

MACRO-PORE MODEL FOR CESIUM TRANSPORT IN SANDY-CLAYED POROUS MEDIA

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ABSTRACT

This paper discusses the type of macro-scale, or Darcy-scale, model suitable for modelling Cesium transport in sandy-clayed soil. While the motivation for the study comes from the context of nuclear risk control, this study may be viewed in the more general framework of surface contaminations with reactive solute transport. The adopted strategy consists in looking at an idealized soil composed of Fontainebleau sand with a few percents of fine particles of Illite du Puy. This leads to a simpler system in terms of geochemical reactions compared to natural systems which present much more chemical components in the solid phases and in water. Two averaged models have been tested. The first model corresponds to a two-equation model involving mainly dispersion in the macro-porosity, and an exchange term with the balance equation for the clay macro-scale domain, which is estimated from the application of a volume averaging upscaling technique. The second model corresponds to a mixed-model coupling a macro-scale equation for the intra-granular fluid phase with a direct simulation of diffusion in the clay particle with special boundary conditions involving the macro-scale concentration.

1. INTRODUCTION

The study of the solute transport in a fully or partially water saturated porous medium is the subject of many works, this field of research has many applications in the context of nuclear waste storage and environmental pollution. In these two areas of application, the simulation of the tracer behavior requires an accurate knowledge of the transport equations to be solved at the Darcy-scale and a thorough understanding of the parameters and their relationships. The presence of several solid phases with different geometric and chemical characteristics involve a phenomenology and processes which have to be described first at the pore-scale in order to deduce the equations to be solved at the macro-scale. For example, in many geochemical studies, the first approximation usually performed in Darcy-scale models for the retention process of the tracer in clay assumes that macro-scale concentrations correspond to equilibrium conditions. However, the comparison between the characteristic times of (1) the reactive and diffusion processes in the clay grain and (2) the advection process in the intragranular porosity may lead to situations where the pore-scale solute concentration is not homogeneous [Alvaro et al., 1997]. This suggests the importance of the two-media effects, and this may be taken into account at the Darcy-scale by a two-equation model. The remaining issue being the connection between Darcy-scale and micro-scale properties.

This work focuses on the reactive transport of cesium in a fully saturated porous medium composed of a sand of Fontainebleau (non-reactive) and one particular type of clay : *illite* (from

Puy, France) [Sawhney, 1972] [Koning and Comans, 2004]. The second section is dedicated to the formalization of the equations to be solved at the Darcy-scale when the diffusion and the sorption processes of the cesium are explicitly taken into account in the clay. The method is based on the application of one particular upscaling technique : the volume averaging with closure problems. Both scales and the three phases are presented in Fig. 1 (Ω_0 and Ω_1). Another approach presented in this section is the mixed approach. These two approaches are compared with direct simulations performed at the pore-scale and used as the reference for validation of the macro-scale models. At the pore scale, the Stokes equation is applied to compute the fluid velocity and a two-equation model to simulate the cesium transport. The third section presents the numerical results.

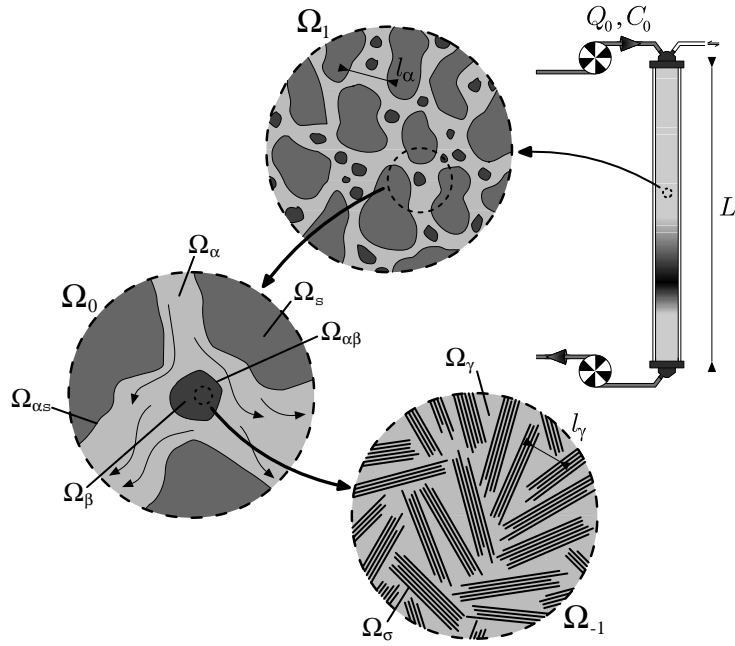


FIGURE 1. Pull-down scales of porous media

2. VOLUME AVERAGING

The system is composed of three phases, one fluid phase and two solid phases : water (ϕ_α), clay (ϕ_β) and sand (ϕ_s). The solid phases are supposed to be immobile with rigid interfaces. Due to low concentrations, phase densities are not modified by the migration of species. At very low Reynolds numbers ($Re = U_\alpha l_\alpha / \nu_\alpha$) the flow can be treated as incompressible. Stokes' equation of motion and boundary conditions can be stated as :

$$-\vec{\nabla} p_\alpha + \nu_\alpha \Delta \vec{u}_\alpha = \vec{0} \quad (1a)$$

$$\vec{\nabla} \cdot \vec{u}_\alpha = 0 \quad (1b)$$

$$\vec{u}_\alpha = \vec{0} \quad \text{at } \Omega_{\alpha\beta} \cup \Omega_{\alpha s} \quad (1c)$$

We consider the solute transfer of a cationic species (Cesium, Cs^+) whose concentration is very low compared to the others major background components (chloride Cl^- , potassium

K^+), constant in space and time. Fontainebleau sand is non-reactive, so no mass transfer can occur through ($\alpha - s$) interface between the liquid and the solid phases ($\Omega_{\alpha s}$). Because the clay particles are considered as micro-porous media, the solute can diffuse and sorbe inside them. We suppose that the kinetic reactions are sufficiently fast compared to the diffusion process. We also consider that thermodynamic equilibrium is reached and we model the cesium transport in ϕ_β by a retarded-diffusive process. In the water phase the solute is advected by the velocity field and molecular diffusion is modeled by the Fick's law. We emphasize that the boundary condition at α - β interface is not simple. Marle [Marle, 1982] has developed a general method for obtaining a macroscopic equations involving jump discontinuities on interfaces. Let's consider a virtual interface $\Omega_{\alpha\beta}$ between bulk and microporous media. c_α and c_β represent the concentration of the species in ϕ_α and ϕ_β . Mass conservation imposes flux continuity through $\Omega_{\alpha\beta}$. Nevertheless, with a low diffusive ratio D_β/D_α and reactive process at equilibrium, the jump condition can be neglected. All these considerations lead to the following local system :

$$\frac{\partial c_\alpha}{\partial t} = -\vec{\nabla} \cdot [\vec{u}_\alpha c_\alpha - D_\alpha \vec{\nabla} c_\alpha] \quad (2a)$$

$$R_\beta \frac{\partial c_\beta}{\partial t} = \vec{\nabla} \cdot [D_\beta \vec{\nabla} c_\beta] \quad (2b)$$

$$\begin{aligned} \text{B.C. 1 :} & \quad c_\alpha = c_\beta & \text{at } \Omega_{\alpha\beta} \\ \text{B.C. 2 :} & \quad \vec{n}_{\alpha\beta} \cdot (D_\alpha \vec{\nabla} c_\alpha) = \vec{n}_{\alpha\beta} \cdot (D_\beta \vec{\nabla} c_\beta) & \text{at } \Omega_{\alpha\beta} \\ \text{B.C. 3 :} & \quad \vec{n}_{\alpha s} \cdot (D_\alpha \vec{\nabla} c_\alpha) = \vec{0} & \text{at } \Omega_{\alpha s} \end{aligned} \quad (2c)$$

In Eq. (2a), D_α is the molecular diffusion of cesium in the water and \vec{u}_α is the microscopic fluid velocity. In (2b), R_β is the retardation factor given by the thermodynamic equilibrium of sorption reaction, and D_β is the effective diffusion coefficient affected by the tortuosity in the micropores.

Following the method given in [Quintard and Whitaker, 1993] and [Quintard and Whitaker, 1994], for any function ψ_i associated to the phase ϕ_i we define superficial average $\langle \psi_i \rangle = \frac{1}{V_0} \int_{\Omega_i} \psi_i d\Omega$ and intrinsic average $\langle \psi_i \rangle^j = \frac{1}{V_j} \int_{\Omega_i} \psi_i d\Omega$, with $V_j = \int_{\Omega_j} d\Omega$. These two quantities are simply related by $\langle \psi_i \rangle = \varepsilon_j \langle \psi_i \rangle^j$ where ε_j is the volume fraction of the j -phase given by $\varepsilon_j = V_j/V_0$. The choice of the classical weighting function is explained by the ordered nature of our idealized porous media. As exposed in [Quintard and Whitaker, 1993] the characteristic length scale l_0 of the averaging volume V_0 can be taken equal to the finite maximum correlation length scale l_α .

The averaging of equations (2a), (2b) and (2c) gives a two-equations model depending on spatial deviations of concentration and velocity. These deviations are given by $\psi_i = \langle \psi_i \rangle^i + \tilde{\psi}_i$. By assuming the following length-scale constraints : $l_\alpha \sim l_0$ and $l_0^2 \ll L^2$ we simplify the equations considerably. Intrinsic average varies little over the scale of the microstructure ($l_\alpha \|\vec{\nabla} \langle c_\alpha \rangle^\alpha\| \ll 1$). This leads to the following superficial volume averaged mass transport equation :

$$\begin{aligned} \varepsilon_\alpha \frac{\partial C_\alpha}{\partial t} &= -\vec{\nabla} \cdot \left[\langle \vec{u}_\alpha \rangle C_\alpha + \langle \vec{u}_\alpha \tilde{c}_\alpha \rangle - D_\alpha \left(\varepsilon_\alpha \vec{\nabla} C_\alpha + \langle \vec{n}_{\alpha\beta} \tilde{c}_\alpha \rangle \right) \right] \\ &\quad + \langle \vec{n}_{\alpha\beta} \cdot \left(D_\alpha \vec{\nabla} \tilde{c}_\alpha \right) \rangle \end{aligned} \quad (3)$$

$$\varepsilon_\beta R_\beta \frac{\partial C_\beta}{\partial t} = \vec{\nabla} \cdot \left[D_\beta \left(\varepsilon_\beta \vec{\nabla} C_\beta + \langle \vec{n}_{\alpha\beta} \tilde{c}_\beta \rangle \right) \right] + \langle \vec{n}_{\alpha\beta} \cdot \left(D_\beta \vec{\nabla} \tilde{c}_\beta \right) \rangle \quad (4)$$

with the simplified notations $\langle c_\alpha \rangle^\alpha \equiv C_\alpha$ and $\langle c_\beta \rangle^\beta \equiv C_\beta$.

2.1. Closure problem. The closure problem is obtained by subtracting the averaged equations from the local equations : (2a)– $\varepsilon_\alpha^{-1} \times (3)$ and (2b)– $\varepsilon_\beta^{-1} \times (4)$ [Crapiste et al., 1986]. We use spatial decomposition in order to develop a boundary condition. We note that deviation fields arise from three sink/source terms. Thus at the first order we introduce spatial deviations which are linear combinations of $\vec{\nabla} C_\alpha$, $\vec{\nabla} C_\beta$ and $C_\alpha - C_\beta$ with the understanding that the macroscopic concentration and its gradient are linearly independent. It allows a simplification of the closure problem by splitting it into three independent problems for closure variables $(\vec{b}_{\alpha\alpha}, \vec{b}_{\beta\alpha})$, $(\vec{b}_{\alpha\beta}, \vec{b}_{\beta\beta})$ and (s_α, s_β) . This way we neglect cross effects of sink/source terms.

$$\tilde{c}_\alpha = \vec{b}_{\alpha\alpha} \cdot \vec{\nabla} C_\alpha + \vec{b}_{\alpha\beta} \cdot \vec{\nabla} C_\beta - s_\alpha (C_\alpha - C_\beta) \quad (5a)$$

$$\tilde{c}_\beta = \vec{b}_{\beta\alpha} \cdot \vec{\nabla} C_\alpha + \vec{b}_{\beta\beta} \cdot \vec{\nabla} C_\beta - s_\beta (C_\alpha - C_\beta) \quad (5b)$$

2.2. Closed form of the averaged equations. Use of the representation for \tilde{c}_α and \tilde{c}_β given by (5a)-(5b) leads to the closed form of the transport equations. Some simplifications can be made on symmetric unit cells.

$$\varepsilon_\alpha \frac{\partial C_\alpha}{\partial t} = -\vec{\nabla} \cdot \left[\varepsilon_\alpha \vec{U}_\alpha C_\alpha - \overline{\overline{\mathbf{K}}}_{\alpha\alpha} \cdot \vec{\nabla} C_\alpha - \overline{\overline{\mathbf{K}}}_{\alpha\beta} \cdot \vec{\nabla} C_\beta + \vec{P}_\alpha (C_\alpha - C_\beta) \right] - \Gamma \quad (6)$$

$$\varepsilon_\beta R_\beta \frac{\partial C_\beta}{\partial t} = -\vec{\nabla} \cdot \left[-\overline{\overline{\mathbf{K}}}_{\beta\alpha} \cdot \vec{\nabla} C_\alpha - \overline{\overline{\mathbf{K}}}_{\beta\beta} \cdot \vec{\nabla} C_\beta \right] + \Gamma \quad (7)$$

with $\Gamma = h_0 (C_\alpha - C_\beta)$. In equations (6) and (7), the second-order tensors $\overline{\overline{\mathbf{K}}}_{\alpha\alpha}$, $\overline{\overline{\mathbf{K}}}_{\alpha\beta}$, $\overline{\overline{\mathbf{K}}}_{\beta\alpha}$, $\overline{\overline{\mathbf{K}}}_{\beta\beta}$ ($[L]^2 \cdot [T]^{-1}$), the \vec{P}_α vector ($[L] \cdot [T]^{-1}$) and the scalar h_0 ($[T]^{-1}$) are coefficients calculated with the closure variables. Some of these effective parameters are usual, like the dispersion tensor $\overline{\overline{\mathbf{K}}}_{\alpha\alpha}$ and the Darcy's velocity $\varepsilon_\alpha \vec{U}_\alpha$, and can be found in many empirical studies. In this study the non-equilibrium behaviour of the system, induced by the presence of the β -phase indicates a coupling between the mass transfer and transport. Thus we refer to the dispersion as active dispersion, and the quantification of deviation from passive dispersion is required. The retardation coefficient R_β is not modified by the averaging. Use of expressions (5a)-(5b) in (3) and (4) generates additional terms such as self-diffusion into the β -phase, cross-diffusion and velocity-like parameters. \vec{P}_α acts as a correction term for the velocity with mass exchange between phases. When diffusion and adsorption occur the advancing of the pollutant is slower than predicted by the Darcy's velocity.

2.3. **Mixed model.** Averaged model can reproduce transport in two-phase system with good agreement when the system is close to equilibrium. If this condition is not satisfied a solution includes higher-order gradients such as $\vec{\nabla}^2 C_\alpha$ which can be of the same order as $(C_\alpha - C_\beta)$. This leads to a new closure problem for s_α and s_β where gradients play a sink/source role [Kechagia et al., 2002].

We expect better results by mixing two equations at different scales [Fesh et al., 1998], following ideas that have been widely used for double-porosity systems. For α -phase transport we solve equation (6) whereas for β -phase we solve local diffusive-retarded equation. According to the spherical geometry of clay particles, this model consists in solving a one-dimensional equation coupled with N local one-dimensional equations (where N is the number of nodes). The special boundary condition which links macroscopic and microscopic variables is given by

$$\begin{aligned} c_\beta &= c_\alpha \\ &= C_\alpha + \vec{m}_1 \cdot \vec{\nabla} C_\alpha + \vec{m}_2 \cdot \vec{\nabla} C_\beta - m_3 (C_\alpha - C_\beta) \text{ at } \Omega_{\alpha\beta} \end{aligned} \quad (8)$$

where $\vec{m}_1 = \frac{1}{S_{\alpha\beta}} \int_{\Omega_{\alpha\beta}} \vec{b}_{\alpha\alpha} d\Omega$, $\vec{m}_2 = \frac{1}{S_{\alpha\beta}} \int_{\Omega_{\alpha\beta}} \vec{b}_{\alpha\beta} d\Omega$, $m_3 = \frac{1}{S_{\alpha\beta}} \int_{\Omega_{\alpha\beta}} s_\alpha d\Omega$ and $S_{\alpha\beta}$ is the area of α - β interface.

3. NUMERICAL MODELLING

One of the key problems in the volume averaging method is the choice of the geometry. In order to get isotropic properties, the three-dimensional periodic unit cell illustrated in Fig 2 is used. The cell is a face-centered cubic network of spherical sand grains with four spherical clay particles on every tetrahedral site. This quite complicated three-dimensional representative elementary volume is meshed by quadratic hexahedral elements. A finite elements method is applied to discretize the continuous equations and the computations are performed with *Cast3M*, a CEA numerical tool.

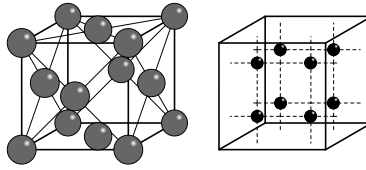


FIGURE 2. Sand grains face-centered cubic network (left), clay particules network (right). Sand radius $r_\alpha = 150\mu m$, clay radius $r_\beta = 50\mu m$, characteristic length scale $l_0 = 233\mu m$

The first step consists in computing the velocity field on a unit cell by solving the Stokes' equations with periodic boundary conditions. As predicted by the linear nature of this motion equations, a linear relation between the Darcy's flux and pressure gradient is obtained. Modifying porosity of the network we find the classical power law for the intrinsic permeability ($[L]^2$) in a saturated porous medium ($\vec{Q}_{Darcy} = -\frac{1}{\mu_\alpha} \overline{\overline{\mathbf{k}}}_{sat} \cdot \vec{\nabla} p_\alpha$).

The equivalent dispersive-reactive tensor $\overline{\overline{\mathbf{K}}}_{\alpha\alpha}$ is the sum of interfacial fluxes (at Ω_{α_s} for tortuous effects and at $\Omega_{\alpha\beta}$ for exchange between phases) and volumic dispersion (cross effects of concentration and velocity spatial deviations) :

$$\overline{\mathbf{K}}_{\alpha\alpha} = \varepsilon_{\alpha} D_{\alpha} \overline{\mathbf{I}} + D_{\alpha} \frac{1}{V_0} \int_{\Omega_{\alpha s}} \vec{n}_{\alpha s} \vec{b}_{\alpha\alpha} d\Omega + D_{\alpha} \frac{1}{V_0} \int_{\Omega_{\alpha\beta}} \vec{n}_{\alpha\beta} \vec{b}_{\alpha\alpha} d\Omega - \frac{1}{V_0} \int_{\Omega_{\alpha}} \vec{u}_{\alpha} \vec{b}_{\alpha\alpha} d\Omega \quad (9)$$

It expresses at the macro scale the competition between diffusion and advection. We focus on the expected behaviour of the effective parameters with respect to the local Péclet number ($Pe = u_{\alpha} l_{\alpha} / D_{\alpha}$). Experiments in unconsolidated sandy soils with one-dimensional flow have shown that passive dispersion can be modeled by a quite simple correlation : at small Péclet numbers a diffusive regime only affected by tortuosity followed first by a transition regime then by a dispersive regime governed by a power law expression. In the case of active dispersion we observe the same behaviour. The two-equation model presented by equations (6) and (7) is governed by ten effective parameters. Four of them can be measured : ε_{α} , ε_{β} , R_{β} and $\varepsilon_{\alpha} U_{\alpha}$. Clearly, an experimental unidimensional study would have difficulties to discriminate cross effective diffusion coefficients or velocity-like coefficient \vec{P}_{α} . As shown in Tab. 1, numerically we observe the same hierarchy with two main parameters : $\overline{\mathbf{K}}_{\alpha\alpha}$ and h_0 .

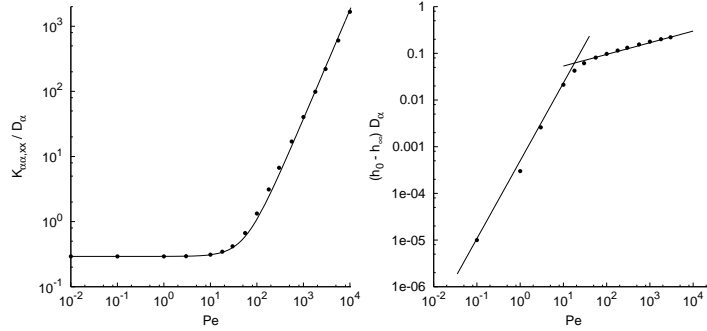


FIGURE 3. Effective active dispersion $K_{\alpha\alpha,xx}$ and exchange rate h_0

The exchange rate as shown in Fig. 3 is very close to h_{∞} where $h_{\infty} = \lim_{Pe \rightarrow 0} h_0$ is a constant. Nevertheless we can distinguish two behaviours expressed by a power law. For low Péclet numbers $h_0 D_{\alpha}$ grows with the power 1.65 whereas for high Péclet numbers with power 0.25.

For given geometry and Péclet number a direct simulation is made as a reference solution of our problem. For this we generate a trellis of N unit cells and duplicate the periodic velocity field. And we solve equations (2a), (2b) and (2c) with the following boundary conditions.

$$\begin{aligned} \vec{n} \cdot \left(\vec{u}_{\alpha} c_{\alpha} - D_{\alpha} \vec{\nabla} c_{\alpha} \right) &= f_0 \quad \text{at } \Omega_{inlet} \\ \vec{n} \cdot \left(-D_{\alpha} \vec{\nabla} c_{\alpha} \right) &= 0 \quad \text{at } \Omega_{outlet} \end{aligned} \quad (10)$$

Then we integrate the concentration field to obtain the macroscopic concentration at the center of every unit cell. Concerning averaged simulation, effective properties are calculated by solving the closure problem for a given Péclet number and boundary conditions expressed as

$$\begin{aligned}
\vec{n} \cdot \left(\varepsilon_\alpha \vec{U}_\alpha C_\alpha - \overline{\overline{K}}_{\alpha\alpha} \cdot \vec{\nabla} C_\alpha \right) &= \int_{\Omega_{inlet}} f_0 d\Omega \quad \text{at } \Omega_{inlet} \\
\vec{n} \cdot \left(-\overline{\overline{K}}_{\alpha\alpha} \cdot \vec{\nabla} C_\alpha \right) &= 0 \quad \text{at } \Omega_{outlet} \\
\vec{n} \cdot \left(-\overline{\overline{K}}_{\beta\beta} \cdot \vec{\nabla} C_\beta \right) &= 0 \quad \text{at } \Omega_{inlet} \cup \Omega_{outlet}
\end{aligned} \tag{11}$$

We tested our methodology for two Péclet number : $Pe_a = 10^1$ for diffusive regime and $Pe_b = 10^3$ for dispersive regime.

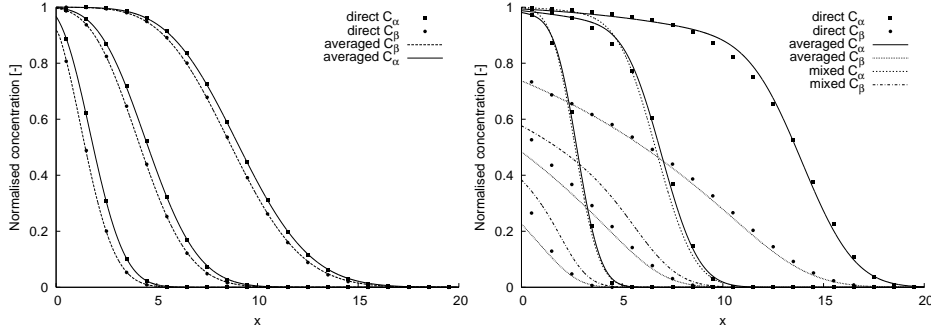


FIGURE 4. Comparison between direct, averaged and mixed models for ($Pe_a = 10^1, R_{\beta,a} = 5$) (left) and ($Pe_b = 10^3, R_{\beta,b} = 1$) (right). $\omega_\alpha = 0.4$ and $\omega_\beta = 4.13 \times 10^{-2}$

	$\varepsilon_\alpha U_{\alpha,x}$	$K_{\alpha\alpha,xx}$	$K_{\beta\alpha,xx}$	$K_{\alpha\beta,xx}$	$K_{\beta\beta,xx}$	$P_{\alpha,x}$	h_0
Pe_a	4.29×10^{-5}	1.13×10^{-9}	-3.29×10^{-13}	3.11×10^{-12}	1.65×10^{-12}	1.6×10^{-6}	1.66×10^{-1}
Pe_b	4.29×10^{-3}	1.47×10^{-7}	6.32×10^{-12}	-1.27×10^{-10}	1.59×10^{-12}	9.61×10^{-5}	1.92×10^{-1}

TABLE 1. Values used in averaged simulations

At low Péclet number diffusion is large enough to balance concentration in α - and β -phase. As C_β is sufficiently close to C_α the one equation model is valid. Under these conditions one can write a one-equation model for transport with a retardation coefficient $R_{eff} = \varepsilon_\alpha + \varepsilon_\beta R_\beta$ and an effective diffusion $\overline{\overline{K}}_{eff} = \overline{\overline{K}}_{\alpha\alpha} + \overline{\overline{K}}_{\alpha\beta} + \overline{\overline{K}}_{\beta\alpha} + \overline{\overline{K}}_{\beta\beta}$. This assumption is often used to fit experimental data with a simple retarded *Convection Dispersion Equation* (CDE) model. At high Péclet number we observe a strong imbalance between phases. The averaged model which uses a unique characteristic time associated to exchange rate have good agreements with direct simulations. Let us notice that the model underestimates the concentration in the β -phase C_β for early times. When the system is very far from equilibrium some of the hypothesis performed in the volume averaging are not exact as argued by Kechagia et al. [Kechagia et al., 2002]. The mass transfer through the surface $\Omega_{\alpha\beta}$ is described by a set of characteristic times, which can be reduced to its first term h_0 only in a steady state regime. Nevertheless if the active dispersion is compared to the passive dispersion we find a relative deviation of about 6.5% for Pe_b ($K_{\alpha\alpha,xx}^{passive} = 1.56 \times 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}$) which means that, for such two-phase porous media under these hydraulic conditions, dispersion and exchange rate can not be estimated independently. For low Péclet numbers the two dispersions are hardly different (0.24%) for Pe_a . The mixed model does not have assumptions in the form of the exchange rate. In Fig. 4 we observe an overestimation of the concentration C_β . Accuracy can be improved by modifying the

boundary condition at $\Omega_{\alpha\beta}$. Direct simulations have shown that the concentration field in clay particles is not concentric. Such a behaviour can not be modeled by a one-dimensional diffusive process. Only a three-dimensional model with an heterogeneous special boundary condition could reproduce it.

4. CONCLUSION

In this work is investigated capability of the two-equation model to predict transient movement of a conserving and sorbing solute in a porous media.

Resulting from a competition between diffusion and advection processes at the micro-pore scale, the Péclet number is the main parameter which permits to distinguish between two mass-transfer behaviours. At low Péclet number, the equilibrium between α - and β -phase is reached, thus transport can be modeled by a single equation model. Exchange rate is sufficiently large, active and passive hydrodynamic dispersions are equal. At high Péclet number transport is represented by two concentrations strongly imbalanced. Active equivalent parameters are computed with a closure problem in the approximation of steady-state and scale separation even for transient the macroscopic problem.

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