

1992

P.M.C. Thoolen, P.W. Hemker

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Department of Numerical Mathematics Report NM-R9223 November

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Approximate Methods for N-component Solute Transport and Ion-exchange

P.M.C. Thoolen and P.W. Hemker

University of Amsterdam, and
CWI

P.O.Box 4079, 1009 AB Amsterdam, The Netherlands

Abstract. We consider the computation of ion-exchange when an ambient groundwater of one uniform composition is displaced by an injection solution of a constant but differing composition. The problem is to sort out the composition change from the initial to the injected compositions. An analytical method for the n -dimensional homoivalent system is described by Rhee, Aris and Amundson (1970). Conditions are given under which this method can be used to calculate an approximate solution to the plateau concentrations in the n -dimensional heterovalent system. Further, two algorithms for the three-component heterovalent system are derived from Charbeneau (1988). Finally, a discretisation method is introduced in which the concept of adaptive mesh refinement is applied. Such a method can be used in more complex situations and it still can represent sharp moving fronts.

The results for the different approximate computations are compared for a real life problem as found in Valocchi(1981).

1991 Mathematics Subject Classification: Primary: 65C20. Secondary: 39-00, 39-04, 68Q22, 68Q35.

1991 CR Categories: G1.8.

Keywords and Phrases: Ion-exchange, approximate computation, heterovalent system, self-adaptive discretisation, time-dependent hyperbolic system.

1 Introduction

Many chemical processes, like complexation, redox, precipitation-dissolution and ion-exchange, affect the transport of reacting solutes in porous media. In this paper it will be assumed that solute transport is uni-directional and isothermal. Also is assumed that the transport takes place in a homogeneous porous medium with constant pore-size, and with virtually constant water-content, water-density and water-viscosity. Furthermore, we only describe the influence of ion-exchange on the transport. Ion-exchange is a chemical process in which ions are migrating between the aqueous- and mineral phase, until a chemical equilibrium has been reached. This chemical equilibrium is described by algebraic equations.

Suppose a solution of reactive contaminants is migrating through a column. The column consist of a porous medium with pore-size ϵ . The migration velocity will be taken v . The diffusion-effects will be assumed to be negligible, compared to the convective transport (this is justified if the flow velocity is not too small).

A chemical process can either be 'fast'(equilibrium-type) or 'slow'(kinetic type), and thus have a very different effect on the migration process. We consider the equilibrium-type, which means that there will always be a local equilibrium between the aqueous and the mineral phase.

In this paper we introduce an adaptive finite volume (FV) method that can be used to approximately solve complex multi-component problems with a good approximation of possible discontinuities in the solution. We compare this method with more common approximate methods based on analytic results. We do not claim that for relatively simple problems FV methods should be used: for more complex problems they will be unavoidable. We only want to show how good FV methods can be made available.

Report NM-R9223

ISSN 0169-0388

CWI

P.O. Box 4079, 1009 AB Amsterdam, The Netherlands

In Section 2 we give a mathematical description of the transport and chemical equilibrium equations. We describe the Riemann problem in the case of ion-transport, and we compute the velocity with which every ion concentration variation propagates.

In the third section we treat two different analytic approximation methods for the equations derived in Section 2. First we describe the method of *Rhee, Aris* and *Amundson*, which can be applied in the n -dimensional homovalent system. We show that, under some conditions, the method yields a first approximation to the solution in the n -dimensional heterovalent system. This approximation can be used as starting value in the iteration process of the method of *Charbeneau*, which is an efficient algorithm for the three dimensional heterovalent system.

In Section 4 we introduce the adaptive discretisation method, which is needed in any case when we want to solve much more complex systems. We show that the adaptive mesh refinement technique is an efficient tool to model n -component solute transport, and especially the discontinuities that can emerge in the solution. The concept of the limiter, known from gas dynamics computations, is introduced in order to construct a difference scheme that is second order in space.

In the last section we apply the approximation methods to cation transport, as described by *Valocchi* [10], in a field project in the Palo Alto Baylands Region, and we compare the results obtained.

2 Mathematical description of the problem

A mathematical description of one-dimensional transport in a column is given by the mass-balance equations. These equations are differential equations, whereas the chemical equations are algebraic. The two equations form a system of basic transport equations that are mathematically 'mixed'. The set of equations is given as follows:

$$\epsilon \frac{\partial c_i}{\partial t} + (1 - \epsilon) \frac{\partial \bar{c}_i}{\partial t} + v \epsilon \frac{\partial c_i}{\partial x} = 0 \quad (1)$$

$$\left(\frac{c_j}{\beta_j}\right)^{1/\nu_j} = K_{ij} \left(\frac{c_i}{\beta_i}\right)^{1/\nu_i} \quad (2)$$

with ϵ and v as introduced above, and

c_i : concentration of ion i in the aqueous phase in eq dm^{-3} ;

\bar{c}_i : concentration of ion i in the mineral phase in eq dm^{-3} ;

$CEC = \sum_{j=1}^n \bar{c}_j$ (Cation Exchange Capacity in eq dm^{-3});

$\beta_i = \bar{c}_i / CEC$ (dimensionless);

ν_i : charge of ion i ;

K_{ij} : The selectivity coefficient defined for the reaction where ion i exchanges for ion j .

Equation (2), the mass-action equation, is an ideal version of the true exchange equation. It makes use of the values of the exchangeable fractions (β), and of the solute concentrations c . In the true mass-action equation one has also to deal with values of the activity (effective concentration) of the ions on the exchanger-surface, and the activity of the ions in solution.

We can rewrite (2) to an equation from which it is possible to determine β_j , if all c_i are known, $i = 1, \dots, n$, as follows:

$$K_{ij}^{\nu_i} c_i \left(\frac{\beta_j}{c_j}\right)^{\nu_j} = \beta_i, \quad (3)$$

$$\sum_{i=1}^n K_{ij}^{\nu_i} c_i \left(\frac{\beta_j}{c_j}\right)^{\nu_j} = 1. \quad (4)$$

As a consequence, if all c_i and only one β_j are known, the other β_i 's can be determined from (4). To solve (4) for β_j , we may use Newton-Raphson iteration. This method will converge if we choose the starting values sufficiently close to the solution, because (4) is twice differentiable with respect to β_j ,

2.1 The Riemann problem

Equations (1) - (2) form a quasi-linear system of n partial differential equations of first order. With the initial and boundary conditions given by

$$\begin{aligned} y > 0, \quad t = 0, \quad \alpha &= \alpha^{init}, \quad \beta = \beta^{init} = f(\alpha^{init}), \\ y = 0, \quad t \geq 0, \quad \alpha &= \alpha^{inj}, \quad \beta = \beta^{inj} = f(\alpha^{inj}), \end{aligned}$$

the system (1) - (2) is called a Riemann problem. In this notation, β and α are vectors. We can rewrite (1) so that the concentrations in both the mineral and the aqueous phase become dimensionless. We therefore define

$$\begin{aligned} y &:= x/v, \\ B_0 &:= CEC(1 - \epsilon)/\epsilon, \\ A_0 &:= \sum_{i=1}^n c_i^{inj}, \\ \alpha &:= c/A_0. \end{aligned} \quad (5)$$

Substitution of (5) into (1) - (2) gives, in conservation form,

$$\frac{\partial \alpha}{\partial y} + \frac{\partial f(\alpha)}{\partial t} = 0, \quad (6)$$

with $f_i(\alpha) = \alpha_i + \beta_i(\alpha)$ and $\beta_i(\alpha)$ such that

$$K_{ij}^{\nu_i \nu_j} = \frac{(A_0 \alpha_j)^{\nu_i} \beta_i^{\nu_j}}{(A_0 \alpha_i)^{\nu_j} \beta_j^{\nu_i}}, \quad (7)$$

We may write (6) also as

$$(I + A) \frac{\partial \alpha}{\partial t} + I \frac{\partial \alpha}{\partial y} = 0, \quad (8)$$

with the matrix A given by $A_{ij} = \frac{B_0}{A_0} \left(\frac{\partial \beta_i}{\partial \alpha_j}\right)$.

The partial derivatives of β can be deduced from the mass-action equation (4) by differentiating (4) with respect to c_k , $k = 1, \dots, n$. This yields after rewriting to the dimensionless variables α and β :

$$\frac{\partial \beta_j}{\partial \alpha_k} = \left(\frac{B_0 \beta_j}{A_0 \alpha_j}\right) \delta_{jk} + \frac{\nu_j \beta_j}{\sum_{i=1}^n \nu_i \beta_i} \frac{B_0}{A_0} \left[\frac{\beta_n}{\alpha_n} - \frac{\beta_k}{\alpha_k}\right], \quad (9)$$

with δ_{jk} Kroneckers delta.

Let $\alpha(y, t)$ be a solution to the system (8) and (7), and the initial and boundary conditions. Then it follows that $\alpha(\rho y, \rho t)$ satisfies these conditions as well. If the solution is unique, $\alpha(y, t) = \alpha(\rho y, \rho t)$, so α is a function of only y/t . We define a parameter θ , $\theta = \theta(y/t)$, such that $\alpha = \alpha(\theta)$. It is then possible to write (1) as

$$\left((I + A) \frac{\partial \theta}{\partial t} + I \frac{\partial \theta}{\partial y} \right) \frac{d\alpha}{d\theta} = 0. \quad (10)$$

System (10) can only have a non-trivial solution if

$$|I + A - I\lambda| = 0, \quad (11)$$

with $\lambda = -(\partial\theta/\partial y)/(\partial\theta/\partial t)$. The solutions $\lambda^{(i)}$ to the algebraic equation (11) are the eigenvalues of $A+I$, so that, when $\lambda = \lambda^{(i)}$, the vector $d\alpha/d\theta$ must be proportional to the right eigenvector $r^{(i)}$ of $A+I$, corresponding to $\lambda^{(i)}$. As system (10) is assumed to be hyperbolic, there will be n distinct real eigenvalues $\lambda^{(i)}$ with n corresponding eigenvectors. Because $d\alpha/d\theta \propto r^{(i)}$, (10) is equivalent with

$$\left(\lambda^{(i)} I \frac{\partial \theta}{\partial t} + I \frac{\partial \theta}{\partial y} \right) \frac{d\alpha}{d\theta} = 0 \quad (12)$$

for each $i = 1, \dots, n$. With the notation

$$\frac{d\cdot}{d^{(i)}} = \lambda^{(i)} \frac{\partial \cdot}{\partial t} + \frac{\partial \cdot}{\partial y}, \quad (13)$$

it follows from (12) that $d\alpha/d^{(i)}=0$, so α is constant along a curve with $dt/dy = \lambda^{(i)}$.

Because β is a function of α only, also β is constant along this curve. Since $\lambda^{(i)}$ is a function of α and β , it must be constant, and the curve is a straight line. We see that for each i , $\lambda^{(i)}$ corresponds to a $C^{(i)}$ -family of characteristic curves, and for the n distinct eigenvalues there are n different $C^{(i)}$ -families.

For the solution of (10) the characteristics of one $C^{(i)}$ -family should not intersect. If intersection takes place, we have to introduce a discontinuity (see Jeffrey [6]) or shock wave. In the y - t plane, the mapping of the shock wave is a curve, whose derivative yields the velocity with which the discontinuity propagates.

Each characteristic in (t, y) space is associated with a state vector α , and hence with a point in the concentration space \mathcal{A} , and each $C^{(i)}$ simple wave maps on a single curve $\Gamma^{(i)}$ (the simple wave path). Together, the curves $\Gamma^{(i)}$ form an arc Γ , the concentration route that connects α^{inj} to α^{init} in \mathcal{A} . If one has one or more shock waves between several simple waves, the arc Γ in the concentration space contains an equal number of gaps, indicating the 'step'-wise changes of the concentration.

2.2 Velocities of simple waves and shocks

Because (12) is a transport equation, we know that $1/\lambda^{(i)}$, physically spoken, is the velocity with which every α variation propagates in the i -th characteristic direction. For all $i = 1, \dots, n$, $\lambda^{(i)}$ is given by

$$\lambda^{(i)} = 1 + \frac{B_0}{A_0} \frac{d\beta_j/d\theta}{d\alpha_j/d\theta}. \quad (14)$$

It is clear that, on each characteristic curve,

$$\frac{d\beta_1/d\theta}{d\alpha_1/d\theta} = \dots = \frac{d\beta_n/d\theta}{d\alpha_n/d\theta}. \quad (15)$$

The equation is the fundamental differential equation of the Riemann's problem, the solution of which generates the curve $\Gamma^{(i)}$, being part of the concentration route in the n -dimensional concentration space.

In case of a discontinuity, the differential equation (8) does not hold any more. Now, from the integral form of the equation, we derive the velocity of the discontinuity as the generalised Rankine-Hugoniot relation. We find

$$[\alpha_j]\dot{s} + \frac{B_0}{A_0}[\beta_j]\dot{s} - [\alpha_j] = 0. \quad (16)$$

The symbol $[\]$ denotes the jump of its argument across the discontinuity.

Since dt/ds must be the same for all j , the following compatibility equation is fulfilled:

$$\frac{[\beta_1]}{[\alpha_1]} = \dots = \frac{[\beta_n]}{[\alpha_n]}. \quad (17)$$

Equations (16) and (17) together form a system of algebraic equations analogous to (14) - (15).

3 Approximate solution methods

To solve the set of equations (1) - (2) for the homovalent case (all $\nu_j = \nu$ equal) we know the method of Rhee, Aris and Amundson [8]. They develop analytical formulas to compute the plateau concentrations α^{p_i} , $i = 0, \dots, n$. These are the concentrations at the end points of every simple- or shock wave path $\Gamma^{(i)}$, that corresponds to the $C^{(i)}$ family of characteristic curves. In the homovalent case it appears that the curves $\Gamma^{(i)}$, are straight lines. as a function of suitably chosen θ . Thus, Rhee, Aris and Amundson succeed in transforming the concentration space \mathcal{A} to a space Ω , in which the curves $\Gamma^{(i)}$ are orthogonal to each other.

In the heterovalent case (different ν_j), no parameter θ has been found for which the curves $\Gamma^{(i)}$ become straight lines. So the above mentioned transformation from concentration space \mathcal{A} to space Ω , cannot be used. However, under conditions, it is possible to approximate the mass-action equation (2) so that the curves $\Gamma^{(i)}$, as a function of θ used in the homovalent case, can be approximated by straight lines. The method of Rhee, Aris and Amundson then yields a first approximation to the plateau concentrations, which may then be used as starting values in the Newton-Raphson iteration process to solve the nonlinear system of equations numerically.

A different approach is followed by Charbeneau [2] who considers the heterovalent case, and develops a method to approximate the plateau concentrations in the case $n = 3$. In the following we describe both approximation methods in more detail.

3.1 Heterovalent ions: an approximation with Rhee e.a.

First we use the method of Rhee et al., to obtain, under conditions, an approximation to the plateau concentrations in the heterovalent case. That means, we drop the restriction that all

valences are equal. From (2) we know that

$$\frac{c_j}{\beta_j} = K_{ij}^{\nu_j} \left(\frac{c_i}{\beta_i}\right) \left(\frac{c_i}{\beta_i}\right)^{\frac{\nu_j}{\nu_i}-1}. \quad (18)$$

Expressing every c_j/β_j in the unknown c_n/β_n , we find

$$\frac{c_j}{\beta_j} = K_{nj}^{\nu_j} \left(\frac{c_n}{\beta_n}\right) \left(\frac{c_n}{\beta_n}\right)^{\frac{\nu_j}{\nu_n}-1}, \quad (19)$$

which written in dimensionless variables gives

$$\frac{\alpha_j}{\beta_j} = (A_0)^{\frac{\nu_j}{\nu_n}-1} K_{nj}^{\nu_j} \left(\frac{\alpha_n}{\beta_n}\right) \left(\frac{\alpha_n}{\beta_n}\right)^{\frac{\nu_j}{\nu_n}-1}. \quad (20)$$

We see that, if we are able to approximate the expression $(\alpha_n/\beta_n)^{\frac{\nu_j}{\nu_n}-1}$ by a suitable constant, we can use the method of Rhee, Aris and Amundson to obtain an approximation to the plateau concentrations.

Therefore, define the function

$$g_j(x/t) = \left(\frac{\alpha_n(x/t)}{\beta_n(x/t)}\right)^{\frac{\nu_j}{\nu_n}-1} =: (\gamma(x/t))^{\frac{\nu_j}{\nu_n}-1}. \quad (21)$$

The Taylor series of $g_j(\gamma)$ in a neighbourhood of $\tilde{\gamma} \neq 0$, is given by

$$\begin{aligned} g_j(\gamma) &= \tilde{\gamma}^{\frac{\nu_j}{\nu_n}-1} + \left(\frac{\nu_j}{\nu_n} - 1\right)(\gamma - \tilde{\gamma}) \tilde{\gamma}^{\frac{\nu_j}{\nu_n}-2} + O((\gamma - \tilde{\gamma})^2) \\ &= \tilde{\gamma}^{\frac{\nu_j}{\nu_n}-1} \left(1 + \left(\frac{\nu_j}{\nu_n} - 1\right) \left(\frac{\gamma - \tilde{\gamma}}{\tilde{\gamma}}\right) + O\left(\left(\frac{\gamma - \tilde{\gamma}}{\tilde{\gamma}}\right)^2\right)\right). \end{aligned} \quad (22)$$

If

$$\left|\frac{\nu_j}{\nu_n} - 1\right| \leq 1, \quad (23)$$

for all j , then $\tilde{\gamma}^{\frac{\nu_j}{\nu_n}-1}$ is a good approximation of g_j , only if

$$\left|\frac{\gamma - \tilde{\gamma}}{\tilde{\gamma}}\right| \ll 1. \quad (24)$$

If maximum and minimum values of γ are known, $\tilde{\gamma}$ can be selected as

$$\tilde{\gamma} = \frac{1}{2}(\gamma^{max} + \gamma^{min}), \quad (25)$$

where γ^{max} and γ^{min} are the extreme values of γ . The approximation (25) will be better as the difference between the maximum and minimum of γ becomes smaller.

3.2 Heterovalent ions: method of Charbeneau

For the case $n = 3$, Charbeneau [2] developed a method to approximate the solution of equation (15), making use of the fact that $d\alpha/d\theta \propto r^{(k)}$ in the k -th characteristic direction. From this it follows that (cf. (10))

$$d\alpha = r^{(k)} d\zeta, \quad (26)$$

for all k , and with $\zeta = f(\theta)$. Integration of (26) gives:

$$\alpha^{(k)} = \alpha^{(k-1)} + \int_{\zeta(\alpha^{(k-1)})}^{\zeta(\alpha^{(k)})} r^{(k)} d\zeta. \quad (27)$$

Because we have no explicit expression for $r^{(k)}$ in ζ , we cannot integrate (27) analytically. Therefore (27) is approximated by the trapezoidal rule. Thus the integral is replaced by the approximation:

$$\alpha^{(k)} = \alpha^{(k-1)} + \frac{1}{2} [r^{(k)}(\alpha^{(k-1)}) + r^{(k)}(\alpha^{(k)})] \Delta\zeta_k, \quad (28)$$

where $\Delta\zeta_k = \zeta(\alpha^{(k)}) - \zeta(\alpha^{(k-1)})$. With the notation

$$r^{(i)}(k) = \frac{1}{2} [r^{(i)}(\alpha^{(k-1)}) + r^{(i)}(\alpha^{(k)})], \quad (29)$$

this approximation may be written

$$\alpha^{(k)} = \alpha^{(k-1)} + r^{(k)}(k) \Delta\zeta_k. \quad (30)$$

We call the vector $r^{(i)}(k)$ the i -th right eigenvector, averaged in the k -th characteristic direction. In the same way is the vector $l^{(i)}(k)$ the i -th left eigenvector, averaged in the k -th characteristic direction. There is one equation (30) for each of the two composition paths $\Gamma^{(k)}$. They are connected by the requirement that

$$\alpha^{inj} - \alpha^{init} = \sum_{j=1}^2 r^{(j)}(j) \Delta\zeta_j. \quad (31)$$

From $l^{(i)} \perp r^{(j)}$ for $i \neq j$ immediately follows $l^{(i)}(k) \perp r^{(j)}(k)$ for $i \neq j$. Making use of this bi-orthogonality relation, the inner product of $l^{(1)}(2)$ and (31) leads to

$$\Delta\zeta_1 = \frac{l^{(1)}(2) \cdot (\alpha^{inj} - \alpha^{init})}{l^{(1)}(2) \cdot r^{(1)}(1)}, \quad (32)$$

with $l^{(1)}(2) = [l^{(1)}(\alpha^p) + l^{(1)}(\alpha^{inj})]/2$ and $r^{(1)}(1) = [r^{(1)}(\alpha^{init}) + r^{(1)}(\alpha^p)]/2$

The plateau concentration α^p is unknown, and has to be calculated. For its approximation Charbeneau proposes an iterative method with initial estimates $l^{(1)}(2) = (l^{(1)}(\alpha^{init}) + l^{(1)}(\alpha^{inj}))/2$ and $r^{(1)}(1) = (r^{(1)}(\alpha^{init}) + r^{(1)}(\alpha^{inj}))/2$. With (32) this gives an estimate of $\Delta\zeta_1$ and we find an approximation of α^p by using

$$\alpha^p = \alpha^{init} + r^{(1)}(1) \Delta\zeta_1. \quad (33)$$

Equations (32) and (33) are iterated until convergence.

Once the point α^p is known, it should be verified that α^p is a simple wave composition. We can distinguish between simple- and shock waves by the ordering of the eigenvalues.

The approximate computation of α^p is only justified for the simple wave - simple wave case. In the other three cases we have to adapt the method to determine the plateau composition. We call the adaptation for shock wave transitions the modified method of Charbeneau.

In this modified method Charbeneau uses the fact that a plateau composition is the intersection of two paths, each of which may be a simple wave or a shock wave path. For the shock wave path equation (17) is used. As before, for a simple wave path we take equation (26), which is approximated by

$$\frac{\Delta\alpha_1}{r_1} = \frac{\Delta\alpha_2}{r_2}, \quad (34)$$

where the components of r are approximated by the components of the average right eigenvector. Equations (7), (17) and (34) form a system of four equations with four unknowns, $\alpha_1^p, \alpha_2^p, \beta_1^p, \beta_2^p$.

This system can be solved by means of Newton-Raphson iteration with starting values either the simple wave-simple wave solution or the values obtained by the method of Rhee, Aris and Amundson.

4 The finite volume approach

In the previous sections we considered essentially analytic solution methods. However, these methods become increasingly harder if more complicated systems have to be treated.

In practice, we have not only to deal with ion-exchange, but also with precipitation, dissolution, minerals, adsorption, temperature and/or pH being not constant etc., which makes the chemical equilibrium equations essentially more difficult. If we want to incorporate the chemical processes described above, a numerical solution method based on discretisation seems unavoidable.

Therefore, in this section we describe an automatic discretisation method that is useful to treat more complex situations as well, and which is also able to represent sharply the discontinuities that emerge in the system of hyperbolic differential equations.

4.1 Discretisation of the differential equations

To discretise the differential equation (1), we use a finite-volume time-stepping technique [3]. The method is applied explicitly in time. Although explicit time stepping has the disadvantage of finite stability intervals, in our case it will be efficient because

- calculation of the inverse fluxes, that would be necessary for *implicit* time stepping, is very complicated for realistic chemical equilibrium equations;
- we can guarantee to easily satisfy a CFL-condition, which makes our method converge.

First we consider the scalar hyperbolic differential equation in conservation form

$$\frac{\partial u}{\partial t} + \frac{\partial f}{\partial x} = 0, \quad f = f(u), \quad (35)$$

$$u_0(x) = \begin{cases} u_L & \text{if } x < 0 \\ u_R & \text{if } x > 0 \end{cases}, \quad u_0(x) := u(0, x)$$

Discretising (35) forward in time and upwind in space, we know that we have to restrict the time step Δt so as to satisfy the CFL-condition

$$\frac{\Delta t}{\Delta x} \max_{n,m \in \mathbb{Z}} \left| \frac{df(u_n^m)}{du} \right| < 1, \quad u_n^m = u(x_n, t_m), \quad (36)$$

in order to make the numerical procedure convergent. However, the convergence of a scheme will not necessarily guarantee that the solution, in the limit $\Delta y \rightarrow 0$, is the physically relevant solution. Therefore we need extra conditions. First of all, the difference scheme has to be in *conservation* form. This is equivalent to request conservation of mass for every cell in the grid. Other conditions are that the scheme must be *monotone* and satisfy the *entropy condition*. For the discussion of these concepts we refer to the paper by *Harten et al.* [4]. In the same paper, it can be seen that linear monotone finite difference schemes in conservation form can be only first order accurate in space. If we yet use a second order linear scheme, just before and after the discontinuity, oscillations will appear in the solution.

To overcome this difficulty we have to resort to nonlinear schemes. For this purpose we can introduce a *limiter* in the difference scheme. To explain the concept of the limiter, we discretise equation (35), as

$$u_n^{m+1} = u_n^m - \frac{\Delta t}{\Delta y} (f_{n+\frac{1}{2}}^m - f_{n-\frac{1}{2}}^m), \quad (37)$$

where $f_{n+\frac{1}{2}}^m = f(u_{n+\frac{1}{2}}^m)$, $f_{n-\frac{1}{2}}^m = f(u_{n-\frac{1}{2}}^m)$, with

$$\begin{aligned} u_{n+\frac{1}{2}}^m &= u_n^m + \frac{1}{2} \psi(R_n^m) (u_n^m - u_{n-1}^m), \\ u_{n-\frac{1}{2}}^m &= u_{n-1}^m + \frac{1}{2} \psi(R_{n-1}^m) (u_{n-1}^m - u_{n-2}^m), \\ R_n^m &= \frac{u_{n+1}^m - u_n^m}{u_n^m - u_{n-1}^m}. \end{aligned} \quad (38)$$

$\psi : \mathbb{R} \rightarrow \mathbb{R}$ is a continuous function, called the limiter. The limiter is introduced in the discretisation, in order to construct a monotone scheme, second order in space. How such limiters are constructed is found in *Spekreijse* [9]. Notice that in equation (38) $\psi \equiv 0$ corresponds to the first order upwind scheme (which is monotone), while $\psi \equiv 1$ yields the one-sided second order upwind scheme. A scheme third-order in space is obtained for $\psi \equiv 1/3$; However, no schemes with constant $\psi \neq 0$ can be monotone. Possible limiters combining the property of second order accuracy and monotonicity are:

- the van Leer limiter: $\psi_{VL}(R) = \frac{R+|R|}{|R|+1}$;
- the van Albada limiter: $\psi_{VA}(R) = \frac{R^2+R}{R^2+1}$;
- Koren's limiter: $\psi_K(R) = \frac{R^2+R}{2-R+R^2}$.

The last limiter by *Koren* [7] even combines the property of third order accuracy and monotonicity. With equation (37)-(38), depending on the choice of the limiter, we can solve equation (35) by different orders of accuracy in space. Whatever order of accuracy we use, reducing the time and/or space step will always improve the solution, as long as the CFL condition (36) is fulfilled.

The system (1,2) can be solved by the same technique as the scalar equation (35) if we apply the interpolation (38) to each component of the system separately.

On the larger part of the domain the solution will be fairly smooth, while discontinuities will occur only at specific locations. Accurate modeling of these discontinuities demands the time-space domain to be partitioned in very fine cells. As a consequence, if we fix the grid points, a fine mesh also appears in regions where a coarse mesh would be satisfactory. To overcome this, we introduce a method that places refined cells with a very small mesh spacing, only at the location where it is needed. Such a method is *adaptive mesh refinement*, which we will explain in the next section.

4.2 Adaptive mesh refinement

Adaptive mesh refinement is a method that adapts its time- and space step in regions where it is necessary according to some user specified (accuracy) criterion. Because we must fulfill the CFL condition, we keep the mesh ratio of time and space step constant. As in the preceding chapters, we consider only one space dimension.

We start with the definition of an initial or *base grid* \mathcal{B} , which is a partition of the *space* domain at $t = t_0$ (the initial time), either uniform or non-uniform. If it is non-uniform, it is of a special type. The base grid is composed of several *subgrids* on different *levels of refinement*. A subgrid on a particular level is a uniform partition in cells of (parts of) the space axis. Cells in a finer grid are always obtained by splitting cells on the next coarser level. Which part of the space axis is partitioned depends on the time, t , and on the shape of the solution of the problem to solve. For the subgrids on the next finer level the mesh size is halved, so that two cells on a fine subgrid always make one cell of the subgrid on the next coarser level. The two coarsest subgrids cover the whole space domain, next finer levels may cover increasingly smaller subdomains. The coarsest refinement levels are numbered as level 0 and level 1. In principle there is no limit to the number of levels.

When proceeding in time, the time step for the approximation of the solution on the subgrid with level j is taken proportional to the cell size of level j , such that the CFL condition is satisfied. In this way all grids in the time-space domain are nested and ordered as in a binary tree. If we denote the subgrids by S_j , with j referring to the refinement level, we have

$$\mathcal{B} = S_0 \cup S_1 \cup \dots \cup S_n, \quad (39)$$

with S_0 denoting the coarsest- and S_n the finest subgrid at $t = t_0$. The precise shape of the base grid depends on the solution. If it is known in advance that at $t = 0$ a discontinuity appears at a specified location, then the user may decide to refine the grid up to a certain level near that location. Anyway, \mathcal{B} is taken so that the initial solution is well represented on \mathcal{B} . Because the initial solution is given, the grid \mathcal{B} can be generated automatically. In principle the integration of the partial differential equation is done by time-stepping on all the available grids S_0, \dots, S_n . Because of the fixed $\Delta x/\Delta t$ ratio, smaller time steps are used on the finer grids. The solutions on the different grids are compared in order to decide, during the computation, where and when the subgrids have to be generated, extended or removed. Because the finer grids yield the more accurate solutions, after comparison the coarse-grid approximations are improved by correcting them with the finer grid solutions. In this way accurate solutions are obtained on the base grids $\mathcal{B}(t)$.

Flux computations and time stepping

The initial- and boundary values are given by the physics of the problem. The value of the fluxes across the cell interfaces are calculated by solving approximately a Riemann problem at the cell interface, with a given left and right state $f = f(u_L, u_R)$. The states u_L and u_R are obtained by interpolation of the known solution (at a particular time t). This interpolation to compute u_L may be piecewise constant for a first order method, or piecewise linear for a second order method. By application of the conservation law (35) for each cell separately (see [5]), the new state at time $t + \Delta t$ is computed.

The algorithm

We use a recursive technique to make the programme adapt its grid where necessary. To perform one time step from t to $t + \Delta t_l$ on level l , we define the algorithm **Timestep**($l, t, \Delta t_l$) as follows:

1. Do one integration step on the subgrid S_l at level l , from t to $t + \Delta t_l$.
2. Make a backup copy of all solutions at levels $k > l$ that are available at t , i.e. make a back-up of the solution at $S_k(t)$, $k = l + 1, \dots$.
3. If the subgrid $S_{l+1}(t)$ exists then apply **Timestep**($l + 1, t, \Delta t_{l+1}$), else return.
4. Apply **Timestep**($l + 1, t + \Delta t_{l+1}, \Delta t_{l+1}$). Notice that we arrive by this time step at $t + \Delta t_l$ on level $l + 1$!
5. Compare the solutions at $t + \Delta t_l$ as obtained by computations on level l and on level $l + 1$, and decide whether $S_{l+1}(t)$ must be further refined or possibly unrefined.
6. Correct the solution on level l by means of the solution obtained at level $l + 1$.
7. If $S_{l+1}(t)$ must be refined then
 - get the back-up copy of all the solutions on $S_k(t)$, $k = l + 1, \dots$ as saved in 2;
 - create subgrid $S_{l+2}(t)$;
 - go to 3.
8. If $S_{l+1}(t)$ must be unrefined then remove such cells from $S_{l+2}(t)$.
9. Return.

Adaptive grid and solute transport

The above adaptive mesh refinement technique, is an efficient method to solve our non-linear system of coupled differential- and algebraic equations. Where the solution is smooth, that is where simple waves appear in the solution or where the solution is constant (plateau concentrations), the programme will use a coarse grid and yet deliver an accurate solution as specified by the user. Where discontinuities appear in the solution (shock waves), the programme refines its grid until a specified minimal resolution of the grid. In this way no unnecessary calculations are made, and a specified accuracy is obtained.

In section 4.1 we saw that we have to satisfy a CFL condition in order to get a stable difference scheme. According to equation (36), this depends on the fastest propagation velocity of u . In the case of N -component solute transport and ion-exchange, we know from Section 2.2 that the fastest propagation velocity is just the migration velocity v . Condition (36) then shows that

$$\Delta t \leq v\Delta x, \quad (40)$$

is a sufficient stability condition.

5 Computational results

In this section we show results, obtained for the equations (1) - (2) by the different methods described in this paper. We consider cation exchange for the ions Na^+ , Mg^{2+} and Ca^{2+} as described in the paper by Appelo [1]. The initial and injected concentrations come from a field project in the Palo Alto Baylands region in 1978, by Valocchi et al. [10]. Because we have to deal with three different cations, we know that only two of them are independent. To simulate the cation transport we have to solve four equations in four unknowns, i.e. a Riemann problem consisting of two differential equations (1), with initial and boundary values given by the measurements of Valocchi, coupled to two chemical equilibrium equations (2).

To this set of equations we first apply the method of Charbeneau, thus assuming that two simple waves exist in the solution (see Section 3.2). The results, which consist of an approximation to the plateau concentrations, are used to verify this assumption. We find that in reality two shocks exist in the solution. That means that the assumption had not been justified. As a consequence, the method of Charbeneau is not appropriate to model the present cation transport. However, the modified method of Charbeneau is appropriate because it covers also the other possibilities (cf. Section 3.2).

We know that the modified method of Charbeneau determines the plateau concentrations in the shock-wave - shock-wave case by means of Newton-Raphson iteration of equations (7) and (17). These equations form a set of four equations in four unknowns. In Section 3.2 we described two ways to apply the iteration. Both iteration methods, applied for the data [10], converge and yield the same approximation to the plateau concentrations. The results are given in the Table 1.

We also computed an approximation by the method of Rhee, Aris and Amundson. This method is justified because the conditions (23) and (24) are satisfied. With the valences of the cations in this field project, it is easily seen that condition (23) is always fulfilled. Furthermore, taking

$$\tilde{\gamma} = \frac{1}{2}(\gamma^{inj} + \gamma^{init}), \quad (41)$$

we satisfy condition (24) because, in this case,

$$\gamma^{min} = \gamma^{init} \text{ and } \gamma^{inj} = \gamma^{max}. \quad (42)$$

The results are summarised in Table 1.

The approximation to the plateau concentrations obtained by Newton-Raphson iteration of equations (17) and (4) agree, within rounding errors, with those found by Appelo [1]. Furthermore, the approximation obtained by the homovalent approximation of the mass action

Table 1: Approximations to the plateau concentrations as obtained by different methods.

plateau concentration (mmol./l)	Method of Charbeneau (simple wave-simple wave)	Modified method of Charbeneau (shock wave-shock wave)	Homovalent approximation of the mass-action equation (Rhee et al.)
Na^+ (aqueous)	9.35	9.47	9.52
Mg^{2+} (aqueous)	1.27	1.68	1.67
Ca^{2+} (aqueous)	1.38	0.92	0.90
NaX (adsorbed)	59.88	64.16	58.70
MgX_2 (adsorbed)	117.50	173.28	175.50
CaX_2 (adsorbed)	227.56	169.64	170.15

equations is surprisingly accurate. Therefore, and because of the ease with which such results are obtained, these approximations can be used as starting values for the Newton-Raphson process in the modified method of Charbeneau.

Finally we solve the equations (1) - (2) numerically, as explained in Section 4. The method is always explicit and first order in time. The space discretisation (38) allows a number of possibilities. We compare three different strategies:

(a) first order upwind in space, $\psi = 0$, (b) second order upwind in space, $\psi = 1$, (c) second order upwind in space, making use of the *van Leer* limiter.

The effect of the adaptive grid technique is shown in Figure 1. We see that the space axis is refined only in regions where it is necessary, namely at the locations of the discontinuities. Furthermore we restricted the maximum number of levels in the two different computations. First we allowed a maximum level of refinement of 6 and later a maximum number of 4. This causes a difference in the minimal size of the grid cells in the neighbourhood of the discontinuities. In the first computation the size is smallest, which results in more accurate modeled shocks, compared to the second computation. Because the numerical error is small in the first figure, the constant region between 0.088 and 0.380 can be more unrefined than in the second figure, where the numerical error is bigger and influences a larger area around the discontinuities.

The effect of a limiter is shown in Figure 2. Figure 2a is first order accurate, whereas Figures 2b and 2c have second order accuracy. Figure 2b shows under- and overshoot in the neighbourhood of the shocks, caused by non-monotonicity. This has disappeared in Figure 2c, where the *van Leer* limiter was used to make the system monotone, while maintaining second order accuracy.

6 Conclusions

We have seen that modeling cation transport with existing *analytic* methods is restricted to rather simple problems. The method of Rhee et al., valid for n -dimensional homovalent systems, can also be applied to the heterovalent system. This yields a first approximation to the plateau concentrations, which in turn can be used as an initial estimate for Newton-Raphson iteration in the modified method of Charbeneau. With the data from [10] it was

shown that this initial estimate can be very accurate in practical situations indeed. However, the homovalent approximation can only be justified if we know something about the extreme values of the quotient α_n/β_n , with α_n and β_n the dependent concentrations.

The method of Charbeneau is efficient for 3-component transport, though extension to more components makes the algorithm complicated while convergence of the iteration processes cannot be guaranteed.

The modified method of Charbeneau can also be applied to cation transport of more than 3 ions, but this method has the disadvantage that it requires a-priori knowledge about the order of appearance of shock waves and/or simple waves in the solution. To obtain information about this ordering, we can determine it for the approximate solution obtained by the method of Rhee et al. before we apply the modified method of Charbeneau, and at the end we have to apply an a-posteriori check again. For complex chemical systems this may become a rather laborious procedure.

Simulation of the time dependent process by discretisation with adaptive mesh refinement is a very flexible method to model n -component solute transport. It can be made efficient when both time and space step are refined only in regions where it is necessary. Then, sharp fronts are accurately modeled with a minimum amount of work. The explicitness of the method makes it easy to use, also for complex chemical models, and it can also be used in combination with existing programmes that model geochemical processes.

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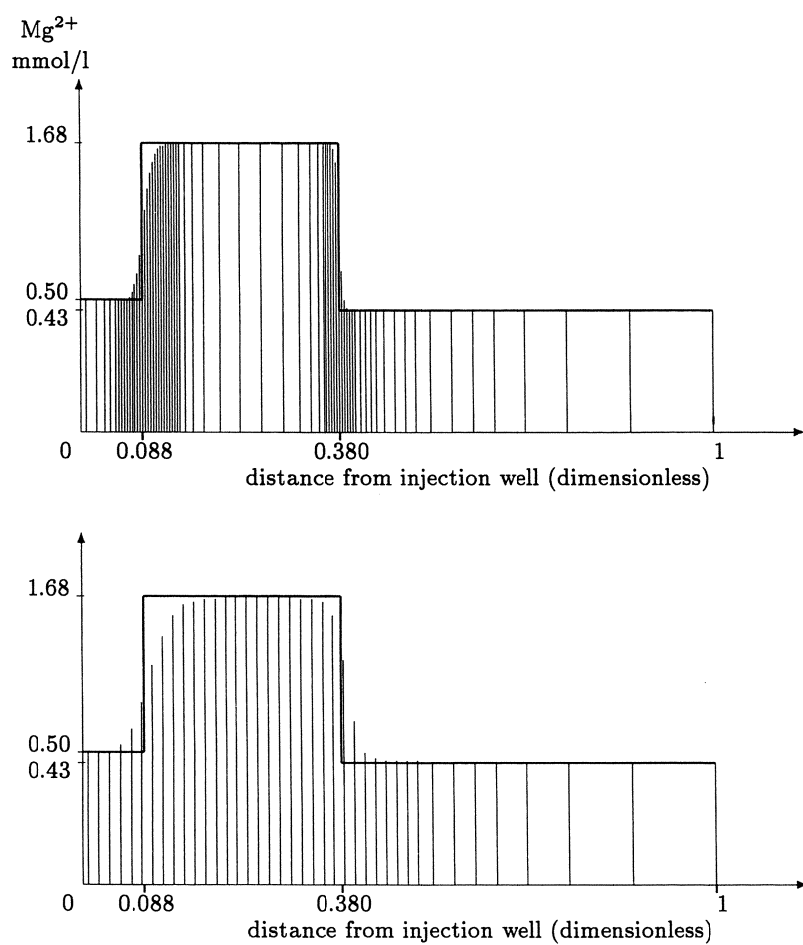


Figure 1: Aqueous concentration of Mg^{2+} .

The vertical lines represent the solution, obtained by the first order method on the composite grid at $t = 10$. Six levels of refinement are used in the first graph, four levels of refinement in the second. The thick horizontal lines show the analytic sharp front solution as obtained by the modified method of Charbeneau. The value of the adaptive procedure is easily observed.

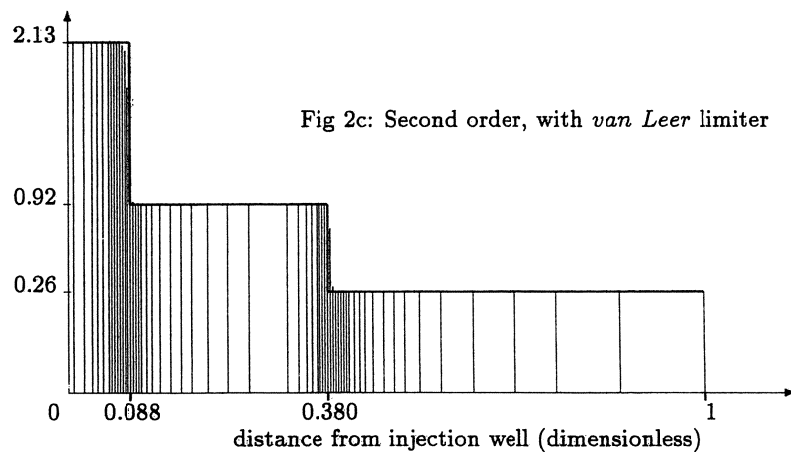
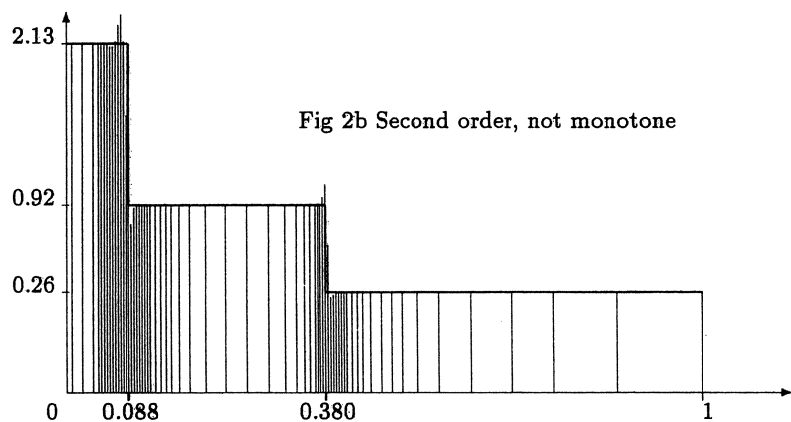
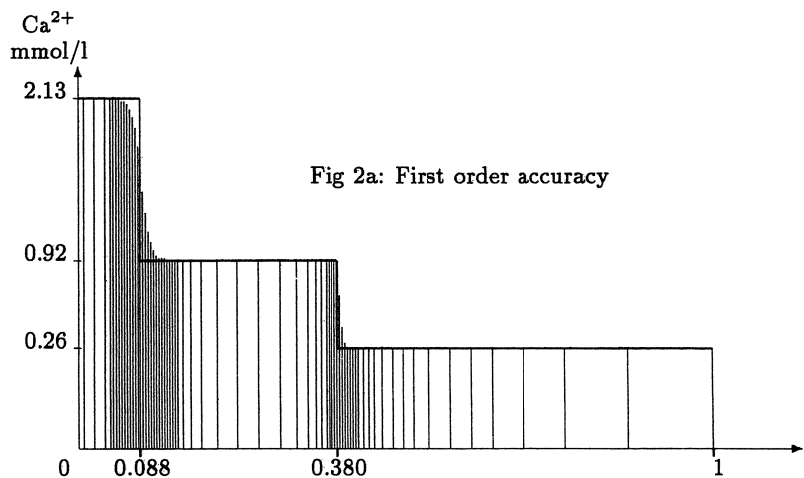


Figure 2: Aqueous concentration of Ca^{2+} .

The value of the different space discretisations: first and second order accuracy, with and without limiter. Here the solution of the equations (1) - (2) is shown for the field problem of Valocchi at $t = 10$.