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COUPLED REACTIVE TRANSPORT MODELING – THE PROGRAM TRANSPORT

VRATISLAV ŽABKA*, JAN ŠEMBERA*

*Institute of new technologies and applied informatics (NTI)
Technical University of Liberec,
Studentská 2, 461 17 Liberec, Czech Republic
e-mail: vratislav.zabka@tul.cz

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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.

Important part of the contribution would be demonstration of results of simulation of real transport column experiments recently realized at the Technical University of Liberec.

1 INTRODUCTION

Modeling of transport processes is becoming increasingly important in recent years. There are many areas where it is necessary to model the transport of heat and water. This paper and the Transport program have been developed for the needs of projects dealing with study of contamination. But the modeling of transport actions is not sufficient for the contamination problem. The reactive processes are also very important, because the contaminants affect their surroundings primarily chemically. Transport and reactive components can interact, that is why we are talking about a coupled problem.

An example of impact of the reactive component to transport may be the precipitation of mineral phase. It can affect mobility of all observed components. An example of the opposite effect may be a dependence of type of ongoing reactions on flow velocity. We study those and other influences using simulations of the Transport program.

Studying of such processes in the underground, about its composition we have only limited information, is extremely difficult or almost impossible. If we want to detect patterns of events that take place under the ground, we must study them in known conditions first. In the laboratory we can split both processes and test them separately. The reactive processes among solutions of different concentrations in flasks and transport processes using column experiments with simple solutions. Only when we can correctly simulate such processes separately, we can begin to combine them. The Transport program is used to simulate the combinations of these processes.

2 GENERAL SPECIFICATIONS

This paper aims to present the Transport program itself and design a methodology of its use for modeling of transport-reactive processes. The paper is divided into four main parts and conclusion. In the section 3 we present the Transport program and possibilities of its configuration. In this section we briefly describe the structure of calculation of the program itself as well as the structure of model problem.

An important part of the transport-reactive modeling is to understand the system from the perspective of chemical reactions. The importance of this phase of simulation will be discussed in the section 4. The Transport program itself does not calculate the reactive component of processes, but it uses the communication with geochemical software package from The Geochemist's Workbench (GWB hereafter). With this software, we can model the state of equilibrium of used solutions. This will give us knowledge of their properties and then we can compare them with changes within the transport.

A major problem in calculating the transport-reactive processes is their time-consuming intensity. In the section 5 we suggest a possible way to help. It is the Method of Contamination Front. This method is based on communication between the Transport program and the React program from GWB package. Presented method does not solve the problem of time-consuming intensity, but helps to properly set up the simulation. The resulting calculation will not be accelerated, but it is an important tool in studying the properties of processes in the stage of setting up the simulation.

The final part of the paper (section 6) will discuss the results of simulations in terms of accuracy and time-consuming intensity.

3 THE TRANSPORT PROGRAM V2.2

The Transport program is being developed at the Technical University in Liberec. It is a 1D model based on the Finite Volume Method. It can be used for simulations of column experiments, where the column is filled with a homogeneous porous rock saturated with homogeneous water solution and there are successively injected up to two different water solution. The model is adjusted so that before and behind the rock column there are so-called input and output chamber without a rock. It is well adapted for different kinds of measurements of output parameters of the solutions.

During its development our task was not to simplify the problem and to create a simple model. On the contrary, we expanded the simple model to resolve various types of experiments. The complexity of the model with more parameters emphasizes the accuracy of the modeled experiments. Then the information about the phenomena occurring in the column can be considerably more accurate.

Beside a detailed model of geometry of the column, it is difficult to improve the simulation of transport processes in any way. But large room for progress still remains in modeling of chemical reactions.

4 CHEMICAL REACTION MODELING

Following [1], 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 than 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 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 to compute the 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 significantly extends the 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 the kind of the applied software if we assume using the operator splitting method.

5 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 flowpath 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. 1). 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.

$$| C_e (t) - C_e (t_{kont})| > (C_e (t) + C_e(t_{kont}))\cdot k \quad (1)$$

where C_e [mg l^{-1}] is concentration of the chosen species in the finite volume 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 of the MCF variant 1.

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

$$\begin{gathered} C_- = C_{e-1}(t) - C_e(t) \\ C_+ = C_{e+1}(t) - C_e(t) \\ | C_- - C_+ | > | C_- + C_+|\cdot K \end{gathered} \quad (2)$$

where C_e [mg l^{-1}] is concentration of the chosen species in the finite volume e, K [1] is the coefficient of the MCF variant 2.

6 MODELING OF REAL EXPERIMENTS

In the previous three sections we have briefly discussed certain points of problems of transport-reactive processes. We will follow this introduction up with a specific example of simulation using the Transport program. In the introduction to this section we will set up a complex real problem, which we will divide into individual subtasks and present possible ways to solve them.

As it will be seen, this problem is very complex. Its solution is just at the beginning. At present, new experiments are still underway, which will help to better understand the issue. Therefore the final results of modeling of the specific task are not included at the end of the section. It is only an example of using the Transport program to simulate a particular phenomenon. Simulations of different systems may be done using the indicated procedure.

6.1 Description of the task

Currently, one of the objectives of our group is the use of iron nanoparticles for decomposition of organic contaminants in groundwater. A huge reactive surface is one of the known qualities of iron nanoparticles. Good migration property is their estimated quality. These miniature particles have the potential to penetrate even the smallest pores directly to the source of contamination. But their actual behavior is not well know, yet.

During the migration of nanoparticles through rock environment, their aggregation or sorption on the rock occurs. The exact physical and chemical principles of these phenomena are not yet sufficiently explained, or even modeled. For their explanation and for the discovery of other deviations from the behavior of larger particles we use the Transport program.

6.2 Simulation of tracer tests

One of the most important parts of the process is identifying the physical parameters of rocks and of the entire experiment. Errors made in their determination can lead to inaccurate or incorrect understanding of the characteristics of migrating nanoparticles.

The tracer test is used to determine the basic parameters of the experiment. To the column saturated with water or a solution of known properties we inject a saline solution and record the characteristics of outlet solution on the output. The most important observed parameter is the electrical conductivity; the secondary outlet is the pH of the solution. If we know the precise parameters of the column and the method of measuring the output characteristics, we can then calculate other properties of rocks. These include porosity, which can have substantial effect on the monitored processes.

Before we start modeling of the transport it is necessary to analyze the reactive components of the processes. By testing chemical properties of individual solutions and their combinations we gain important information about progress of the experiment. In the case of tracer tests using a saline solution and distilled water does not occur any complex chemical processes. From this analysis, we found the estimated value of pH.

6.3 Outputs of the experiment

The values of conductivity can be modeled very accurately. Conductivity for low concentration of the solution depends directly on the concentration of salt. Simulation of the pH of the output solution was not accurate (Figure 1). The difference of pH values in order of tenths is indeed very difficult to measure and thus very difficult to compare with the model. In our case a variation in the trend of changes in pH was observed. It was a problem as in general the trend of development of a certain quantity is more important than its specific value in geochemistry.

The measured change in pH occurred when the composition of output solution was changing. But the change was always more distinctive at the beginning of this change than supposed the model. The expected value was approached after a certain time. Using the Transport program, we tried to assess what might cause this unexpected deviation. By testing known options, we concluded that the determining phenomenon is the exchange of sodium and calcite ions at aluminosilicate clays that were present in the rock in the experiment. As can be seen from the chart, when the simulation included the sorption of sodium, the trend of the simulation corresponds much better to the measured values.

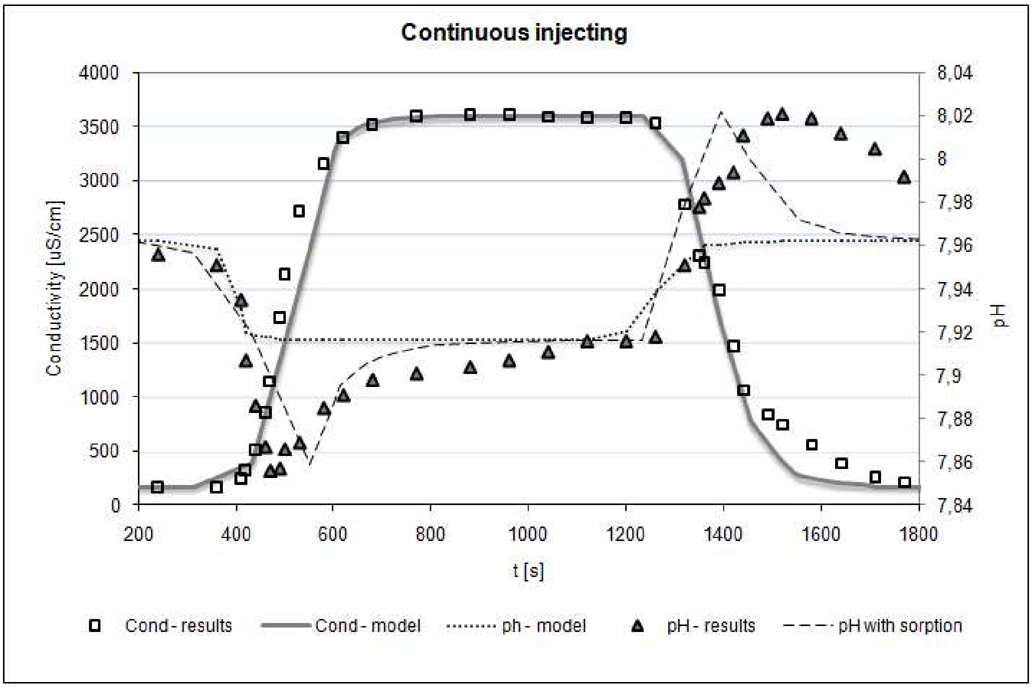

Figure 1: Continuous injecting – dependence conductivity and pH on time of the experiment.

To verify the correctness of our hypothesis, we proposed a further test experiment. Instead of rock, the column was filled with glass balls of size of tens of micrometers. Parameters of the column corresponded, but the exchange between ions in solution and ions of geological environment was excluded. The trend in pH during the experiment with balls and with rock remained unchanged, the hypothesis was thus refuted. We are still trying to attempt this phenomenon. Experiments are in progress.

6.4 Analysis of results and discussion

On this simple example, we wanted to demonstrate some of the ideas that are important in modeling of coupled problems not only in geochemistry. Also on this problem, we tested the time required for the calculation and compared it with the calculations using the method of front contamination.

The basis for modeling of coupled processes is a detailed knowledge of the various components of these processes. For this case of modeling of nanoiron migration, the first necessary is to test the transport and chemical properties of the monitored system. That is in our case the tracer test and monitoring of interactions between particles of nanoiron with different solutions and rock environment.

Although we believe that we know the observed system and we are able to describe its deviations from the normal state, it is useful to doubt our results and perform test simulations under various conditions over and over again. Only by the reactions of the system under various conditions we can learn more about it.

On the model tracer tests, we also compared the influence of the coefficient of the method of contamination front and its other settings to its time-consumption. The calculated results were then compared with the total calculation time without using the previously mentioned method (Table 1). The comparison is only approximate, because the computing time can vary with the complexity of simulated systems. The faster calculation method can be used, the system is the simpler. For example, variant 1of MCF with K = 0.01 can be used for complex actions including precipitation. And even this version is many times faster than the complete calculation.

Table 1: Examples of computation times using two variants of MCF with different coefficients. Average deviation is comparing of results of the MCF variant and complete reactive transport computation.

Variants of the method	Computation time	Average deviation [%]
Complete reactive transport	19h 16min 57s	
MCF Variant 2, K=0.1	9h 8min 39s	0.01
MCF Variant 2, K=0.3	2h 43min 32s	1.58
MCF Variant 1, k=0.01	44min 29s	0.21
MCF Variant 1, k=0.1	16min 27s	5.52

7 CONCLUSION

This paper contains a brief description of the Transport program. This program is a powerful tool for studying both simple and complex processes occurring during the column experiment. This is achieved by the wide range of setting transport and reactive parameters of the experiment. The paper also briefly describes the methodology for modeling of transport-reactive processes.

The paper also proposes a method of speeding up the work on modeling of transport-reactive processes by looking for the contamination front. Although the method itself speeds up the resulting simulation only at the cost of losing some information, it still can be a valuable tool in finding the correct parameters resulting simulation. It does not need to be limited just to the 1D problem. Currently we are working on its extending to more complex problems.

Last part of the paper is a demonstration of some simple simulation of column experiments. Their example demonstrates a possible way to work with the Transport program. The results were also compared to time simulations using the method of contamination front.

Besides introducing suitable instruments for the study of transport-reactive processes, the authors of this paper wanted to draw intention to the complexity of the modeled processes. Without proper understanding of elementary processes, it is not possible to adequately simulate complex actions that are dependent on elementary ones.

When creating models of complex systems it is necessary to simplify them. But we often certainly do not know if we can make some simplification. If it is a study of coupled problems of transport-reactive processes, the Transport program is a suitable tool for studies of these systems.

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