rate still precipitating/diluting before the system reach the equilibrium (Fig. 1.*f,i*). This finding explains the long tailing in breakthrough curves. The system behaves quite similar to homogeneous one when the system is in equilibrium (Fig. 1.*c*) (when the reaction rates are large). This particular set-up can be easily developed in laboratory experiments to check the results in the near future research, allowing for benchmarking.
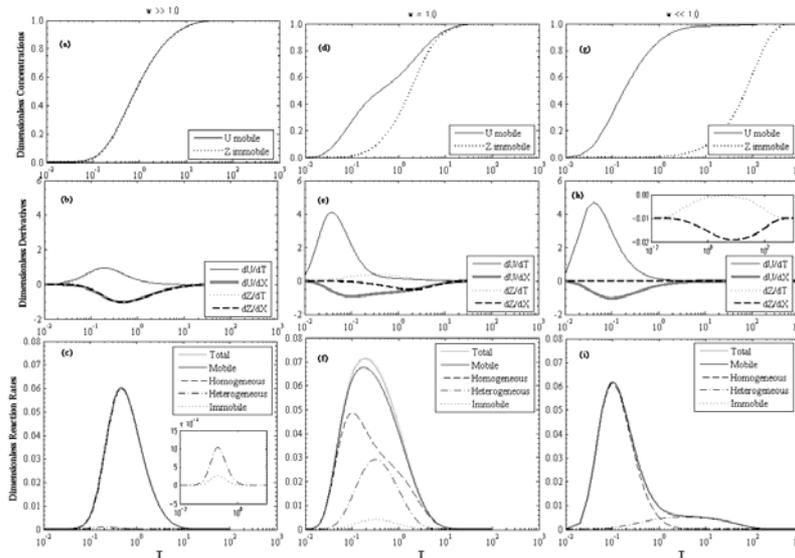

Fig. 1. Dimensionless reaction rate in $X = 0.5$ with a system setup of $P_e = 1.0$, $\beta_{tot} = 5.0$ and $\varphi = \frac{5}{7}$

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