

A DUAL CONTINUUM REACTIVE TRANSPORT MODEL WITH N-TH ORDER SOLUTE TRANSFER TERM FOR STRUCTURED UNSATURATED SOILS

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ABSTRACT

Compacted bentonite is foreseen to be used as backfill and sealing material for high-level radioactive waste disposal. Experimental evidence indicates that bentonite has a macro-porous domain containing free water and a micro-porous domain mainly occupied by interlayer and sorbed water. Geochemical non-equilibrium between macro- and micro- pores calls for a fully coupled reactive transport Dual Continuum Model (DCM) to describe water flow and reactive transport of bentonites. Most DCMs assume a lumped first-order solute transfer term between both domains. However, it is well known that such a term is not correct at all times. Here we present a formulation for dual continuum flow and reactive transport model with an n th-order solute transfer term derived from an approximation of the analytical solution of diffusion through a thin slab. Such formulation has been implemented in a finite element code which solves for both forward and inverse problems. The n th-order transfer term improves greatly the ability and accuracy of DCM to simulate reactive transport in bentonites. Solute transfer terms of different orders (n) are evaluated for a 2-D synthetic case. The order and the empirical coefficients of the solute transfer term are estimated by inverse modelling. Optimum results for bentonite are achieved with $n = 0.72$.

1. INTRODUCTION

The porous system of compacted bentonite exhibits different types of pores: interlayer, intraggregate and interaggregate pores (Fernández et al., 2004). Chemical non-equilibrium between double layer water and free water calls for a Dual Continuum Model (DCM) to study geochemical transport through bentonite.

‘Dual continuum’ or ‘dual domain’ is a term generally used to denote a conceptual model in which the medium is divided into two domains which are coupled by an interaction term for modelling flow and solute transport. A porous medium consists of two separate but connected continua. The first continuum is associated with a network of fractures, fissures, macropores or interaggregate pores while the second involves porous matrix blocks or soil aggregates.

The dual continuum concept has been commonly used to describe the preferential movement of solutes at the macroscopic scale, a phenomenon that is widely believed to occur in most natural (undisturbed) media. In most DCM transport models, solute transport in both domains is described by two coupled advection-dispersion equations. Their complexity depends on the purpose and dimension of model, the solid phases considered (Šimunek et al., 2003; Larsson and Jarvis, 1999; Lichtner, 2000; Ray et al., 1997), the chemical reactions

involved, the occurrence of microbial processes (Kim and Corapcioglu, 2002), the purpose of the model, and the complexity of the conceptual model.

One of the key points of DCM is the evaluation of the solute transfer term. Most researchers have used a first-order transfer term which is either the sum of convective and diffusive fluxes (Gerke and van Genuchten, 1993; 1996; Jarvis et al., 1991; Larsson and Jarvis, 1999; Ray et al., 1997; Saxena et al., 1994; Schwartz et al., 2000) or only a diffusive flux (Hantush et al., 2002; 1998; Kim and Corapcioglu, 2002; Lichtner, 2000). However, the first-order solute transfer is not accurate at all time scales (for example, Gwo et al., 1998). Another challenge of DCM is parameterization. DCM requires more parameters than a single continuum model (SCM). Direct measurement as well as calibration of these parameters is difficult. Recently, some researchers have called for the use of inverse modelling techniques (Kätterer et al., 2001; Schwartz et al., 2000). However, very little experience is available on inverse modelling for compacted bentonite, a swelling clay having geochemical properties different than those of undisturbed soils.

In this paper we present a formulation of dual continuum non-isothermal multiphase flow and reactive transport with an n th-order solute transfer term. Details of the flow features of our DCM are described in Zheng and Samper (2005) and its validation and application are presented by Zheng et al. (2005). A general form of the solute transfer term is derived from an approximation to analytical solution of the diffusion through a thin slab. Depending on the exponent $1/n$, this solute transfer term can be first-, second- or n th-order. By solving the inverse problem we show that $n = 0.72$ leads to the best approximation of the solute transfer across the two domains.

2. MATHEMATICAL FORMULATIONS

2.1 Solute transport for DCM

It is assumed here that the micro-porous domain includes interlayer and intraaggregate pores while the macro-porous domain includes interaggregate pores. The external surface of aggregates is the interface between macro- and micro-porous domains.

The solute transport model accounts for advection, molecular diffusion and mechanical dispersion. Each of these processes produces a solute flux per unit surface and unit time. There are as many transport equations as chemical components (primary species) in the system. Mass balance equation for the j -th component in the macro-porous domain is given by,

$$\begin{aligned} & \rho_l^{ma} X_{wl}^{ma} \theta_l^{ma} \frac{\partial C_j^{ma}}{\partial t} + \frac{\partial (\rho_l^{ma} X_{wl}^{ma} \theta_l^{ma} P_j^{ma})}{\partial t} + \frac{\partial (\rho_l^{ma} X_{wl}^{ma} \theta_l^{ma} W_j^{ma})}{\partial t} + \frac{\partial (\rho_l^{ma} X_{wl}^{ma} \theta_l^{ma} Y_j^{ma})}{\partial t} \\ & = L^* (C_j^{ma}) + r_i^{ma} (C_j^0 - C_j^{ma}) + \frac{\rho_l^{ma} \Gamma_w (\cdot)}{f^{ma}} - \frac{\Gamma_j^s}{f^{ma}} \end{aligned} \quad (1)$$

where

$$L^* (\cdot) = \nabla \cdot (\rho_l^{ma} X_{wl}^{ma} \theta_l^{ma} \underline{\underline{D}}_j^{ma} \nabla (\cdot)) - \rho_l^{ma} X_{wl}^{ma} \mathbf{q}_l^{ma} \nabla (\cdot) + (r_e^{ma} - r_c^{ma}) (\cdot) \quad (2)$$

superscript ‘ ma ’ denotes macro-porous domain. C_j^{ma} is the total dissolved concentration of the j -th species, $\underline{\underline{D}}_j^{ma}$ is the dispersion coefficient, \mathbf{q}_l^{ma} is liquid flow rate, r_e^{ma} and r_c^{ma} are evaporation and condensation rates, respectively, r_i^{ma} is a sink/source term, C_j^0 is the dissolved concentration of j -th species in the sink term r_i . ρ_l^{ma} is liquid density, X_{wl}^{ma} is the mass fraction of

water in the liquid, θ_l^{ma} is water content, W_j^{ma} is the total exchanged concentration of j-th component, Y_j^{ma} is the total sorbed concentration of j-th component, P_j^{ma} is the precipitated concentration of the j-th component, N_c is the number of solutes, Γ_w is the second-order water transfer (see Zheng and Samper, 2005), Γ_j^s is the solute transfer term (which is defined below), and f^{ma} is the volumetric weighting factor which is given by,

$$f^{ma} = V^{ma} / V^{tot} \quad (3)$$

where V^{ma} is the total volume of macro-porous domain and V^{tot} is the total volume of medium.

The mass balance equation in the micro-porous domain is given by,

$$\begin{aligned} & \rho_l^{mi} X_{wl}^{mi} \theta_l^{mi} \frac{\partial C_j^{mi}}{\partial t} + \frac{\partial (\rho_l^{mi} X_{wl}^{mi} \theta_l^{mi} P_j^{mi})}{\partial t} + \frac{\partial (\rho_l^{mi} X_{wl}^{mi} \theta_l^{mi} W_j^{mi})}{\partial t} + \frac{\partial (\rho_l^{mi} X_{wl}^{mi} \theta_l^{mi} Y_j^{mi})}{\partial t} \\ & = L^* (C_j^{mi}) + r_i^{mi} (C_j^0 - C_j^{mi}) - \frac{\Gamma_w}{1-f^{ma}} C_j^{mi} + \frac{\Gamma_j^s}{1-f^{ma}} \end{aligned} \quad (4)$$

where

$$L^* (\cdot) = \nabla \cdot (\rho_l^{mi} X_{wl}^{mi} \theta_l^{mi} \underline{D}_{\underline{j}}^{mi} \nabla (\cdot)) - \rho_l^{mi} X_{wl}^{mi} \mathbf{q}_l^{mi} \nabla (\cdot) + (r_e^{mi} - r_c^{mi}) (\cdot) \quad (5)$$

superscript ‘mi’ denotes the micro-porous domain. Parameters in Equations (4) and (5) are similar to those in Equations (1) and (2) but for the micro-porous domain.

2.2 Mass transfer term

Here we adopt an approach similar to that of Dykhuizen (1990) to derive the diffusive solute transfer term. Solute diffusion in a matrix block is governed by:

$$\frac{\partial C}{\partial t} = D \nabla^2 C \quad (6)$$

The mass flux, Γ_s , can be found by integrating the flux out of the boundary of the matrix block,

$$\Gamma_s = \frac{-1}{V_m} \int_{\partial V_m} D \frac{\partial C}{\partial n} dA \quad (7)$$

The average concentration in the matrix block, \bar{C}_m , is given by:

$$\bar{C}_m = \frac{1}{V_m} \int_{V_m} C_m dV \quad (8)$$

Integrating in space Equation (6) and using divergence theorem one obtains the following expression for the time derivative of \bar{C}_m :

$$\frac{\partial \bar{C}_m}{\partial t} = \frac{1}{V_m} \int_{\partial V_m} D \frac{\partial C}{\partial n} dA \quad (9)$$

From (7) and (9) it follows that:

$$\frac{\partial \bar{C}_m}{\partial t} = -\Gamma_s \quad (10)$$

One of the most commonly used expressions for Γ_s is that of Warren and Root (1963):

$$\Gamma_s = D(C_f - C_m) \quad (11)$$

A more general exchange equation can be derived from the exact analytical solution of Equation (6) (see Crank, 1975):

$$\frac{\bar{C}_m - C_{ini}}{C_0 - C_{ini}} = 1 - \frac{6}{\pi^2} \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left[-\frac{D(2n+1)^2 \pi^2 t}{4l^2}\right] \quad (12)$$

where C_{ini} is the initial concentration in the block and C_0 is the concentration imposed at the outer boundary at $t = 0$. Vermeulen (1953) found that Equation (12) can be approximated by:

$$\frac{\bar{C}_m - C_{ini}}{C_0 - C_{ini}} = \left[1 - \exp\left(-\frac{D(2n+1)^2 \pi^2 t}{4l^2}\right)\right]^n \quad (13)$$

where $n = 0.5$.

However, a more detailed comparison of Vermeulen approximation with the exact analytical solution reveals that the analytical solution is approximated better with an exponent n equal to 0.72 (see Figure 1).

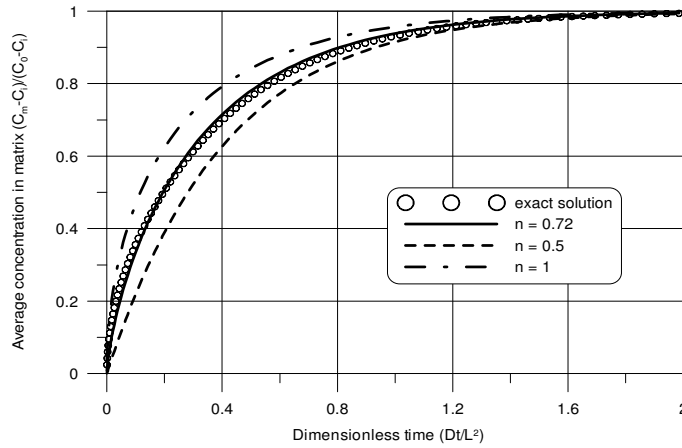


FIGURE 1. Normalized average concentration in the matrix calculated with the exact analytical solution of Equation (12) and Vermeulen approximation in Equation (13) for different values of exponent n .

Differentiating Equation (13) with respect to t , and eliminating t leads to:

$$\frac{d\bar{C}_m}{dt} = \frac{nD\pi^2}{4l^2} \frac{(C_0 - C_i)^{1/n} - (C_m - C_i)^{1/n}}{(C_m - C_i)^{1/n-1}} \quad (14)$$

This expression can be generalized by assuming that C_0 is equal to the concentration in the macro-porous domain and C_i is the initial concentration in the micro-porous domain:

$$\frac{d\bar{C}_m}{dt} = \frac{nD\pi^2}{4l^2} \frac{(C^{ma} - C^{ini})^{1/n} - (C^{mi} - C^{ini})^{1/n}}{(C^{mi} - C^{ini})^{1/n-1}} \quad (15)$$

In order to ensure that $d\bar{C}_m/dt$ has the same sign as $(C_j^{ma} - C_j^{mi})$, a coefficient δ is defined in such a way that $\delta = 1$ when $C_j^{ma} > C_j^{mi}$ and $\delta = -1$ otherwise. In addition, absolute values are used for exponential terms. The final expression of the diffusive flux, Γ_s^d , becomes:

$$\Gamma_s^d = \alpha_s^* \bar{D}_j \delta n \frac{\left| (C_j^{ma} - C_j^{ini})^{1/n} \right| - \left| (C_j^{mi} - C_j^{ini})^{1/n} \right|}{\left| (C_j^{mi} - C_j^{ini})^{1/n-1} \right|} \quad (16)$$

where α_s^* is an empirical shape coefficient which is given by (Gerke and van Genuchten, 1993):

$$a_s^* = \frac{\beta}{\alpha^2} \gamma_s \quad (17)$$

where β is a geometry-dependent coefficient and α is the radius for spheres (or cylinders) or the half width for cubes (m), and γ_s is a dimensionless scaling term. \bar{D}_j in (16) is the weighted arithmetic average of effective diffusion coefficients of macro- and micro-pores, D_e^{ma} and D_e^{mi} , respectively:

$$\bar{D}_j = (D_e^{ma} + wD_e^{mi})/(w+1) \quad (18)$$

where w is a weighting factor.

The diffusive solute transfer term for $n = 1$ coincides with the first-order equation of Warren and Root (1963). For $n = 0.5$, one has a second-order term. A value of $n = 0.72$ will provide the best approximation in most cases.

The advective solute transfer Γ_s^a is given by:

$$\Gamma_s^a = \rho_l^* \Gamma_w C_i^* \quad (19)$$

where c_i^* is the solute concentration at the macro- or micro-porous domain depending on the direction of water transfer and ρ_l^* is the average liquid density of both domains.

The total solute flux between macro- and micro-porous domains for the j -th species is the sum of the advective flux in Equation (19) and the diffusive flux in Equation (16).

3. EVALUATION OF SOLUTE TRANSFER TERM

DCM can be solved in two ways. The first method requires solving a flow and a transport equation with two transfer terms accounting for water and solute exchange. It assumes the two domains coexist in the same element but occupy different volumes. The drawback of this method is the inaccuracy of transfer terms. The second method requires solving two flow and two transport equations (Dai and Samper, 2004; Lichtner, 2000). For 1-D problems it requires a 1-D grid for the macro-porous domain and a 2-D grid for the micro-porous domain (see Samper *et al.*, 2005). This method not only requires more CPU time than the first method, but it is hard to be used for 2- and 3-D problems.

The second method has been widely used to verify water and solute transfer terms of the first method (Gerke and van Genuchten, 1993; Köhne *et al.*, 2004). Here we adopt a similar procedure to evaluate the n th-order solute transfer term of a DCM for compacted bentonite.

A synthetic case is used which corresponds to a 0.05 m \times 0.1 m bentonite block. This case is simulated with both a 2-D SCM (reference model, Figure 2 left) and a 1-D DCM (Figure 2 right). Material 1 in the SCM represents the macro-porous domain while material 2 corresponds to the micro-porous domain. The macro-porous domain accounts for 5% of total volume. Therefore, in the DCM the volumetric weighting factor is 5%.

This case has been used to validate the second-order water transfer term by Zheng *et al.* (2005). Initial and boundary conditions of the reference model are:

$$P_L(z = 0.1, 0 \leq x \leq 0.05, t \geq 0) = 100 \text{ kPa} \quad (20)$$

$$P_L(0 \leq z < 0.1, 0 \leq x \leq 0.05, t = 0) = -125000 \text{ kPa} \quad (21)$$

$$Q(z = 0, t \geq 0) = 0 \quad (22)$$

$$C(0 \leq z < 0.1, 0 \leq x \leq 0.05, t = 0) = 0.45 \text{ mol/L} \quad (23)$$

$$-\theta D \nabla c \cdot n \Big|_{\Gamma_2} (z = 0.1, 0 < x < 0.05, t \geq 0) = Q \cdot C^0 \quad (24)$$

While the initial and boundary conditions for the DCM are:

$$P_L^{ma}(z = 0.1, t \geq 0) = 100 \text{ kPa} \quad (25)$$

$$P_L^{mi}(z = 0.1, t \geq 0) = 100 \text{ kPa} \quad (26)$$

$$P_L^{mi}(0 \leq z < 0.1, t = 0) = -125000 \text{ kPa} \quad (27)$$

$$Q(z = 0, t \geq 0) = 0 \quad (28)$$

$$C^{ma}(0 \leq z < 0.1, t = 0) = 0.45 \text{ mol/L} \quad (29)$$

$$C^{mi}(0 \leq z < 0.1, t = 0) = 0.45 \text{ mol/L} \quad (30)$$

$$-\theta D \nabla c \cdot n|_{\Gamma_2}(z = 0.1, t \geq 0) = QC^0 \quad (31)$$

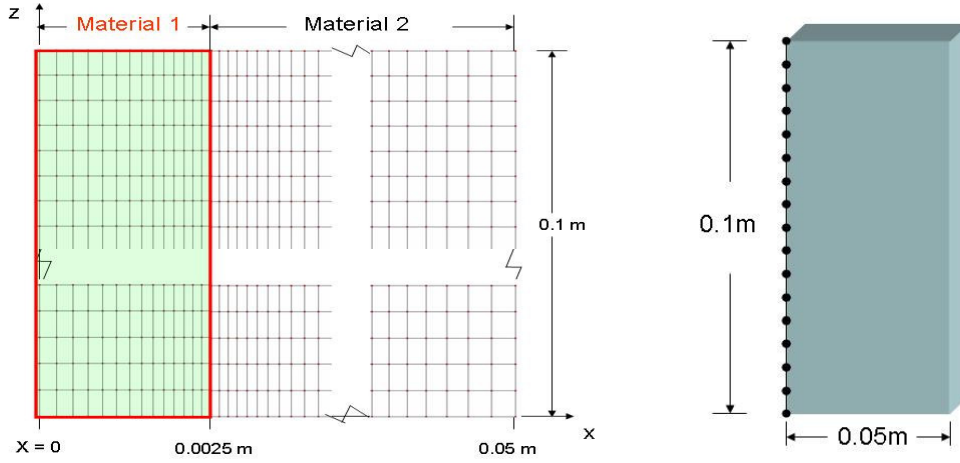


FIGURE 2. Finite element mesh used in the 2-D ‘reference’ SCM (left) and 1-D grid for DCM (right).

Table 1 summarizes the main flow and transport parameters of this synthetic case. A Neuman boundary condition is used at the upper boundary ($z = 0.1$). Solute flux is equal to water flux times boundary concentration C^0 which is equal to $1.31 \cdot 10^{-5}$ mol/L. Water in the macro-porous domain (material 1) is diluted first. Then, the solute migrates from the micro- to the macro-porous domain (material 2) afterwards.

TABLE 1. Parameters used in SCM (reference) and DCM.

Parameter	Intrinsic permeability m^2	Porosity	Effective diffusion coefficient m^2/s
Material 1 (macro-porous domain)	$2.075 \cdot 10^{-20}$	1.0	$2.5 \cdot 10^{-11}$
Material 2 (micro-porous domain)	$2.75 \cdot 10^{-22}$	0.378	$6.88 \cdot 10^{-12}$

The weighting factor, w , is assumed to be equal to 1 while the exponent n is taken equal to its optimum value of 0.72. The scaling term γ_s is estimated from the results of the SCM reference model. Its optimum value is equal to 3.42. Figure 3 shows the average concentration in the micro-porous domain obtained with SCM and DCM. The excellent agreement between the results of both models indicates that the solute transfer term of DCM provides an accurate estimate of the solute transfer flux across the two domains. Figure 3 shows also the spatial variation of the solute flux across the interface of the two domains at two times. Negative values indicate that solute flux is from micro- to macro-porous domain. Although the DCM

model catches the total solute transfer, it overestimates slightly the results of the ‘reference’ model at the upper part at early times. This is caused by the calculation of water transfer between micro-porous and macro-porous domain (Zheng et al., 2005).

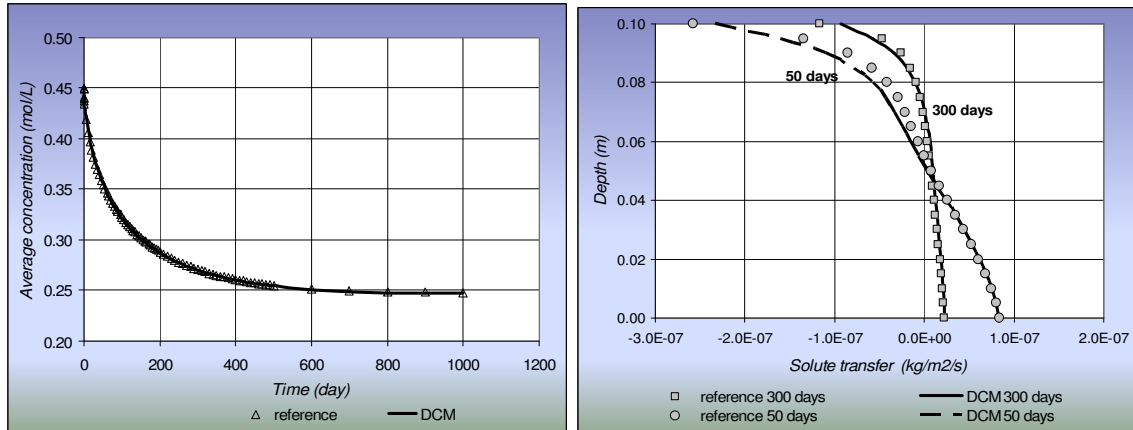


FIGURE 3. Average concentration in the micro-porous domain (left) and spatial distribution of solute flux (right) computed with SCM (‘reference’) and DCM.

4. CONCLUSIONS

Experimental evidence indicates that bentonite exhibits different types of porosity, which calls for the need of using dual continuum models. A n th-order solute transfer term has been implemented in a dual-domain reactive transport model. The solute transfer term has been evaluated for a 2-D synthetic case involving hydration and dilution of a bentonite block. The optimum exponent n is 0.72. Taking advantage of an inverse algorithm, optimum values of the scale term in the solute transfer term have been derived. A scale term around 3.4 leads to a sufficiently accurate calculation of solute transfer across the two domains.

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