

## 1-D Reactive Transport Modeling in Heterogeneous Porous Media

Ouacil Saouli\*, Mossaab Bencheikh-Lehocine, Abdessalam Hassen Meniai

Constantine University, Laboratoire de l'Ingénierie des Procédés d'Environnement,  
Route ain elbey Constantine. saouli\_ouacil2000@yahoo.fr

The quantitative prediction of solute transport presents a great interest in many fields where numerical modelling of solute transport through heterogeneous porous media may be regarded as an efficient tool. In the present study, numerical experiments of a 1D model were performed by means of a method based on the Finite Volume (FV) scheme using operator splitting method to solve transport and chemistry equations, separately at each time step.

The reliability of the method is assessed by comparing the obtained results with the one-dimensional analytical solution and experimental data reported in the literature and an excellent agreement between the different sets of values was obtained.

### 1. Introduction

The simulation of reactive solute transport in heterogeneous porous media is of importance in various areas of research and industry. Modeling reactive transport needs the resolution of both transport and the chemistry equations. This work deals with numerical method for solving the coupled problem. The transport of reactive solute in porous media is described by partial differential equation of convection-diffusion type and is solved using Finite Volume (FV) method based on operator splitting scheme, where each part are solved separately (Carrayrou et al., 2004) with different time step discretizations for the convective and dispersive parts. Specifically, the dispersive term should be treated implicitly, and the convective term is better handled explicitly. The splitting scheme works by tacking several small time steps of convection, controlled by a CFL condition, within a large time step of dispersion. The scheme has been shown to be unconditionally stable, and has a good behavior in convection-dominated situations (Amir and Kern, 2010). In the literature, two types of methods have been described to simulate the coupled problem: the Sequential Approaches (SA) (Yeh and Tripathi, 1991) which decomposes the full system into sub problems of transport and reaction ones and the Global Approach (GA) (Krautle and Knaber, 2007) which solves simultaneously the whole system. In the present work a sequential method is adopted and the fixed point is used for solving the nonlinear system at each time step.

### 2. Reactive Transport Equation

In this section, the transport of reactive solute in a single phase flow through a heterogeneous porous media is considered. The solute may react in the phase and with

the porous matrix. The mathematical model describing the transport in 1D is given by the following convection-dispersion equation (Bear and Verruijt, 1982):

$$\omega \frac{\partial c}{\partial t} + \frac{\partial}{\partial x} \left( -D \frac{\partial c}{\partial x} + uc \right) + (1-\omega) \frac{\partial F}{\partial t} = 0, \quad 0 < x < L, \quad 0 < t < T \quad (1)$$

where  $c$  is the solute concentration,  $\omega$  the porosity,  $D$  the longitudinal dispersion coefficient,  $u$  the velocity and  $F$  the solute concentration on the solid phase.

It should be noted that a local fluid-solid equilibrium is assumed, justifying the used present form of Equation 1.

The initial condition is  $c(x, 0) = 0$  and the boundary conditions are a Dirichlet condition  $c(0, t) = c_i$  at the inlet ( $x=0$ ) and zero dispersive flux  $\partial c / \partial x = 0$  at the outlet ( $x=L$ ).

For the discretization step, a cell-centered finite-volume scheme is used (Eymard et al., 2000) where the domain  $[0, L]$  is divided into  $N$  intervals  $[x_{i-1/2}, x_{i+1/2}]$  of length  $h_i$ ,

where  $x_{1/2} = 0$ ,  $x_{N+1/2} = L$ ,  $x_i$  the center of element  $i$  and  $c_i$  the approximate solution in the element  $i$ . The flux  $\varphi(x, t) = -D \partial c / \partial x + uc$  is made of a diffusive flux  $\varphi_d = -D \partial c / \partial x$  and a convective flux  $\varphi_c = uc$ .

Integrating Equation 1 over a cell  $[x_{i-1/2}, x_{i+1/2}]$ , leads to the following:

$$\omega_i h_i \frac{dc_i}{dt} + (1 - \omega_i) h_i \frac{dF_i}{dt} + \varphi_{d,i+1/2} + \varphi_{c,i+1/2} - \varphi_{d,i-1/2} - \varphi_{c,i-1/2} = 0 \quad (2)$$

The dispersive and the convective fluxes need values for the dispersion coefficient and velocity and one can write:  $\varphi_{d,i+1/2} = -D_{i+1/2} (c_{i+1} - c_i) / h_{i+1/2}$ ,

$\varphi_{c,i+1/2} = u_{i+1/2} c_i$  with  $h_{i+1/2} = (h_i + h_{i+1}) / 2$ ,  $D_{i+1/2} = 2D_i D_{i+1} / (D_i + D_{i+1})$  and  $u_{i+1/2} = 2u_i u_{i+1} / (u_i + u_{i+1})$  for heterogeneous porous media.

$\Delta t$  is the time step used to discretize the time interval  $[0, T]$  and  $c_i^n$  the value of  $c_i$  ( $n\Delta t$ ).

To solve Equation 2 a splitting technique (Mazzia et al., 2000) was adopted that enables the use of different spatial and temporal approximations for different transport processes (convection and dispersion) and hence avoiding problems associated with numerical dispersion. The dispersive term should be treated implicitly, and the convective term is better handled explicitly.

### 2.1. Convection step

The dispersion time step  $[t_n, t_{n+1}]$  is divided into  $M$  time steps of convection

$\Delta t_c = [t_{n,m}, t_{n,m+1}]$ , where  $m=0, \dots, M-1$ .  $c_i^{n,m}$  is defined as an approximation of  $c$  at time  $t^{n,m}$ . Equation 1 simplifies as follows:  $\omega \frac{\partial c}{\partial t} + \frac{\partial}{\partial x}(uc) + (1-\omega) \frac{\partial F}{\partial t} = 0$

Integrating this equation over an element  $i$  using Euler's explicit scheme gives:

$$c_i^{n,m} = c_i^{n,0} + \frac{u_{i+1/2} \Delta t_c}{\omega_i h_i} \sum_{m=0}^{M-1} c_{i-1}^{n,m} - \frac{u_{i-1/2} \Delta t_c}{\omega_i h_i} \sum_{m=0}^{M-1} c_i^{n,m} - \frac{1-\omega_i}{\omega_i} (F_i^{n+1} - F_i^n)$$

This step has a Courant-Friedrichs-Lewy (CFL) restriction that takes the form  $CFL = u \Delta t_c / (\omega \max h_i) \leq 1$ . The splitting scheme works by taking several small time steps of convection, controlled by a CFL condition.

### 2.1 Dispersion step

When  $c_i^{n,M}$  is obtained in convection step after  $M$  time steps  $c_i^{n+1}$  is calculated and

$$\text{Equation 1 becomes: } \omega \frac{\partial c}{\partial t} + \frac{\partial}{\partial x} \left( -D \frac{\partial c}{\partial x} \right) = 0$$

The integration of this equation over an element  $i$  using implicit scheme gives:

$$\left( -\frac{D_{i-1/2}}{h_{i-1/2}} \Delta t \right) c_{i-1}^{n+1} + \left( \omega_i h_i + \frac{D_{i+1/2}}{h_{i+1/2}} \Delta t + \frac{D_{i-1/2}}{h_{i-1/2}} \Delta t \right) c_i^{n+1} - \left( \frac{D_{i+1/2}}{h_{i+1/2}} \Delta t \right) c_{i+1}^{n+1} = \omega_i h_i c_i^n$$

## 3. Solution of the Coupled Problem

The final discrete coupled system can be written as:

$$c^{n+1} = \Psi_T(c^n, F^n, F^{n+1}) \text{ for transport and } F^{n+1} = \Psi_C(c^{n+1}) \text{ for chemistry. This}$$

non nonlinear system can be solved by various methods where the classical way is based on a fixed-point method (Carrayrou et al., 2004). Recently, more global approaches have been used (Krautle and Knaber, 2007). In this work, results are presented for a fixed-point method.

Assuming that  $c^n, F^n$  are known (initials conditions),  $F^{n+1,0} = F^n$  is initialized, and an iteration corresponding to the step number  $k$  is as follows:

1. Compute  $c^{n+1,k+1} = \Psi_T(c^n, F^n, F^{n+1,k})$
2. Compute  $F^{n+1,k+1} = \Psi_C(c^{n+1,k+1})$
3. Set  $k=k+1$  and go back to 1 unless the norm  $\|F^{n+1,k+1} - F^{n+1,k}\|$  is small enough and the iterative is halted.

To assess the obtained results, a comparison with the analytical solution and experimental data reported in Katia (2005) for inert and reactive transport respectively, was performed.

## 4. Numerical Results

### 4.1 Transport of an inert solute

In this section, inert transport is considered and the concentration profile is compared with the corresponding analytical concentration given by (Ogata and Banks, 1961) as follows:

$$\frac{c(x, t)}{c_i} = 0.5 \left[ \operatorname{erfc} \left( \frac{x - ut / \omega}{2 D t / \omega} \right) + \exp \left( \frac{ux}{D} \right) \operatorname{erfc} \left( \frac{x + ut / \omega}{2 D t / \omega} \right) \right] \quad (3)$$

where  $\operatorname{erfc}$  is the complementary error function.

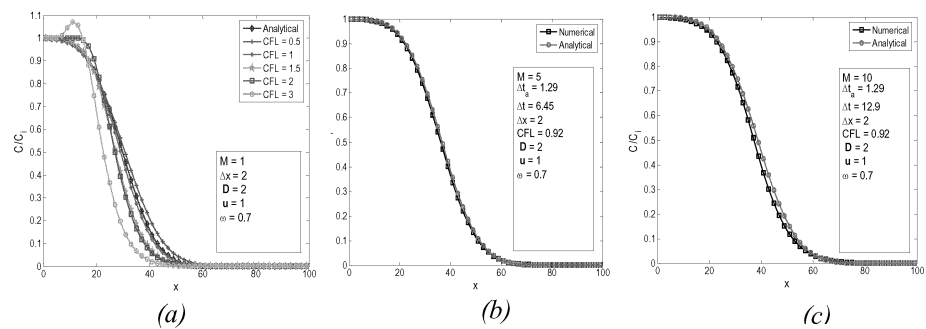


Figure 1: Comparison between analytical and numerical solutions.

Figure 1a shows that for CFL values close to unity, the numerical and analytical solutions are nearly confounded. Also to investigate the influence of the splitting factor  $M$ , values of 5 and 10 were tested and the results of Figures 1b & c clearly show that this parameter has not a great influence, the small deviations between the two curves may be just due to splitting errors.

### 4.2 Reactive transport

In the experimental work of Katia (2005), the adsorption of copper ions onto glass balls was considered. For this purpose, a column in Altuglas of 5cm in diameter and 100 cm in height is filled with these balls, leading to a mean porosity value of 0.31. A solution of copper is injected and the ions concentration was measured by spectrophotometry. The results indicated that the adsorption isotherm of the copper onto glass balls was best represented by Freundlich equation ( $F = k_F c^n$ ), where the chemical reaction constant  $k_F$  is equal to 5.7 and the exponent  $n$  which describes the adsorption intensity takes the value of 0.487.

The study of the adsorption in dynamic mode was made according to the flowrate, for a single installed capacity (9 meq) and a single concentration ( $9 \cdot 10^{-3} \text{M}$ ).

Figure 2 shows the copper concentration at the exit of the column, measured experimentally whereas Figures 2b and 2c present results obtained numerically, for various BE values (volume of solution got back in mL/capacity installed in meq). It can clearly be seen that the agreement between the experimental values and the results obtained from the model is reasonable. We can also see that when we act on the dispersion by reducing, the agreement is greatly improved and this confirms the reliability of the model.

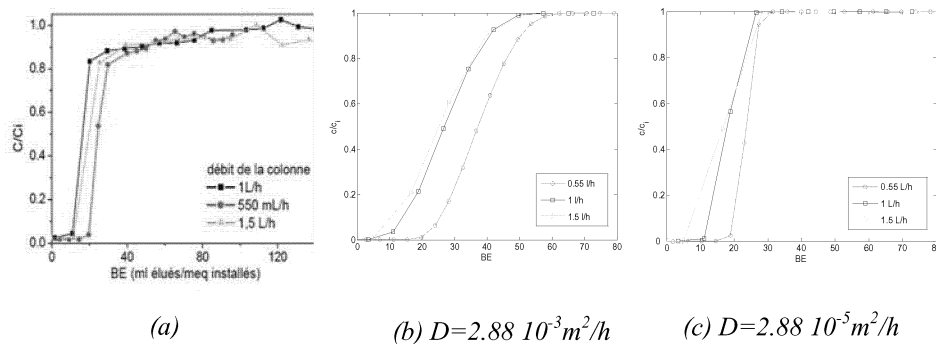


Figure 2: Breakthrough curve (function of volume) of  $\text{Cu}^{2+}$  for different rates.

Figure 3, shows the breakthrough curves, for both cases with and without adsorption. These curves enable the calculation of the breakthrough time which is a relevant parameter corresponding to the necessary time for the medium saturation ( $0.95 \times c/c_i$ ). From the curve of Figure 3b, it can be seen that a low adsorption is shown, since there is no great difference between both cases (with and without adsorption). This confirms the results of Katia (2005) where in fact the glass had low copper retention (retardation factor between 1.26 and 1.37).

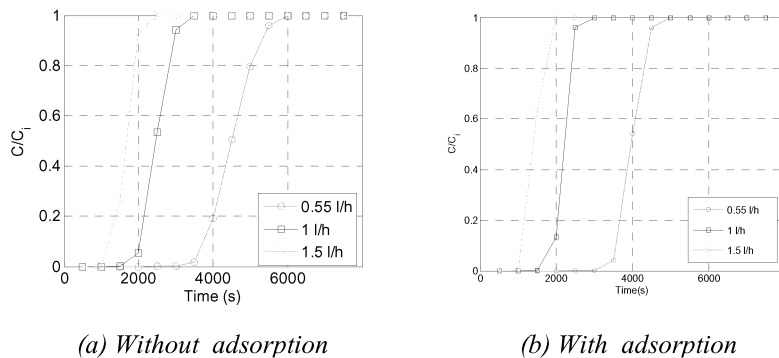


Figure 3: Breakthrough curve of  $\text{Cu}^{2+}$  for different rates ( $D=2.88 \cdot 10^{-5} \text{m}^2/\text{h}$ ).

## 5. Conclusions

In this study the reactive transport of solute in porous media was performed numerically. For this purpose, a calculation code was developed under Matlab environment to solve the corresponding model equations. The calculations were performed on 1D case and the results were compared to the reported experimental data, in order to assess the model. This latter has shown great capabilities to handle this complex physical problem. However it needs refinements in order to take into account heterogeneity and other factors like physico-chemical interactions.

Finally, it can be recommended to extend the transport model to 3D case and to introduce dissolution-precipitation, kinetic reactions.

## References

- Amir L. and Kern M., 2010, A global method for coupling transport with chemistry in heterogeneous porous media, *Computational Geoscience*, 14, 465-481.
- Bear J. and Verruijt A., 1982, *Modeling Groundwater Flow and Pollution*, D. Reidel, the Netherlands.
- Carrayrou J., Mosé R. and Behra P., 2004, Operator splitting procedures for reactive transport and comparison of mass balance errors, *Journal of Contaminant Hydrology*, 68, 239-268.
- Eymard R., Gallouët T. and Herbin R., 2000, *Finite Volume Methods*, vol. 7: *Handbook of Numerical Analysis*, Eds. Ciarlet P.G. and Lions J.L., North-Holland, Amsterdam, the Netherlands, 713-1020.
- Katia B., 2005, *Reactive transport modeling in heterogeneous porous media. Application to nonlinear adsorption process*, PhD Thesis, University of Rennes 1 (in French).
- Krautle S. and Knabner P., 2007, A reduction scheme for coupled multicomponent transport-reaction problems in porous media: Generalization to problems with heterogeneous equilibrium reactions, *Water Resources Research*, 43, 3115-3124.
- Mazzia A., Bergamaschi L. and Putti M., 2000, A time-splitting technique for the advection-dispersion equation in ground-water, *Journal of Computational Physics*, 157, 181-198.
- Ogata A. and Banks R., 1961, A solution of differential equation of longitudinal dispersion in porous media, *United States Geological Survey*, 21, 1-7.
- Yeh G. T. and Tripathi V. S., 1991, A model for simulating transport of reactive multispecies components: model development and demonstration, *Water Resources Research*, 27, 3075-3094.
- Yeh G. T. and Tripathi V. S., 1991, A model for simulating transport of reactive multispecies components: model development and demonstration, *Water Resources Research*, 27, 3075-3094.