Transport program and simulation of transport column experiments

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Abstract The contribution presents the program Transport, which serves to simulation of column transport experiments. Its main function is not to predict results of experiments but to compare influence of individual physical and chemical processes to the experiment results. The one-dimensional advection-diffusion model is based on Finite Volume Method; it includes the triple porosity concept, sorption, retardation, and chemical reactions simulated using connected program React from The Geochemist's Workbench package or PhreeqC. Due to these geochemical programs, the user has extensive possibilities of chemistry simulation during transport. The program Transport simulates not only the processes inside the column but also preparation of entering solutions and measurement methods of outgoing solution parameters.
Keywords column experiment; contamination front; groundwater modelling

INTRODUCTION AND BACKGROUND INFORMATION

Importance of modelling is rising due to frequent contamination of the groundwater. In the last twenty years, the coupling of hydrologic transport and reactive chemistry has been fast developed. The observed influence of chemical and biochemical reaction to transport is the reason for the effort to coupling of hydrologic transport and reactive chemistry.

Column experiments are important for correct set up of 3D model parameters. With column experiment we evaluate properties of the tested rock (like sorption capacity, pore volume etc.). Good understanding of processes in the column is required for correct differentiation of individual processes. Thus, the most comprehensive model of the column is needed for accurate estimation of parameters.

The Transport program includes some innovations comparing to conventional models. Three groups of innovations are described: (1) more precise geometrical and physical model of the column experiment; (2) major attention to the reactive component of the process; and (3) communication between transport and reactive component of the process based on *the method of contamination front (MCF)*.

Inclusion of these three groups of innovations has led to extension of model complexity but runtime has not changed. While using MCF causes a significant computation time reduction. In this time, we work on inclusion of MCF to a 3D transport model. We suppose a more significant computation time reduction for 3D case.

COLUMN MODEL INNOVATION

The simplest model of column experiment is a cylinder consisting of porous medium (Fig. 1). In our case, we have used one-dimensional model based on the Finite Volume Method. The inlet is modelled by a boundary condition defining species concentrations as piecewise constant functions in time. The result of the simulation is the chemical composition of the solute outgoing from the column.

The real column experiment looks slightly different and some simplifications affect computed parameters. In this chapter we briefly describe correction of two simplifications that are most relevant: (1) input and output chamber of the column and (2) output flask.
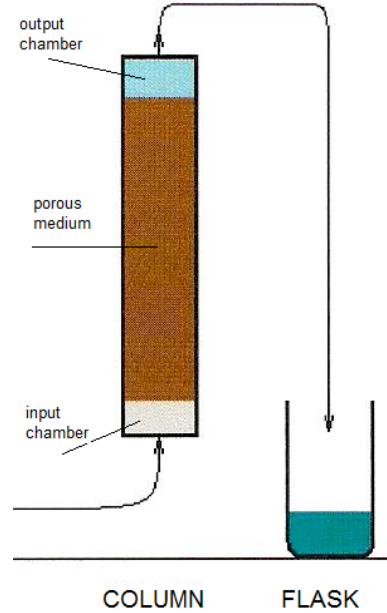

Fig. 1: **Scheme of laboratory column experiment.**

By the terms input and output chamber of the column we mean the volumes ahead of the porous medium cylinder and behind this cylinder. Those parts of the column are formed due to technology of column creation and they have various effects in various column experiments. Both chambers frequently contain another material than the column cylinder. When we do not include chambers into the model of column experiment, the parameters can be calibrated incorrectly. For better understanding we present the equation for computation of concentration of one species in the input chamber:

$$C_0(t + \Delta t) = C_0(t) + \frac{\Delta t \cdot Q(t)}{V_0}(C_{vst}(t) - C_0(t)) \tag{1}$$

where C_0 [mg l^{-1}] is concentration of one specie in the input chamber, t [s] is the actual time, V_0 [l] is volume of the input chamber, C_{vst} [mg l^{-1}] is concentration of the input solution and Q [l t^{-1}] is flow rate. Another type of the simplest model extension is the model of the output flask. The solute concentrations and properties in the real column experiment are measured in the output flask. The solution outflows from the output chamber into the output flask. At a certain time the flask is replaced and analyzed. Composition of the solution in the output flask is different than composition of the solute outflowing from the column computed by the simplest model. This is the reason why we include the computation of the output flask into the model. It is described by equations [2] and [3]:

$$V_{N+2}(t + \Delta t) = V_{N+2}(t) + \Delta t \cdot Q(t) \tag{2}$$

$$C_{N+2}(t + \Delta t) = \frac{C_{N+2}(t) \cdot V_{N+2}(t) + \Delta t \cdot Q(t) \cdot C_{N+1}(t)}{V_{N+2}(t + \Delta t)} \qquad (3)$$

where the index *N+1* refers to the output chamber, and the index *N+2* refers to the output flask.

CHEMICAL REACTION MODELLING

Following (Fang Y., 2003), while the coupling of hydrologic transport and chemical reaction models is an active area of research, the development of chemical reaction batch models has received much less attention. Whereas reactive parameters setting is more difficult then setting of transport parameters. Reactive transport program can not only compute with species concentrations. Information about other solute properties is important to include. Those properties are changing along the column experiment depending on current reactions and ambient conditions.

For example, setting of the solute and external atmosphere equilibrium is important for solute properties and inside chemical reactions. Otherwise setting of precipitation processes have an effect to solute composition and sometimes also transport properties. E. g. when column experiment takes only few days, it is not possible for hematite to precipitate; the mineral hematite is the final product of precipitation for solution including oxygen and iron but its precipitation needs at least hundreds of years (Zeman J., 2007) and column experiments do not last as long, so we have to suppress this mineral in the thermodynamic equilibrium computations.

The Transport program includes some setups to operate with given aqueous solutions. Setting of concentrations and solute properties is an important part of operation with reaction component of the process. The Transport program user can perform complete analysis of given solutions before he starts the computing of main simulation of the column experiment. The user can also compute the equilibrium of the solute and the atmosphere. Another program option is setting of different ambient conditions in different parts along the column model. For example, the user can prohibit the access of oxygen inside of column but he can allow the calculation of equilibrium with the atmosphere in the output flask.

Coupling of reactive chemistry with transport extends computation time significantly. In this time, some trends can be observed in the effort to deal with this problem (parallel programming or development of numerical methods). Our approach to this problem is different. It is based on finding the contamination front which is almost independent of kind of the applied software if we assume using the method of operator splitting.

THE METHOD OF CONTAMINATION FRONT

The method of contamination front is based on reduction of the number of chemical equilibrium computations. By the "contamination front" we mean the situation where the solute concentrations significantly change in time. For example, this situation occurs when two different solutions mix because of advection. In such a situation, many chemical processes take place so it is important to compute the chemical equilibrium there. In other places of the column we can suppose that simulation of chemical processes can be omitted. The Method of Contamination Front (MCF) is

based on looking for elements where the concentrations rapidly change. In this time, we are evolving two variants of the MCF: (1) testing the concentration change in time in each element, or (2) testing the concentration change along the streamline in one time.

In the first case (variant 1), we are searching the contamination front in every single element. We wait for a significant change of concentration of the chosen species. The level of importance depends on the coefficient k (Eq. 4). If we set up the coefficient $k=0.5$, change of the specie concentration has to be larger than arithmetic mean of the past and the present specie concentration.

$$|C_e(t) - C_e(t_{kont})| > (C_e(t) + C_e(t_{kont})) * k \tag{4}$$

where C_e [mg l^{-1}] is concentration of one specie in the element e, t_{kont} [s] is the time when the last concentration front was found, t [s] is the actual time, k [1] is the coefficient the MCF variant 1.

In the second case (variant 2), we are searching for the contamination front according to the situation in neighbouring elements. We check concentration of one species in every element using the equations (Eq. 5, 6, 7). Variant 2 uses only the concentrations in present time which can be an advantage for large 3D models.

$$C_- = C_{e-1}(t) - C_e(t) \tag{5}$$

$$C_+ = C_{e+1}(t) - C_e(t) \tag{6}$$

$$|C_- - C_+| > (C_- + C_+) * K \tag{7}$$

where C_e [mg l^{-1}] is concentration of one specie in the element e, K [1] is the coefficient of the MCF variant 2.

TESTING OF THE MCF

The MCF was tested on real column experiment that lasted about 340 hours. Flow lasted about 30 hours and the rest of the time, the column balance was stabilized. At the first time, the column was filled by the aqueous solution modelling original groundwater in the site. After the equilibrium reaching (start of the counting the time) an acid solution (contaminant) was injected into the column (it took about 10 hours). After the balance restoring (it took 310 hours) an alkaline solution was injected into the column (it took 20 hours). The alkaline solution was supposed to neutralize the contaminant. (Gombos L., 2006)

We computed reactive transport simulation for both variant of the MCF with different coefficients k and K. We compared results of those simulations with the complete reactive transport model. Complete reactive transport model consisted of 30 elements, and time step was 200 s. Consumed computation times of both variants with different coefficients are shown in the Tab. 1.

Here we present the last part of the experiment time interval (Fig. 2 and 3). In this part, the alkaline solution was mixed with acid solution inside of the column. The results of computations following individual variants differ mostly in this part of the experiment simulation time (among others, because of Alunite precipitation). For the

same reason, we present the results of computation of K^+ concentration and pH. Variances of other solute concentrations and properties are not so significant.

Table 1 **Time comsuption of computations using several variants of MCF.**

Variants of the method	Computation time [min]
MCF variant 2, K=0.3	4
MCF variant 2, K=0.01	69
MCF variant 1, k=0.1	5
MCF variant 1, k=0.01	18
Complete reactive transport	90
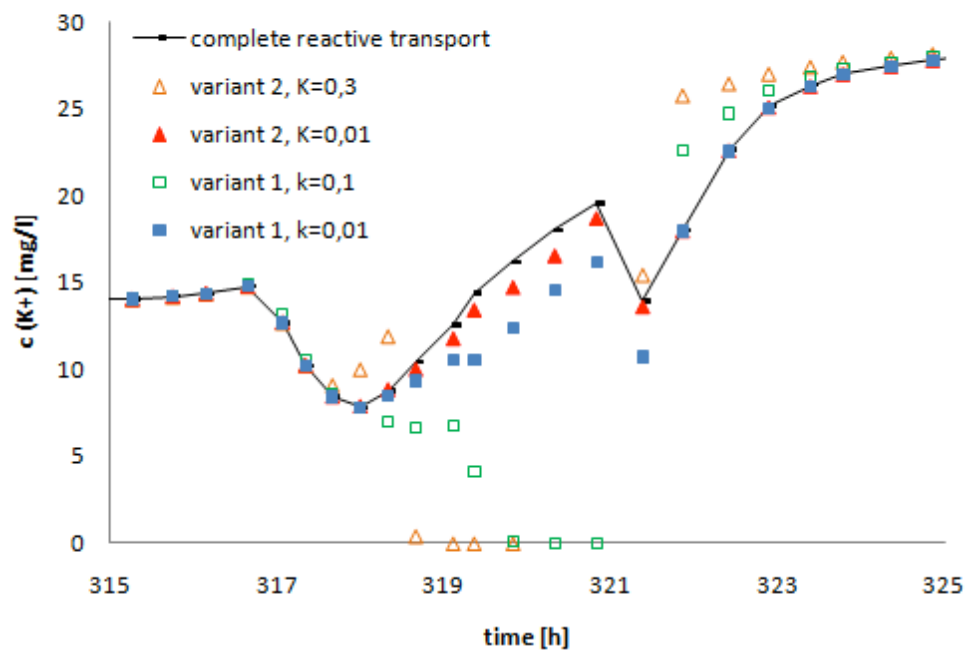
Fig. 2 **Dependence of concentration of K^+ ion on time computed using several variants of MCF compared to the "complete reactive transport".**
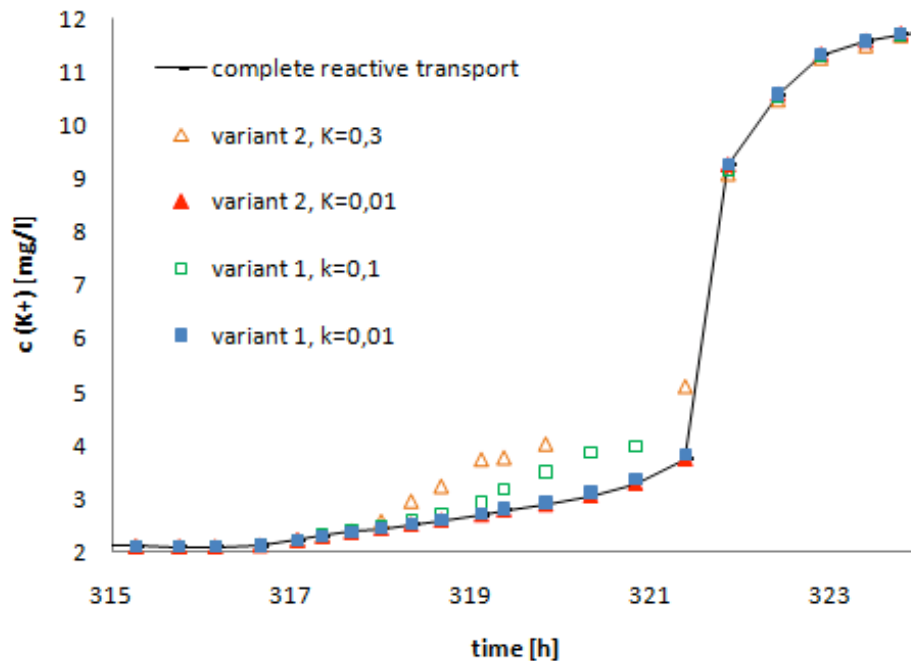
Fig. 3 **Dependence of pH on time computed using several variants of MCF compared to the ”complete reactive transport“.**

On Fig. 2 and Fig. 3, we can see that lowering of the coefficient *k* or *K* makes the computation more precise. The Tab. 1 shows that also the computation time is growing with growing accuracy. But if we compare accuracy of the MCF with complete reactive transport, computation time reduction can be significant.

CONCLUSIONS

This paper presented changes in column experiment model that were done to improve understanding to reactive transport processes. Parameters of real column experiment can be more precisely estimated and better implemented to 3D groundwater simulation.

The Method of Contamination Front reduced the computational time from hours to tens of minutes maintaining the accuracy of calculations of reactive transport.

At this time, the MCF is being tested on real column experiments and we are planning its implementation to a 3D reactive transport model.

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