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An efficient time scaling technique for coupled geochemical and transport models

Ivars Neretnieks *, Ji-Wei Yu, Jinsong Liu

Department of Chemical Engineering and Technology, Royal Institute of Technology, S-100 44, Stockholm, Sweden

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Abstract

In earlier work using coupled geochemical and transport models such as CHEQMATE, HYDROGEOCHEM, PHREEQM and other codes, we have found that, when the mass of mineral phases in the system is large compared with the solubilities of the minerals in the water, computing times become prohibitively large. These problems have been found for several systems of interest for radionuclide migration. In a study of the coupled formation and movement of redox fronts, hydrolysis fronts and dissolving and precipitating secondary minerals, scaling of the amounts of the minerals could be made without influencing the results. This is not possible in general.

In these circumstances the computations would typically need millions or many millions of time steps to have the fronts move through one "cell" in a finite difference based code. It has been noted, however, that this also leads to stationary states, developing in the system. This has been pointed out and utilised by Lichtner. We have developed a code, CHEMFRONTS, which utilises this property. The drawback is that it is not easy to incorporate diffusion/dispersion using this approach. It can only handle advection dominated transport. For such cases however it is extremely fast compared with conventional codes.

We have now developed a technique whereby the stationary state approximation can be superimposed on and incorporated in finite difference and finite element codes. This speeds up the computations considerably. So far we have used it successfully in CHEQMATE, HYDROGEOCHEM and PHREEQM.

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* Corresponding author. Tel.: +46-8-790 8229. Fax: +46-8-10 52 28. E-mail: niquel@chemeng.kth.se.

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In this paper we show the method and give some examples of its application using previously addressed problems.

Keywords: Diffusion–dispersion; Chemical reactions; Numerical models; Finite difference analysis; Finite element analysis; Quasi-stationary approximation; Time scaling techniques

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1. Introduction

In the concept of final disposal of nuclear waste, coupled geochemical and transport models are used to model the water/rock interaction in geological formations. The models usually consist of two parts: the geochemistry part and the mass transport part. The transport part describes the diffusive/dispersive and advective mass transport of solute; the geochemistry part describes the various geochemical reactions, including sorption/desorption, precipitation/dissolution, acid/base neutralisation, aqueous species complexation, redox reactions, etc. The transport is represented mathematically by a set of partial differential equations (PDEs). The chemical reactions, under the assumption of local equilibrium, are described by a set of nonlinear algebraic equations (AEs). For a comprehensive review of the coupled geochemical and transport models, see e.g. Yeh and Tripathi (1989) and Neretnieks (1993).

Most of the available coupled transport/reaction codes have difficulties in handling the situations when mass of the mineral phases in the system is large compared with the solubilities of the minerals. The computation time will become prohibitively large. There are several reasons for this. When the PDEs describing the transport are solved with finite difference approximations with the explicit method, e.g. in CHEQMATE (Haworth et al., 1988) and PHREEQM (Appelo and Willemsen, 1987), there is always a numerical stability constraint for the length of time steps (Lapidus and Pinder, 1982). For those codes which use finite element approach, like HYDROGEOCHEM (Yeh and Tripathi, 1991), local equilibrium assumption also poses limitations to the length of time steps, as too large a perturbation from equilibrium can easily cause the program to tumble into convergence problems.

To ease these kind of time-step restrictions, various techniques have been proposed. By adapting the spatial grid to moving boundaries, in advection-dominating systems of coupled transport and reactions, the calculation can be readily speeded up (Lichtner, 1992). It is difficult, however, to use the moving boundary technique in diffusion-dominating systems. Recently, a general scaling technique has been proposed (Lichtner, 1993) to be used in systems of mass transport coupled with chemical reactions of finite rates. It has been demonstrated that scaling the rate constants of such reactions by a common factor and the diffusion coefficient by the reciprocal factor is equivalent to scaling the time and space coordinates by the same factor. The scaling techniques do not, however, influence the numerical stability criteria discussed below, which we set out to circumvent. When the quasi-stationary approximation applies, even in diffusion-dominating systems, we can still take advantage of the quasi-stationary properties of the transport to speed up the calculations, in a simple and straightforward way.

In this paper we present an efficient time scaling technique to speed up the calculations of coupled transport/reaction models. The technique is theoretically based on the quasi-stationary state approximation (Lichtner, 1988). It can, however, be applied to other codes that are not directly based on this approximation. This technique has been tested in several codes, and it works properly and increases the computing speed substantially.

2. Numerical stability and local equilibrium constrains on length of time steps

In most of the coupled codes, the explicit finite difference method is used to solve the PDEs. There is a numerical stability limitation in the length of time steps for the explicit method (Lapidus and Pinder, 1982). The criterion is that the numerical procedure is stable only when

$$\Delta t \leq \frac{0.5(\Delta x)^2}{D_L} \tag{1}$$

where Δt is the length of the time step, Δx is the length of the discretised cell and D_L is the dispersion coefficient of the transported species.

Another necessary criterion (Walter et al., 1994) is that the Courant number

$$\mathrm{Co} = \frac{u \Delta t}{\Delta x} \leq 1 \tag{2}$$

where u is the velocity of the flow ($\mathrm{m\,s^{-1}}$).

Physically this means that in one time step one cannot move more water from one cell to the next than the water volume in the cell. This is a very severe limitation as also the mineral in a cell must be depleted by dissolution, because many time steps will be needed to dissolve the mineral in the cell. In those codes which use finite element method, there are similar limitations of the length of time steps.

In itself the time step restrictions, Eqs. (1) and (2), are not very severe if there are no reactions with solid phases. Then only the water in the flowpath has to be displaced a few times. A few hundred to thousand time steps usually suffice for one-dimensional problems to simulate the breakthrough curves. The complication arises when there is a large mass of solid that reacts and only a very small fraction of the solid dissolves (or precipitates) at every passage of a pore volume of water. Not uncommonly the solubilities of many interesting minerals are very small compared with the amounts of minerals residing, per volume of water, in the flowpath. This means that many, often thousands to millions, of pore volumes must flow through the system before all of a mineral can be dissolved. This easily gives numbers of time steps of the order of millions to billions or more in typical problems. Not even the largest computers suffice for this. The situation is even more complex when many different minerals dissolve and precipitate.

3. Direct implementation of the quasi-stationary state approximation

The code CHEMFRONTS (Bäverman, 1993 and Bäverman et al., 1995) has a direct implementation of the quasi-stationary state approximation. The approximation is based on the following reasoning. When the quantities of minerals are very large compared with the species in the water, it is often possible to neglect the local accumulation of species in the liquid. In CHEMFRONTS, diffusion and dispersion are not considered. The amount of advective transport is then set to be equal to the reaction (dissolution or precipitation) rate of minerals. The mineral reaction rates are assumed to be proportional to the difference between the ion activity product (IAP) and the solubility product of the mineral. The reaction rate can be made very large if one wants to simulate local equilibrium as is done in most other models. The governing equations are:

$$\bar{\bar{A}}\frac{\mathrm{d}\bar{C}}{\mathrm{d}z}=\bar{F} \tag{3}$$

where $\bar{\bar{A}}$ is a square matrix whose elements consist of stoichiometric coefficients of the various aqueous phase reactions, $\bar{C}$ is a column vector of the concentrations of primary species, and $\bar{F}$ is another column vector describing the mineral reaction rates. As the mineral reaction rate equation contains the IAP of the mineral, $\bar{F}$ is also a function of $\bar{C}$. For more detailed description of the code, see Bäverman (1993).

For a given mineral pattern in a system, aqueous concentration profiles can be calculated by solving Eq. (3) and the mineral reaction rates can also be calculated in each region. The mineral patterns will change as a result of the dissolution and precipitation reactions. The new patterns are determined and one time step is taken. After sufficiently many time steps, the rate of propagation of the mineral reaction fronts, e.g. redox fronts, becomes constant and can be extrapolated to a later time. It is demonstrated that the propagation rate of the fronts is practically constant when steady-state is achieved if the reaction rates are fast. This steady-state propagation of dissolution/precipitation waves has also been shown in other systems (Walsh et al., 1984; Bryant et al., 1987).

The CHEMFRONTS code is very suitable to handle the development and movement of sharp fronts such as redox fronts. The code is also very fast compared with other available codes. The code, however, has some drawbacks. It is not easy to incorporate diffusion/dispersion when using the quasi-stationary state approximation directly. There is also some numerical problem when the concentrations become extremely low, as e.g. in the case for oxygen under strongly reducing conditions. Negative concentrations can sometimes be generated in the iterations. Below we will present a novel approach which can avoid the generation of negative concentrations. The idea is to use logarithmic concentrations instead of the free concentrations as independent variables in the model. The logarithmic concentration is defined as $c=\ln C$ and the spatial derivative of the logarithmic concentration is

$$\frac{\mathrm{d}c}{\mathrm{d}z}=\frac{1}{C}\frac{\mathrm{d}C}{\mathrm{d}z} \tag{4}$$

where c is the logarithmic concentration and C is the free concentration of the component.

The introduction of the logarithmic concentration leads to a new governing equation system

$$\overline{\overline{B}}\,\overline{\frac{\mathrm{d}c}{\mathrm{d}z}} = \overline{F} \tag{5}$$

The elements of $\overline{\overline{B}}$ are defined as

$$b_{jk} = \begin{cases} C_j + \sum\limits_i v_{ij} v_{ik} C_{xi} & \text{for } j = k \\ \sum\limits_i v_{ij} v_{ik} C_{xi} & \text{for } j \neq k \end{cases} \tag{6}$$

where C_j is the concentration of primary species, C_{xi} is the concentration of complex, v_{ij} is the stoichiometric coefficient of complex reactions.

The variation range of the logarithmic concentration is much smaller than that of the original concentration during the calculation. When the logarithmic concentration returns to the original concentration, the concentration is calculated as the exponential function of the logarithmic concentration, which will never be negative.

4. The time scaling technique and its applications to various programs

In circumstances where the quasi-stationary state approximation does not apply, and when dispersion/diffusion is important, other computer codes that do not directly implement the quasi-stationary state approximation are more applicable. The computation times of these codes are usually prohibitively large for real-case problems. Below we present an efficient time scaling technique, which enables many codes to be free from the restrictions of directly assuming the quasi-stationary state approximation, but still to benefit from the acceleration of computing speed that the quasi-stationary state approximation gives. We first present the theoretical basis, the generic logic and algorithm of the time scaling technique, followed by examples of implementation of the technique in several widely used codes.

The basic rationale of the time-scaling technique is as follows (Liu, 1995). When the system is in local chemical equilibrium both within the aqueous phase and between the aqueous and the mineral phases, the aqueous phase composition is primarily determined by the minerals present, but not by the quantities of the minerals. When the mineral sequence does not change in the system, i.e. neither new minerals emerge nor any existing minerals are exhausted, the composition of the aqueous phase does not change.

The generic logic and algorithm of the time scaling technique are as follows. During one time step, the amounts of different minerals precipitated and dissolved are calculated. If there is no change of mineral sequence in this time step in any of the discretised cells in the system, it is assumed that there will be the same aqueous phase compositions (the same concentration profiles spatially), and the same amounts of minerals precipitated or dissolved, in the next time step. This can be extrapolated to the time steps that

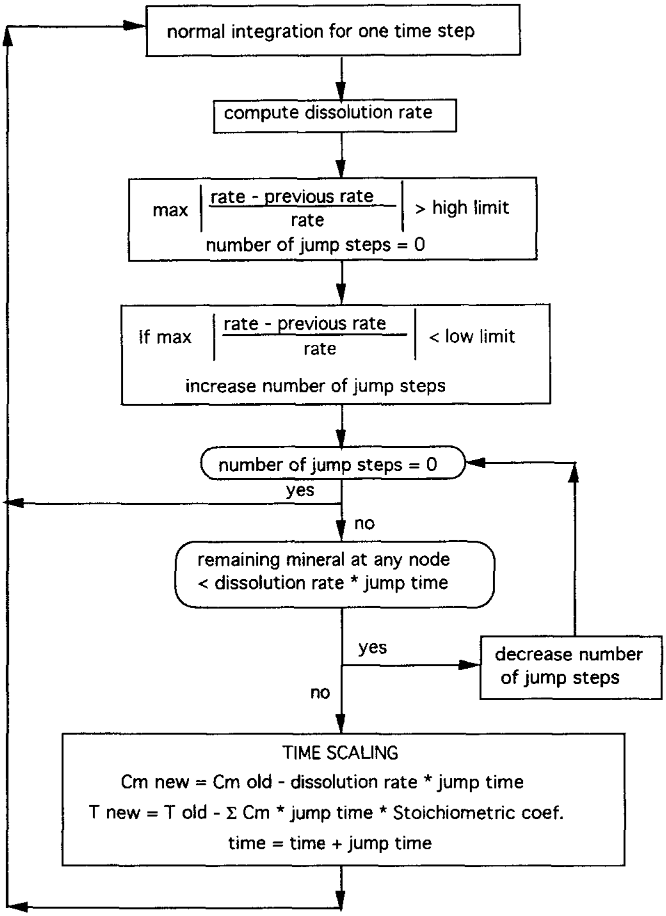

Fig. 1. The logic of the time scaling approach.

still follow, until the mineral sequence in any of the cells changes. Then the concentration profiles of aqueous species are re-calculated and the above procedures are repeated. Another criterion to take the jump of time steps can be the relative difference of mineral depletion/generation rates between two time steps. If the relative difference is small, the scaling technique is applied, otherwise it is not. A flow sheet of the logic of the scaling approach is shown in Fig. 1.

4.1. Test in CHEQMATE

The time scaling technique has so far been tested in three widely used codes: CHEQMATE, HYDROGEOCHEM and PHREEQM. The CHEQMATE code (Haworth et al., 1988) models one-dimensional diffusion and advection of aqueous species with chemical equilibrium. The chemical part is based on PHREEQE (Parkhurst et al., 1985). The transport part is solved by an explicit forward finite difference method. The code includes an automatic mineral accounting procedure, so that solid phases may be added or removed from the system as precipitation or dissolution occurs.

In version 6.25 of CHEQMATE, the time scaling technique is tested. It is coded in the main program before and after the calling of the PHRQCL subroutine. The modified version has been used to model the near-field of the Cigar Lake uranium deposit, and the results obtained agree with other simulations and do not contradict field observations.

4.2. Test in PHREEQM

PHREEQM (Appelo and Willemsen, 1987) can model the multi-component transport in a one-dimensional column, coupled with chemical equilibria between the aqueous phase and the mineral and gas phases, including redox, complexation, precipitation/dissolution and cation exchange. The advective transport process is simulated by flushing aqueous solution through the discretised cells, i.e. by replacing the aqueous solution in one cell with that in the upstream cell. The axial dispersion is modelled using partial exchange and mixing of the water contents in the adjacent cells. This replacing and mixing is just another way to implement the finite difference method. Except for this, the code has similar features as CHEQMATE.

The time scaling technique is coded in subroutine COLUMN in the July, 1987, MOS-DOS version of PHREEQM. Preliminary test of the modified code has been carried out for several problems, including solid waste leaching and a simplified case of the Poços de Caldas uranium mineral, and the technique works well with the code.

4.3. Test in HYDROGEOCHEM

The code HYDROGEOCHEM models the transport of soluble species in water flowing through a porous medium composed of solid phases. The chemical reactions between the species in the aqueous phase and the solid phases are assumed to be of local equilibrium. To the numerical solution, a weighted-residual finite element method is used for spatial discretisation and finite difference approximation is used for time integration.

The time scaling technique has been tested and works with the examples used.

4.4. Examples of applications of the time-scaling technique

The time-scaling technique discussed in this paper has been applied to several studies with coupled transport/reaction models. Examples of these applications will be given below. For more details, we refer to the references.

In the natural analogue studies of the Cigar Lake uranium deposit (Liu, 1995), the coupled transport/reaction models have been tested, to simulate the various geochemical reactions and mass transport, especially the observed hematisation (oxidation of pyrite to hematite) in the clay surrounding the ore body. The oxidants was assumed to be generated through water radiolysis in the ore body. As the ore body was formed 1.3×10^9 years ago, the numerical simulations with coupled codes should also cover this time span. Because of the stability criteria discussed above, most of the available codes would need billions of time steps in the simulations.

The time-scaling technique was applied. The code used there was CHEQMATE (Haworth et al., 1988). A time scaling factor of 10^4–10^5 was used. With the time-scaling technique, the simulation could be carried out within a few hours and a few tens of hours on a normal desktop computer. Analytical solutions were used to compare with the numerical results, but for different subsets of the problem. The results did not contradict the field observations.

Another example of the application of time-scaling was in the coupled transport/reaction modelling of the long-term stability of the bentonite buffer surrounding a spent-fuel canister in a final repository (Liu and Neretnieks, 1996). In this study, scaling factors of 10 and 100 was used. With these factors, the simulation could readily be done to cover a time period of about one million years. The results agree with those obtained without time scaling. But the computation is 10 and 100 times faster, respectively.

5. Discussions and conclusions

Real-case modelling of coupled mass transport with geochemical reactions by most of the available codes often takes prohibitively long computation time. With the quasi-stationary state approximation, the computation can be speeded up, but the widely used codes do not fully implement this approximation. There are also cases in which the approximation may not be applicable.

The time scaling technique presented in this paper can speed up the numerical calculations of codes that do not a priori assume the quasi-stationary state approximation to be valid. The technique is theoretically based on the quasi-stationary approximation. Its implementation in codes is relatively easy and straight forward. It has been tested in several widely used codes and seems to work well.

When coded in a program, the time scaling technique does not necessarily require the code to implement the quasi-stationary state approximation. The accumulation of species in the aqueous phase, therefore, need not be neglected. The dynamic evolution of water composition as well as mineral patterns can both be simulated.

The reasoning of the time scaling technique is that, when local equilibrium is assumed, and when the solubility of mineral is small compared with the species present in the solid phases, steady-state propagation of the mineral reaction fronts can be achieved. This has been demonstrated in CHEMFRONTS when the quasi-stationary state approximation is fully implemented (Bäverman, 1993), and in some special systems (Walsh et al., 1984; Bryant et al., 1987). Whether it is still true in other circumstances still needs to be demonstrated.

In this paper, the logarithmic concentration approach to avoid negative concentrations has been applied to CHEMFRONTS. It has helped to avoid over- or under-flow problems.

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