

Three-dimensional Modelling of Reactive Solutes Transport in Porous Media

Ouacil Saouli^a, Mosaab Bencheikh Lehocine^b

^aUnité de recherche URSMA, Constantine University, Algeria

^bLaboratoire LIPE, Constantine University 3, Algeria
 saouli_ouacil2000@yahoo.fr

The simulation of solutes transport in porous media is of importance in many disciplines including CO₂ sequestration simulations, the evaluation of underground water quality, nuclear waste simulations, and petroleum reservoir engineering. We present a numerical method for coupling 3D transport with equilibrium reactions. Our method is based on a fixed-point algorithm that enables us to couple different transport and chemistry modules. A splitting technique is used for transport that enables us to use different spatial and temporal approximations for different transport processes. The Newton's method is used to solve the chemical system. The reliability of the method is assessed by comparing the obtained results in a column with the one-dimensional problem.

1. Introduction

The simulation of reactive solutes transport in porous media is of importance in different domains: in CO₂ sequestration simulations, in petroleum reservoirs, and in groundwater flow and pollution.

This paper is a follow up in three-dimensional of the one-dimensional modeling described in (Saouli et al, 2011). The coupled transport and chemistry problem is solved in a three-dimensional column having uniform hydraulic conductivity under LifeV library (C++ finite element code). The flow is described by the Darcy law, the transport of solutes is described by the convection-dispersion equation, and whereas solutes chemistry involves the solution of nonlinear algebraic equations (local equilibrium is assumed). We have used operator splitting method (Samper et al, 2009), where transport and chemistry are solved separately at each time step.

The outline of this paper is as follows. In Section 2, we describe the discretization of the flow equations using mixed finite element method. In Section 3, we use splitting technique that enables us to use different time approximation for convection and dispersion. Convection is approximated by finite volume method while dispersion is approximated by mixed finite element method. Section 4, presents the chemistry model in which we consider equilibrium reactions and in Section 5 the full transport-chemistry problem is modeled and solved with fixed point method. Finally, numerical results are shown in section 6.

2. Flow model

For incompressible Darcy flow problem with no sink and source terms, the equations are given by

$$\text{div } \mathbf{u} = 0$$

$$\mathbf{u} = -\mathbf{K}\nabla P \quad (1)$$

where \mathbf{u} is the Darcy velocity, P is the pressure or the hydraulic head, and \mathbf{K} is the hydraulic conductivity. We have used mixed finite element method. It leads to the linear system

$$\begin{bmatrix} B & 0 \\ A & B^T \end{bmatrix} \begin{bmatrix} \mathbf{u} \\ P \end{bmatrix} = \begin{bmatrix} 0 \\ f \end{bmatrix} \quad (2)$$

3. Transport model

The advection-dispersion equation is used to model transport problem

$$\frac{\partial c}{\partial t} + \text{div}(-\mathbf{D}\nabla c + \mathbf{u}c) = r \quad (3)$$

where c is the concentration of solute, \mathbf{D} is dispersion tensor, and r are sources/sinks term. The dispersion tensor is given by

$$\mathbf{D}_{ij} = \alpha_T u \delta_{ij} + \frac{(\alpha_L - \alpha_T)(u_i u_j)}{u} + D_m \tau \delta_{ij} \quad (4)$$

where D_m is molecular diffusion coefficient, α_L and α_T are longitudinal and transversal dispersivities respectively, τ is the tortuosity of the porous medium, and δ is the delta kroneker. In fact, molecular diffusion can be neglected in comparison with mechanical dispersion.

To solve Eq(3), we have used a splitting technique.

3.1 Convection step

We define $c^{n,m}$ an approximation of c at time $t^{n,m}$. Eq(3) will come

$$\frac{\partial c}{\partial t} + \text{div}(\mathbf{u}c) = 0 \quad (5)$$

The convection step can be written as

$$|h| \frac{c^{n,m+1} - c^{n,m}}{\Delta t_c} + \sum c_F^{n,m} \xi_{h,F} u_F = 0 \quad (6)$$

where Δt_c is convection time step. Δt_c must satisfy a CFL condition that in 1D takes the form

$$CFL = u \cdot \frac{\Delta t_c}{\Delta x} \leq 1$$

3.2 Dispersion step

Once $c^{n,M}$ is obtained from the convection step after M time substeps. We introduce $\varphi = -\mathbf{D}\nabla c$ then the dispersion step is to find c and φ such that

$$|h| \frac{c^{n+1} - c^{n,M}}{\Delta t} + \sum \varphi_F^{n+1} \xi_{h,F} = 0 \quad (7)$$

Given a righthandside r a transport step from c^n to c^{n+1} is denoted in compact form as

$$c^{n+1} = \phi_T(c^n, r)$$

4. Chemical equations

In this study, we assume a local chemical equilibrium with both aqueous and sorption reactions at every point. We use the Morel formalism, where each chemical equation describes how a set of secondary species is formed from a set of primary species (Morel and Hening, 1993). The general Morel's table is

Table 1: Morel's table for chemical system

	c	s	K
x	A ₁	0	K _x
y	A ₃	A ₄	K _y
Total	T	W	

where c is the vector of concentrations of the N_c primary aqueous species, s is the vector of concentrations of the N_s sorbed species, A_1 , A_3 and A_4 are stoichiometric matrices, K_x , K_y are the equilibrium constants, x is the vector of concentrations of the N_x secondary aqueous species, y is the vector of concentrations of

the N_y secondary sorbed species, T is the vector of total concentrations of the aqueous species c_i and W is the vector of the total concentrations of the sorbed species s_i .

Each chemical reaction satisfies a mass action law (for each secondary aqueous and sorbed specie):

$$\begin{aligned} \log(x_i) &= \sum_{j=1}^{N_c} A_{1ij} \log(c_j) + \log(K_{xi}), i = 1, \dots, N_x \\ \log(y_i) &= \sum_{j=1}^{N_c} A_{3ij} \log(c_j) + \sum_{j=1}^{N_s} A_{4ij} \log(s_j) + \log(K_{yi}), i = 1, \dots, N_y \end{aligned} \quad (8)$$

Moreover each component (primary specie) satisfies a conservation law:

$$\begin{aligned} T_i &= c_i + \sum_{j=1}^{N_x} A_{1ij}^T x_j + \sum_{j=1}^{N_y} A_{3ij}^T y_j, i = 1, \dots, N_c \\ W_i &= s_i + \sum_{j=1}^{N_y} A_{4ij}^T y_j, i = 1, \dots, N_s \end{aligned} \quad (9)$$

For a given T and W , Eq(8) and Eq(9) form a nonlinear system whose unknowns are the vectors c , s , x , and y . After solving this system, we calculate

$$C = c + A_1^T x, \quad F = A_3^T y \quad (10)$$

We will use the compact notation $F = \phi_C(T)$.

5. Coupled transport and chemistry

To obtain the coupled model between transport and chemistry, we write Eq(3) for each specie. We assume that the transport operator is the same for all species. Standard manipulations lead to the coupled system

$$\begin{aligned} \frac{\partial c}{\partial t} + \frac{\partial F}{\partial t} + L(c) &= 0, \\ T &= C + F \\ F &= \phi_C(T). \end{aligned} \quad (11)$$

where ϕ_C is the solution operator for the chemical problem defined in the previous section. After discretization in time and space, one obtains the final discrete coupled system, expressed in terms of the solution operator ϕ_T for transport introduced in section 3.

$$\begin{aligned} C^{n+1} &= \phi_T(C^n, F^{n+1}, F^n) \\ T^{n+1} &= C^{n+1} + F^{n+1} \\ F^{n+1} &= \phi_C(T^{n+1}) \end{aligned} \quad (12)$$

This nonlinear can be solved by various methods. The classical way is based on a fixed-point method (Amaziane et al, 2008). Suppose that C^n , F^n and T^n are given. We start by initializing $F^{n+1,0} = F^n$, and we iterate with the step number k . The algorithm involves the following steps:

1. Compute $C^{n+1,k+1} = \phi_T(C^n, F^{n+1,k}, F^n)$ (using the transport solver, once for each aqueous species),
2. Compute $T^{n+1,k+1} = C^{n+1,k+1} + F^{n+1,k}$,
3. Compute $F^{n+1,k+1} = \phi_C(T^{n+1,k+1})$ (using the chemical solver, once for each degree of freedom of the mesh),
4. 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 we stop the iterations.

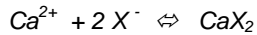
6. Numerical results

We represent here a 3D calculation design. The example of transport in presence of cation exchangers is adopted. This example is used in the documentation of PHREEQC (Parkhurst and Appelo, 1999) as Example 11. The flow and transport parameters used are presented in Table 2.

Table 2: Physical parameters

Length of column	0.5 m
Diameter of column	0.1 m
Hydraulic conductivity	$1.16 \cdot 10^{-7}$ m/s
Pressure difference	0.5 m
α_L	0.05 m
α_T	0.005 m

The chemical reactions for this example are:



where X^- is the exchanger. The initial and injected concentrations are :

Table 3: Initial and injected concentrations [mol/l].

Component	C_{initial}	C_{in}
Ca^{2+}	0	$6.0 \cdot 10^{-4}$
Cl^-	0	$1.2 \cdot 10^{-3}$
K^+	$2.0 \cdot 10^{-4}$	0
Na^+	$1.0 \cdot 10^{-3}$	0

The actual chemical system is given by

Table 4: Morel's table for the actual chemical system

	Ca^{2+}	Na^+	Cl^-	K^+	X^-	K
NaX	0	1	0	0	1	1
KX	0	0	0	1	1	5.01
CaX_2	1	0	0	0	2	$2.86 \cdot 10^3$
Total	T_1	T_2	T_3	T_4		

Figure 1 shows the pressure and the velocity curves. It can easily be seen that a linear distribution of pressure is obtained, when imposing the pressure difference of 0.5 m. The velocity obtained here is $0.01 \text{ m/d} = 1.16 \cdot 10^{-7} \text{ m/s}$ which is in agreement with Darcy's law.

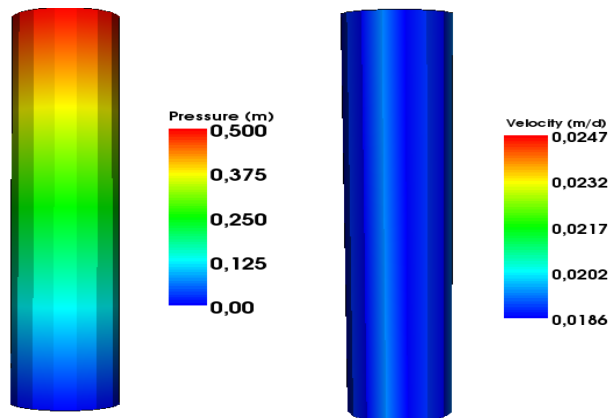


Figure 1: Pressure and velocity distributions.

In order to follow the solutes concentrations along the column, Figure 2 shows the calculated concentrations of the four species.

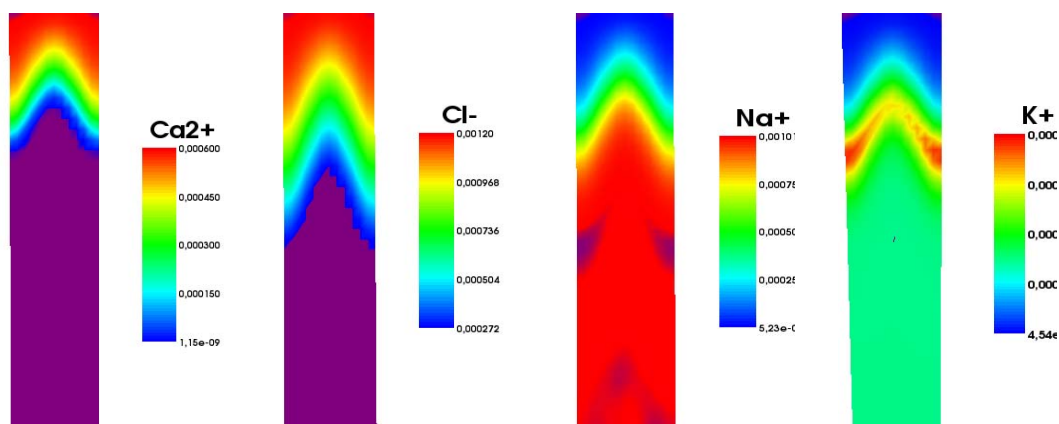


Figure 2: Concentration profiles of Ca^{2+} , Cl^- , Na^+ , and K^+ at time $t = 25$ d.

These concentrations can be represented in better form (see Figure 3).

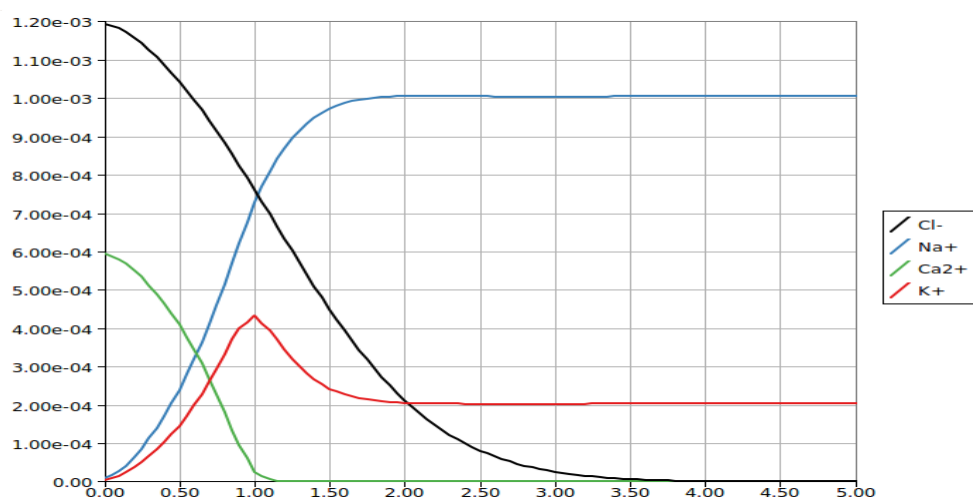


Figure 3: Concentrations of solutes vs height (dm) at radius $r = 0$ and time $t=25$ d.

The sorbed potassium and sodium ions are successively replaced by calcium. Because potassium exchanges more strongly than sodium (as indicated by a larger value of $\log K$ in the exchange reaction), sodium is released first, followed by potassium. Finally, when the entire concentration has been released, the concentration of calcium increases to its steady-state value, the potassium is displaced from the exchanger, and the concentration in solution increases to balance the Cl^- concentration (Amir and Kern, 2010). These results are in good agreement with those obtained by (Xu et al, 1999) and computed by PhreeqC software.

7. Conclusions

In this paper, the reactive solutes transport in a porous column with constant flow velocity field is examined using computational simulations. For this purpose, a calculation code was developed under LifeV environment to solve the corresponding model equations. It enables the determination of various relevant fields such as pressure, velocity and solutes concentrations and hence the dispersion tensor. The calculations were performed on 3D case and the results were compared to those obtained by PhreeqC software.

Finally, it can be recommended to take into account precipitation-dissolution and kinetic phenomena in the chemical model.

References

- Amaziane B., Ossmani M.E., Serres C., 2008, Numerical modeling of the flow and transport of radionuclides in heterogeneous porous media, *Compu. Geosci.*, 12, 437-449.
- Amir L., Kern M., 2010, A global method for coupled transport with chemistry in heterogeneous porous media, *Comput. Geosci.*, 14, 465-481.
- Morel F.M.M., Hering J.G., 1993, *Principles and applications of aquatic chemistry*, Wiley, New York.
- Parkhurst D.L., Appelo C., 1999, *User's guide to PHREEQC- a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*, Tech. Rep., 99-4259.
- Saouli O., Bencheikh Lehocine M., 2011, 1-D reactive transport modeling in heterogeneous porous media, *Chem. Eng. Trans.*, Vol. 24, 415-420.
- Samper J., Xu T., Yang C., 2009, A sequential partly iterative approach for multicomponent reactive transport with CORE2D, *Comput. Geosci.*, Vol. 13, 301-316.
- Xu T., Samper J., Ayora C., Manzano M., Custodio E., 1999, Modeling of non-isothermal multicomponent reactive transport in field scale porous media flow system, *J. Hydrol.*, 214, 144-164.