Numerical modelling of reactive transport processes in fractured porous media

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Abstract A number of environmentally relevant problems require the analysis of reactive contaminant transport in subsurface systems, e.g. disposal of hazardous waste in rock formations or infiltration of leachates from landfills. This paper deals with the transport of chemically reactive components in fractured porous media. We investigate transport processes where chemical reactions occur either under equilibrium or under non-equilibrium conditions. The mathematical description of reactive transport processes is given in a set of nonlinear partial differential equations, which are discretized by using the finite element method in combination with different time-stepping schemes. Automatic grid adaptation is suitable for problem-related discretization. Adaptive grid adjustment is of particular benefit for dynamic problems with moving sharp fronts, such as nonlinear sorption. The new finite element (FE) kernel RTM (Reactive Transport Module) for the numerical simulation of reactive transport processes is embedded in the more general simulator ROCKFLOW. We present benchmark studies for the verification of the numerical code. Further, we present calculations to demonstrate the impact of non-equilibrium effects. Finally, first results for the study site Münchehagen—a former waste depository—are presented.

SOFTWARE CONCEPT OF ROCKFLOW

The finite element (FE) kernel RTM (Reactive Transport Module) described below is embedded in the simulator ROCKFLOW-3. This finite element program has been developed to simulate flow and transport processes of one and more fluid phases in subsurface hydrosystems (Kolditz et al., 1997). The software is written entirely in ANSI-C. Dynamic memory allocation and pointer technique are particularly important for the utilization of automatic grid adaptation and the coupling of different FE kernels. The code consists of several FE kernels, which assemble the matrix equation for the specific partial differential equations of a physical problem, e.g. saturated groundwater flow, gas flow, multiphase flow, tracer transport, and reactive transport. As the software concept allows the coupling of several FE kernels, chemical processes can be simulated for different hydrological systems, so e.g. reactive components can be transported by saturated groundwater gas, or multiphase flow.

GOVERNING EQUATIONS

From the large number of transport models with kinetic reactions, we have chosen a chemical non-equilibrium model to simulate the sorption reaction. It can be described...
by the governing solute transport equation with rate-limited sorption and first-order decay in both phases. The set of equations in three-dimensional Cartesian coordinate system is written as follows (Selim & Amacher, 1988; Bajracharya & Barry, 1992):

\[
\frac{\partial C}{\partial t} + \rho_h \frac{\partial S}{\partial t} + q_a \frac{\partial C}{\partial x_a} = \theta \frac{\partial}{\partial x_a} \left( D_{ab} \frac{\partial C}{\partial x_b} \right) - \lambda_c \theta C - \lambda_a \rho_p S
\]

(1)

\[
\frac{\partial S}{\partial t} = \alpha \left[ f(C) - S \right]
\]

(2)

where \( C \) is the aqueous solute concentration (M L^{-3}), \( S \) is the sorbed phase concentration (M M^{-1}), \( \rho \) is the soil bulk density of the porous medium (M L^{-3}), \( \theta \) is the porosity (L^3 L^{-3}), \( D_{ab} \) is the local hydrodynamic dispersion tensor (L^2 T^{-1}), \( q_a \) is the Darcy velocity (L T^{-1}), \( \lambda_c \) and \( \lambda_a \) is the first-order decay rate coefficient in the aqueous and sorbed phase, respectively (T^{-1}), \( \alpha \) is the sorption rate coefficient (T^{-1}), \( x \) is the distance (L) and \( t \) is the time (T). The function \( f(C) \) represents any sorption isotherm for a chemical species (linear or nonlinear).

Equation (2) describes the kinetic submodel for this chemical non-equilibrium model. It gives the time rate for the change of the adsorbed concentrations. This equation is necessary to close the problem. If the reaction is considered to be in equilibrium, then it can be taken into consideration by setting the parameter \( \alpha \) equal to infinity. Only steady state water flow is considered. Further, it is assumed that the transport of the solute takes place in saturated porous media, and any effect of concentration on the fluid properties is neglected. Details of the mathematical model can be found in Knabner (1991) or Habbar et al. (1998).

**NUMERICAL METHOD**

In the numerical approximation of the governing equations (1) and (2) we begin with the discretization of time. A semi-discretization method is applied. A superscript \( n + 1 \) refers to the time level \( t^{n+1} = t^n + n\Delta t \), \( n = 0, 1, 2, \ldots \). For simplicity, the decay terms are neglected. The resulting equations are:

\[
\frac{C_{n+1} - C^n}{\Delta t} + \rho_h \frac{S_{n+1} - S^n}{\Delta t} + \omega q_a \frac{\partial C_{n+1}}{\partial x_a} + (1 - \omega) q_a \frac{\partial C^n}{\partial x_a} = 0
\]

(3)

\[
\omega \theta \frac{\partial}{\partial x_a} \left( D_{ab} \frac{\partial C_{n+1}}{\partial x_b} \right) + (1 - \omega) \theta \frac{\partial}{\partial x_a} \left( D_{ab} \frac{\partial C^n}{\partial x_b} \right)
\]

where \( \omega \) is an implicit parameter (time weighting coefficient). This allows us to use several schemes (e.g. \( \theta = 0 \) for explicit scheme, \( \theta = 1 \) for implicit scheme and \( \theta = 1/2 \) for Crank-Nicolson). Equation (4) can be resolved explicitly for \( S_{n+1} \), and substitution in (3) leads to:
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\[
C^{n+1} + \frac{\rho_b}{\theta} \frac{\omega \Delta t \alpha}{1 + \omega \Delta t \alpha} f(C^{n+1}) + \frac{\omega \Delta t}{\theta} \frac{q_a}{\partial x_{\alpha}} - \frac{\omega \Delta t}{\theta} \frac{\partial}{\partial x_{\alpha}} \left( D_{ab} \frac{\partial C^{n+1}}{\partial x_{\beta}} \right) = \\
- \frac{\rho_b}{\theta} \frac{(1 - \omega) \Delta t \alpha}{1 + \omega \Delta t \alpha} f(C^n) + \frac{\rho_b}{\theta} \left( \frac{\Delta t \alpha}{1 + \omega \Delta t \alpha} \right) S^n - (1 - \omega) \Delta t \frac{q_a}{\theta} \frac{\partial C^n}{\partial x_{\alpha}} + (1 - \omega) \Delta t \frac{\partial}{\partial x_{\alpha}} \left( D_{ab} \frac{\partial C^n}{\partial x_{\beta}} \right) \tag{5}
\]

\[
S^{n+1} = \frac{\omega \Delta t \alpha}{1 + \omega \Delta t \alpha} f(C^{n+1}) + \frac{(1 - \omega) \Delta t \alpha}{1 + \omega \Delta t \alpha} f(C^n) + \frac{1 - (1 - \omega) \Delta t \alpha}{1 + \omega \Delta t \alpha} S^n \tag{6}
\]

Various methods can be applied at this stage as finite differences or finite elements. Independent of the formulation, either as finite element or using the finite difference method the problem has reduced to the nonlinear equations for \( C^{n+1} \):

\[ M(C)C = r(c) \tag{7} \]

where \( M \) denotes a matrix, \( C \) and \( r \) are vectors. There are several methods to solve the nonlinear problem such as fixed point (or Picard iteration) or Newton method (Istok, 1989). Details of the above described and alternative methods can be found, e.g. in Habbar et al. (1998).

**BENCHMARK EXAMPLES**

A number of numerical studies is presented to demonstrate the ability of the simulator: e.g. porous media models for studying nonlinear sorption resulting in convex or concave breakthrough curves, and fracture matrix models for investigation of the matrix diffusion effect (see Habbar et al., 1998; Kolditz, 1997). The code development is aimed to interpret laboratory and field data (e.g. from the Münchehagen site). For this purpose, identification of the parameters for reactive transport processes is important, such as the coefficient of isotherms or

![Image](image.png)

Fig. 1 Mg breakthrough curve for Ca-Mg transport in Yolo loam (Lai & Jurinak, 1972) using (a) linear isotherm and (b) nonlinear isotherm.
exchange coefficients for heterogeneous (interphase) reactions. The procedure of parameter fitting is more complicated for fractured porous media, with zones containing mobile as well as immobile water. Furthermore, sorption works quite differently in fractures and in rock matrix. This process is governed by the so-called intraparticle diffusion.

The first example illustrates the validation of our model using experimental data of solute transport with cation exchange. We investigate the influence of the cation exchange on Mg transport. Data were taken from the experiment of Lai & Jurinak (1972). A comparison of the observed and simulated Mg breakthrough curves is given. The observed data are represented by the circles, while the ROCKFLOW simulation is shown as the solid line. First, only a linear isotherm is used (Fig. 1(a)). By introducing a slightly nonlinear isotherm a better data fit can be achieved which provides a closer match in front of the pulse peak as shown in Fig. 1(b).

The purpose of the next example is to illustrate the influence of the reaction parameter $\alpha$ (see equation (2)) on the transport of the solute. The value of $\alpha$ can be applied in order to control the conditions for which the reactions are in equilibrium or not. While for the greatest value of $\alpha = 10^5$ the processes take place in equilibrium (the curves C/C0 and S/S0 overlap each other, Fig. 2), for $\alpha = 10^8$ (the smallest value of $\alpha$) a non-equilibrium case is achieved (sorbed concentration is much lower, Fig. 2).

![Fig. 2 Kinetic model: concentration distributions in aqueous and sorbed phases computed using different rates of reactions $\alpha$.](image_url)
FIELD STUDY MÜNCHENHAGEN

The former waste depository at Münchhagen is located in Lower Saxony about 40 km westward from Hannover. Recently, an extensive research programme to study the geology as well as hydraulic and transport characteristics of the subsurface of the depository was carried out. A comprehensive summary of the field investigations can be found e.g. in Dörhöfer et al. (1994).

Numerous organic pollutants show hysteresis in adsorption-desorption reactions, e.g. in the case of the laboratory batch experiments with benzoic acid in Valangin from Münchhagen site (experiments were conducted by J. Maier, Geological Survey of Lower Saxony). The data presented in Fig. 3 show that the sorption and desorption have different characteristics. In addition, the desorption behaviour depends on the initial concentration of the desorption process. In order to model these kinetic behaviour, only a non-equilibrium model is appropriate. Geological investigations show that the fracture system of the clay formation determines flow and transport behaviour. Different approaches have been proposed to model the subsurface system, such as equivalent porous media and parallel fracture array models (Dörhöfer et al., 1994; Lege et al., 1996; Kosakowski, 1996). The present study is based on a more realistic description of the fractured clay. As can be seen in Fig. 4(a) and (b), the fracture system is quite complex. We have three different sets of intersecting fracture populations. The purpose of this study is twofold. At first, we show that transport simulations in those fracture systems are possible using the method of grid adaptation, i.e. meshes are refined in regions with large concentration gradients and are coarsened in areas of small gradients (Barlag, 1997; Kaiser et al., 1998). Second, the comparison of the contaminant migration within the fracture network shows the effect of retardation due to sorption (Fig. 4). Details of this site study can be found in Habbar et al. (1998).

![Graph showing benzoic acid adsorption and desorption isotherms in Valangin](image-url)

**Fig. 3** Benzoic acid adsorption and desorption isotherms in Valangin (data from J. Maier, Geological Survey of Lower Saxony).
Fig. 4 Distribution of concentration within the fracture network at a simulated time of 6 days: (a) migration of a conservative tracer ($K_D = 0$) and (b) migration of a sorbing tracer ($K_D = 0.107 \text{ m}^3 \text{ kg}^{-1}$).
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