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A MIXING CELL SOLUTE TRANSPORT MODEL WITH EXCHANGE OF CATIONS
IN SOILS

Modelling and parameter estimation of transport and
exchange of Na, Ca and Mg ions in soils applied to
microcolumn experiments and to the reuse of drainage
water in Egypt

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C O N T E N T S

1. INTRODUCTION

This report has been written in partial fulfilment of the study in land and water management at the Agricultural University in Wageningen and complies very well with the research carried out by the Institute for Land and Water Management Research in Wageningen and the Drainage Research Institute in Cairo, Egypt. A study has been conducted to the transport and accumulation of salts in the soils with emphasis on the Na, Ca and Mg ions. Besides salinization aspects sodification of soils often poses a threath to agricultural practices in arid and semi arid regions with agriculture depending partly or completely on irrigation. The effect of increasing salinization is an increase of osmotic pressure in the plant root zone and reduced plant growth. Besides physiological effects also poisonous effects of high concentrations of salts play a role. The effect of sodification (dominance of Na^+ on the adsorption complex) enhances the swelling of clay minerals reducing the effective permeability of the soil. Under these circumstances plant growth is reduced by limited water availability as well as by oxygen shortage.

The hazarduous effects of both salinization and sodification are in the field frequently noticed only after a long period. It is therefore important to develop methods to predict these long term effects before irrigation projects are constructed or land reclamation programmes are initiated. Timely taken measures may then prevent a serious decrease in the farmers' income, in project economics, or even prevent the project implementation.

In Egypt agriculture completely depends on irrigation and both processes of salinization and sodification became an important subject of study, because the reuse of drainage water in the Nile Delta in Egypt has been adopted an official policy of the Ministry of Irrigation to supply a great part of the newly to be reclaimed agriculture land with irrigation water.

Knowledge of water quantity and -quality influencing processes are essential for the assessment of a long term justified reuse strategy. At the present, the majority of the water from this potential source still flows to the sea.

This study presents a simple model for water quality forecasting. Two processes are taken into consideration: transport and dispersion caused by the convective flow and the adsorption of Sodium, Calcium and Magnesium. The transport phenomena have been approached by the 'mixing-cell' concept, which is a numerical solution of the general Fokker-Planck equation, presented earlier by GOUDRIAAN (1973) and VAN OMMEN (1985). The adsorption equilibria have been assumed at the end of each time interval. The ternairy adsorption system has been approached by two adsorption isotherms, a 'Gapon' and a 'Kerr' equation and a mass balance.

Two column experiments which enabled to verify the model have been performed at the ICW Laboratory.

The first experiment has been done with a fine sand soil, having a low cation exchange capacity to gain experience with the new and rapid technique with High Performance Liquid Chromatography columns. The second experiment has been carried out with three different feed solutions by Dr. Sammia El Guindy and Mr. J. Harmsen. Long term estimations were made about the effects of the reuse of drainage water.

The conclusions in this report are tentative because the data used in the calculations are based on several assumptions and preliminary data. The two dimensional transport of solutes has been approached with a model presented by ROEST and RIJTEMA (1983). Attention has been paid to other transport and adsorption models for comparison, but no calculations were performed because of their complexity.

A computer programme in FORTRAN for the simulation of a three cations column experiment is presented and techniques for finding optimum parameters from experimental results originating from systems analysis are explained.

A programme for the HP 41 CV calculator for a two cation system is also presented but the required simulation time of an experiment prohibits extensive use of this programme and the storage capacity of this calculator is insufficient for all variable required.

2

2. TRANSPORT MODEL

The transport process of a solute through a soil system follows the theory of exchange chromatography. The exchange process interacts with the transport of ions and the interaction of both processes can be presented by a conservation equation (REINIGER and BOLT, 1972):

$$\frac{\partial(q_i + \varepsilon c_i)}{\partial t} = - \text{div } J_i + \text{prod}(i) \tag{1}$$

where q_i is the amount adsorbed of ion i in meq per cm^3 of the system. The quantity of the same ion in the liquid phase is given by εc_i with ε as the effective posity in cm^3 per cm^3 of the system. The salt concentration c_i is expressed in the same units as the solid phase and salt flux J_i is given in meq $cm^{-2}.sec^{-1}$. The production term prod(i) represents a source or a sink of the ion from e.g. dissolving or precipitating solid salts. However, these processes will not be considered in this report. The transport of the ions considered takes place in the liquid phase. The flux J consists of at least two terms, a convective flux $(J)_{con}$ and a diffusion/dispersion flux $(J)_{di}$ can be distinguished:

$$(J_i)_{con} = v\, c_i \tag{2a}$$

$$(J_i)_{di} = - D_i \text{ grad } c_i \tag{2b}$$

D_i is the effective diffusion coefficient of the ion considered and may be estimated from the self-diffusion coefficients of all ions involved applying a correction for the liquid filled porosity and tortuosity of the pores. The convective flux of the solution is expressed by v in $cm^3 \, sec^{-1}.cm^{-2}$. The ion flux due to mechanical dispersion must be taken into account for heterogeneous porous systems. The dispersion coefficient D_{disp} is usually taken to be proportional to the velocity for low flow rates.

The total effect of diffusion and dispersion is defined as the apparent diffusion and the effect of this phenomenon is given by:

$$D' = D_{diff} + D_{disp} \tag{3}$$

The substitution of eq. 2a into eq. 1 neglecting the production

term and reduction of the system to one dimension yields the following equation:

$$\frac{\partial(q_i + \varepsilon c_i)}{\partial t} = - v \frac{\partial c_i}{\partial x} + D' \frac{\partial^2 c_i}{\partial x^2} \tag{4a}$$

with x as the distance relative to the entrance of the system in cm. The differentiation of the left hand side term to time leads to the following expression:

$$(q_i'(c) + \varepsilon) \frac{\partial c_i}{\partial t} = - v \frac{\partial c_i}{\partial x} + D' \frac{\partial^2 c_i}{\partial x^2} \tag{4b}$$

where $q_i'(c)$ is the differential capacity of the exchanger. The equation can can be solved analytically for an ion with linear adsorption behaviour, when a constant value for $q_i'(c)$ is found (Section 3.2).

2.1. Transport of non retarded ions

At low macroscopic stream velocities molecular diffusion is the main cause of the apparent diffusion, at high velocities dispersion dominates. The Peclet's number gives an indication for the contribution of each process and is defined as:

$$Pe = \frac{D_{disp}}{D_{diff}} \tag{5}$$

Mechanical dispersion is the main process for $Pe \gg 1$ and the total effect is mainly due to diffusion for $Pe \ll 1$.

In this chapter two mathematical methods for solving the differential equation will be considered and attention will be paid to parameter estimation.

2.1.1. Analytical solution

When the adsorption of an ion is absent, the term $q'(c) = 0$ and D^* is defined as D'/ε and $v^* = v'/\varepsilon$.

The following boundary conditions applied to equation 4b can be defined for an one-dimensional flow:

4

initial salt content: $x > 0$, $t = 0$, $c = c_o$

boundary condition : $x = 0$, $t > 0$, $c = c_f$

infinite depth : $x \to \infty$, t_{finite} , $c = c_o$

infinite time : x_{finite} , $t \to \infty$, $c = c_f$

where c_o is the initial concentration of the soil solution and c_f is the concentration of the feed solution.

For a block feed and a constant initial column concentration the solution is found by means of the Laplace transformation method as has been done by WALTER (1945):

$$c(x,t) = c_o + \frac{1}{2}(c_f - c_o)\left[\operatorname{erfc}\frac{(x-v^*t)}{2\sqrt{D^*t}} - \exp\left(\frac{v^*x}{D^*}\right)\operatorname{erfc}\frac{(x+v^*t)}{2\sqrt{D^*t}}\right] \qquad (6)$$

The second erfc term represents the reflection caused by the entrance boundary and for greater values of $x + v^*t$, this term tends to zero:

$$c(x,t) = c_o + \frac{1}{2}(c_f - c_o)\left[\operatorname{erfc}\frac{(x-v^*t)}{2\sqrt{D^*t}}\right] \qquad (7)$$

The slope at a certain point on this curve is obtained by the differential of equation 7:

$$\frac{\partial c(x,t)}{\partial t} = \frac{(c_f - c_o)}{4\sqrt{\pi D^*t}}\left(\frac{x}{t} + v^*\right)\exp\left(-\frac{(x-v^*t)^2}{4D^*t}\right) \qquad (8)$$

The ratio $\alpha_L = \frac{D^*}{v^*}$ is defined as the dispersion length or characteristic length. This parameter can be found in symmetrical curves by the determination of the tangent of the break through curve at $\frac{1}{2}(c_o + c_f)$. (fig. 1).

The occurrence of a blind pore system or a stagnant phase in the column affects the symmetry of the curve. The curve shows a symmetric course for an ideally behaving column. The top of the tangent curve is given by the slope of the break through curve at the time of occurrence of its centre of gravity. When the column has been refreshed once by the feed solution the concentration of the effluent equals $\frac{1}{2}(c_f + c_o)$.
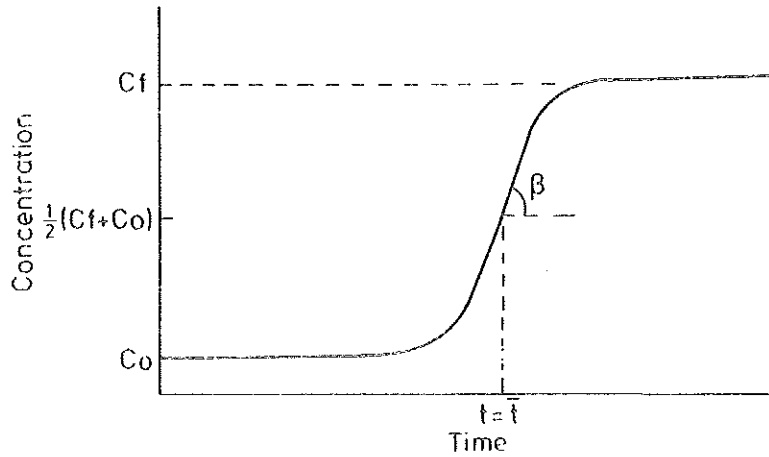
Fig. 1. Calculation of the dispersion length from the slope at the flexure point

For $\bar{t} = \dfrac{L}{v^*}$ and $x = L$, where L gives the length of the column, the dispersion length is given by:

$$\alpha_L = \frac{(c_f - c_o)^2 L}{4\pi \bar{t}^{-2}(tg\ \beta)^2} \tag{9}$$

2.1.2. Numerical solution

GOUDRIAAN (1973) solved the general convection dispersion equation by assuming the apparent dispersion equal to zero. Theoretically, a soil column can be divided in n layers, each with thickness Δx. Within each layer, the salt concentration is supposed to be uniform and the mixing of the solution is complete.

The change of the salt concentration in the i-th layer can be given by:

$$\frac{dc(i)}{dt} = -u\ \frac{c(i) - c(i-1)}{\Delta x} \tag{10}$$

where u is the pore water velocity, $c(i-1)$ is the concentration of the entering solution and $c(i)$ represents the concentration within the layer and of the out flowing solution.

The inflow of salt is dependent on the salt content of the previous layer, the outflow is proportional to its own content. When a solute with concentration zero enters the first layer, the compartment will loose salt proportional to its concentration. The differential equation

for this situation is given by:

$$\frac{dc(1)}{dt} = - u \frac{c(1)}{\Delta x}$$ (11a)

with solution:

$$c(1) = c_{1,o} \exp\left(- \frac{ut}{\Delta x}\right)$$ (11b)

with $c_{1,o}$ as the initial salt concentration in the first layer. The salt flux into the second layer equals $u.c(1)$ and the differential applied to this situation is:

$$\frac{dc(2)}{dt} = - u \frac{c(2)}{\Delta x} + u \frac{c_{1,o} \exp\left(- \frac{ut}{\Delta x}\right)}{\Delta x}$$ (12)

The general solution of equation 10 can be derived by using the mentioned reservoir concept and can be expressed by:

$$c(n) = \exp\left(- \frac{ut}{\Delta x}\right) \sum_{i=o}^{n} c_{i,o}(i)\left(\frac{ut}{\Delta x}\right)^{n-1} \frac{1}{(n-1)!}$$ (13a)

When the initial concentration in the second and succeeding layers is taken zero and the concentration in the first layer (i=o) is taken to be the concentration of the feed solution the expression for $c(n)$ becomes:

$$c(n) = c_o\left(\frac{ut}{\Delta x}\right)^n \frac{1}{n!} \exp\left(- \frac{ut}{\Delta x}\right)$$ (13b)

This equation applies to a Poisson probability distribution if the concentration of the feed solution is set at unity.

The expectation value equals $\frac{ut}{\Delta x}$ and the standard deviation of the one-dimensional spatial distribution is given by:

$$\sigma_s = \left(\frac{ut}{\Delta x}\right)^{\frac{1}{2}}$$ (14)

If the number of layers is large enough, the Poisson distribution can be substituted by a normal (Gauss) type of distribution having the

same standard deviation and represented by:

$$c(n) = c_o \left(\frac{1}{2\sigma_s^2 \pi}\right)^{\frac{1}{2}} \exp\left(-\left(n - \frac{ut}{\Delta x}\right)^2 / \left(2\sigma_s^2\right)\right) \qquad (15)$$

The separation of the column into theoretical layers introduces a numerical dispersion which is similar to the flattening of a sharp front due to diffusion/dispersion in the continuous column. According to the theory of diffusion, a quantity of salt $c_o\Delta x$ entering a porous medium at time t=0 will be distributed at time t=t as:

$$c_t = c_o \Delta x \left(\frac{1}{4\pi Dt}\right)^{\frac{1}{2}} \exp \frac{(\lambda-ut)^2}{4Dt} \qquad (16)$$

An expression for the diffusivity D is obtained from the comparison of the numerical and continuous concentration distribution formulations. Equation (16) is similar to (15) if the multiplier equals:

$$D = \frac{\sigma_s^2 (\Delta x)^2}{2t} \qquad (17)$$

When time t is set at the average time of outflow $\bar{t}$ and the layer thickness is taken as unity the standard deviation in space σ_s equals the product of the stream velocity and the standard deviation in time:

$$\sigma_s = u\sigma_t \qquad (18)$$

The combination of eq. (17) and (18) yields an expression for the dispersion length:

$$\alpha_L = \frac{D}{u} = \frac{u\sigma_t^2}{2\bar{t}} \qquad (19)$$

2.1.3. The mixing cell concept

Supposing that within a time interval Δt a solute volume $Au\Delta t$ enters a compartment with moisture volume $A\Delta x$, the quantity of moisture remaining in this compartment has the volume $A\Delta x - Au\Delta t$ (see fig. 2).
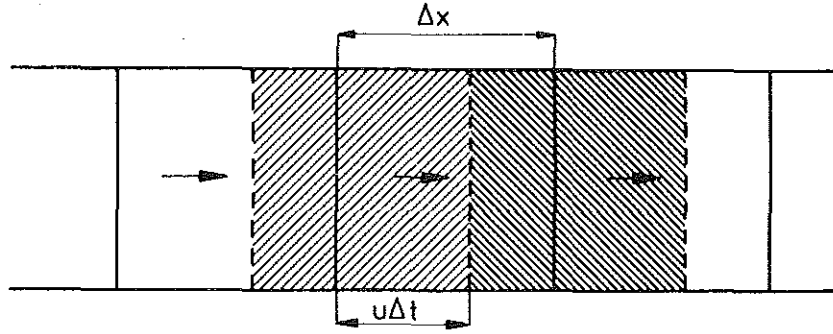
Fig. 2. Schematization of a moving solute through a column

The entering solution mixes completely with the remaining moisture. The concentration will be composed of the two previous concentrations of the compartments i-1 and i and is given by a simple mass balance:

$$A\Delta x \; c(x,t+\Delta t) = Au\Delta t \; c(x,t) + A(\Delta x-u\Delta t) \; c(x-\Delta x,t) \tag{20a}$$

Dividing by $A\Delta x$ and rearranging gives the same equation as the convective dispersion equation, written in finite difference notation and the apparent diffusion set at zero (VAN OMMEN, 1985):

$$c(x,t+\Delta t) = c(x,t) + \frac{u\Delta t}{\Delta x}(c(x-\Delta x,t) - c(x,t)) \tag{20b}$$

The mixing ratio $\frac{u\Delta t}{\Delta x}$ represents a measure for displacement of a cell moisture volume by the volume of a previous compartment. The first and second order terms of equation 4b can be derived numerically by the method of Taylor expansion. The terms are given by:

backward with respect to place:

$$\frac{\partial c}{\partial x} = \frac{c(x) - c(x-\Delta x)}{\Delta x} \qquad + \frac{\Delta x \partial^2 c}{2!\partial x^2} - \frac{(\Delta x)^2 \partial^3 c}{3!\partial x^3} + \dots \tag{21a}$$

foreward with respect to place:

$$\frac{\partial c}{\partial x} = \frac{c(x+\Delta x) - c(x)}{\Delta x} \qquad - \frac{\Delta x \partial^2 c}{2!\partial x^2} - \frac{(\Delta x)^2 \partial^3 c}{3!\partial x^3} - \dots \tag{21b}$$

central:

$$\frac{\partial c}{\partial x} = \frac{c(x+\Delta x) - c(x-\Delta x)}{2\Delta x} \qquad - \frac{(\Delta x)^2 \partial^3 c}{3!\partial x^3} - \frac{(\Delta x)^4 \partial^5 c}{5!\partial x^5} - \dots \tag{21c}$$

backward with respect to time:

$$\frac{\partial c}{\partial t} = \frac{c(t) - c(t-\Delta t)}{\Delta t} + \frac{\Delta t \partial^2 c}{2! \partial t^2} - \frac{(\Delta x)^2 \partial^3 c}{3! \partial t^3} + \ldots \qquad (21d)$$

foreward with respect to time:

$$\frac{\partial c}{\partial t} = \frac{c(t+\Delta t) - c(t)}{\Delta t} - \frac{\Delta t \partial^2 c}{2! \partial t^2} - \frac{(\Delta t)^2 \partial^3 c}{3! \partial t^3} - \ldots \qquad (21e)$$

central:

$$\frac{\partial c}{\partial t} = \frac{c(t+\Delta t) - c(t-\Delta t)}{2\Delta t} - \frac{(\Delta t)^2 \partial^3 c}{3! \partial t^3} - \frac{(\Delta t)^4 \partial^5 c}{5! \partial t^5} - \ldots \qquad (21f)$$

the second order term is given by:

$$\frac{\partial^2 c}{\partial x^2} = \frac{c(x+\Delta x) - 2c(x) + c(x-\Delta x)}{(\Delta x)^2} - \frac{2(\Delta x)^2 \partial^4 c}{4! \partial x^4} - \ldots \qquad (21g)$$

Substitution of equations (21a) and 21e) into (20b), neglecting the third and higher order derivates and terms and assuming $\frac{\partial^2 c}{\partial t^2} \simeq u^2 \frac{\partial^2 c}{\partial t^2}$ yields a similar relation to eq. (4b):

$$\frac{\partial c}{\partial t} = - \frac{u\partial c}{\partial x} + \left(\frac{u\Delta x}{2} - \frac{u^2 \Delta t}{2} \right) \frac{\partial^2 c}{\partial x^2} \qquad (22)$$

The numerical dispersion is given by the error introduced by the finite difference approach. The dispersion length is expressed as:

$$\alpha_L = \frac{\Delta x}{2} - \frac{u\Delta t}{2} \qquad (23)$$

If the layer thickness and dispersion length parameters are known, the time interval required in a computional model can be calculated. The size of the artificial dispersion can be controlled by the choice of the proportion between the layer thickness, the time interval and the velocity.

This concept is only valid if the condition $\alpha_L < \frac{\Delta x}{2}$ is met.

10

2.1.4. Finite difference approach including diffusion

Other discretizations of equation 4b are possible. When a diffusion term is taken into account, the discrete form of 4b can be found from an extension of (20b) with the expression for the second order term (21g):

$$\frac{c(x,t+\Delta t) - c(x,t)}{\Delta t} = - u \frac{c(x,t) - c(x-\Delta x,t)}{\Delta x} +$$

$$+ D \frac{c(x+\Delta x,t) - 2c(x,t) + c(x-\Delta x,t)}{(\Delta x)^2} \tag{24}$$

Multiplying by Δt and rearranging results in the following formula:

$$c(x,t+\Delta t) = \lambda_1 c(x+\Delta x,t) + \lambda_2 c(x,t) + \lambda_3 c(x-\Delta x,t) \tag{25}$$

with:

$$\lambda_1 = D \frac{\Delta t}{(\Delta x)^2} \tag{25a}$$

$$\lambda_2 = 1 - \frac{u\Delta t}{\Delta x} - 2 \frac{D\Delta t}{(\Delta x)^2} \tag{25b}$$

$$\lambda_3 = \frac{u\Delta t}{\Delta x} + \frac{D\Delta t}{(\Delta x)^2} \tag{25c}$$

For the first compartment $c(x-\Delta x,t)$ equals the concentration of the feed solution C_o and for the last compartment another computation schedule can be used:

$$c(x=n,t+\Delta t) = (\lambda_1+\lambda_2) \, c(x=n,t) + \lambda_3 c(x=n-1,t)$$

where n is the number of imaginary compartments with equal size in the column.

The term $\frac{\partial^2 c}{\partial t^2}$ is assumed to be equal to $u^2 \frac{\partial^2 c}{\partial x^2}$ (VAN OMMEN, 1985) and the third and higher order derivates are neglected.

Consideration of the introduced difference errors yields the following relation:

$$\frac{\partial c}{\partial t} = - u \frac{\partial c}{\partial x} + \left(D + \frac{u\Delta x}{2} - \frac{u^2\Delta x}{2} \frac{\partial^2 x}{\partial x^2} \right) \tag{26}$$

with $D + \dfrac{u\Delta x}{2} - \dfrac{u^2 \Delta x}{2}$ as a formulation for the apparent diffusion coeffi-cient. The mathematical coefficient is similar to the expression found in the mixing cell approach (Chapter 2.1.3).

For computational stability reasons the following condition have to be met (VAN DEN AKKER et al, 1984):

$$0 \leq 1 - \frac{u\Delta t}{\Delta x} - 2\frac{D\Delta t}{(\Delta x)^2} \leq 2 \qquad\qquad (27a)$$

or:

$$\frac{u\Delta t}{\Delta x} + 2\frac{D\Delta t}{(\Delta x)^2} \leq 1 \qquad\qquad (27b)$$

2.2. More column systems

Frequently a good structured soil exhibits a bi or multi modal pore size distribution, due to the difference of spatial structure of the particles. A part of the solute can have permanently a lower flow velo-city and therefore the micro velocity distribution will deviate from the Gauss distribution. The breakthrough curve will show an asymmetric behaviour and reach slowly the final concentration. Systems with blind pores will behave in a similar way, the mixing of the solutions between the mobile phase and stagnant phase is due to diffusion only.

It is possible to divide the system in two or more imaginary paral-lel columns in order to simulate this phenomenon (fig. 3). Each soil column distinguished has its own geometrical configuration with its own properties. The assumption of non-transversal interaction seems plausible for micro-columns with high velocities. At the inlet of the system, the total flux is divided into parts proportinal to the contri-bution of each sub-system. The effluents of the imaginary systems are mixed at the outlet.
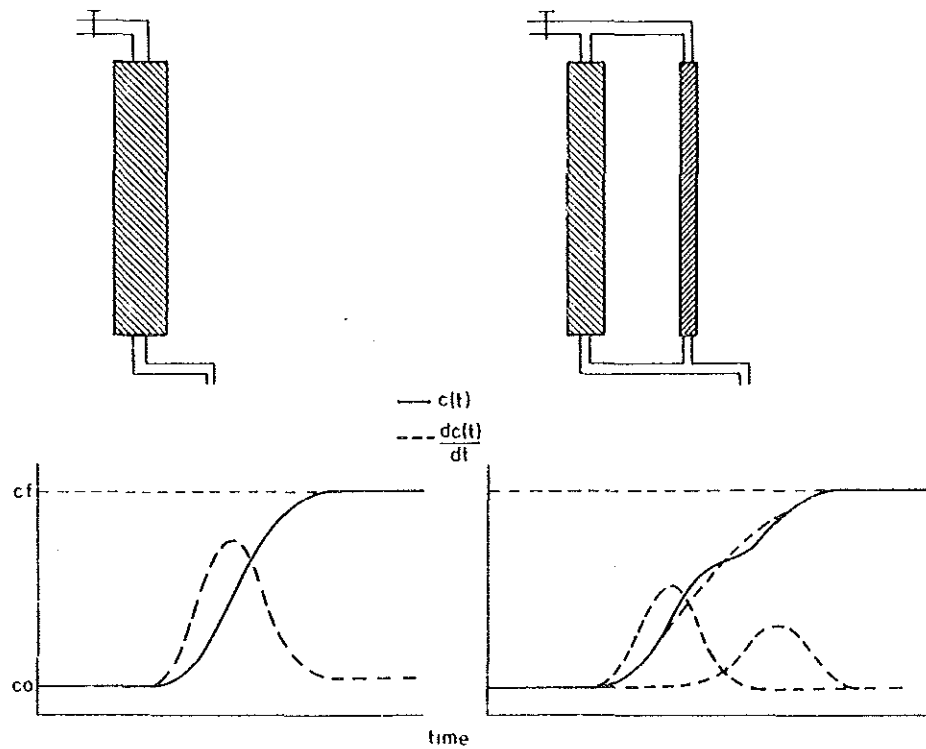
Fig. 3. Schematic representation of the more column system

2.3. Parameter estimation

The passage of a non-retarded tracer is similar to the systems response activated by a certain input in the theory of hydrology. The breakthrough of a solute can be described in terms of a linear time invariant process. The concentration of the feed solution is normally kept constant in a colum experiment. If a non-reactive solute is supplied continuously the course of the concentration at the outlet of the system can be defined as:

$$c(t) = (c_f - c_o) \int_o^t h(t) \, dt + c_o \tag{28}$$

where $h(t)$ is the instaneous unit salino response which characterises the systems operation. This curve can be derived by the first order derivative of an experimentally obtained breakthrough. VAN DE NES (1973) defines the moments of the impuls response relative to the origin as:

$$M_i = \frac{\int_o^\infty t^i\, h(t)\, dt}{\int_o^\infty h(t)\, dt} \tag{29}$$

where M_i is an expression for the ith moment.

The 'average breakthrough time' at the outlet of the column is given by the first moment. In a symmetric system, the centre of gravity of the impuls response curve has been reached at time $\bar{t}$ when:

$$c(\bar{t}) = \frac{1}{2}(c_f + c_o) \tag{28a}$$

The statistical variance in time is given by:

$$\sigma_t^2 = M_2 - M_1^2 \tag{30}$$

If the method of statistical moments is applied to the concentration course described by the Poisson distribution, expressions are obtained for the average breakthrough time and variance:

$$\bar{t} = (n+1)\left(\frac{\Delta x}{u}\right) \tag{31a}$$

$$\sigma_t^2 = (n+1)\left(\frac{\Delta x}{u}\right)^2 \tag{31b}$$

If the first layer is considered to be the reservoir of the feed solution, counting of the layers may start with 1 instead of zero, the number of layers (n), the layer thickness (Δx) and the effective porosity (ε_e) are given by:

$$n = \frac{\bar{t}^2}{\sigma_t^2} \tag{32a}$$

$$\Delta x = L_t\, \frac{\sigma_t^2}{\bar{t}^2} \tag{32b}$$

$$\varepsilon_e = \bar{t}\, \frac{v}{L_t} \tag{32c}$$

14

with L_t as the total length of the column. and v as the flux.

The same method can be applied to the parameter determination of the parallel column system. The main salino response curve may be devided in k symmetrical sub-curves. The relative contribution ϕ_j of each column to the system is given by the area of each curve:

$$\phi_j = \int_0^\infty h_j(t)\, dt \qquad (33)$$

with $\displaystyle\sum_{j=1}^{k} \phi_j = 1$

The effective posity and the velocity in each column are found from:

$$u_j = \frac{L_t}{\bar{t}_j} \qquad (34a)$$

$$\varepsilon_{ej} = \frac{v\phi_j \bar{t}_j}{L_t} \qquad (34b)$$

where the suffix j stands for the number of the column.

The salino response curve can be adjusted by plotting a symmetric curve as large as possible beneath the experimental curve. If diffusion is expected to play an important role, its effect can be estimated by the subtraction of the adjusted apparent diffusion from the total apparent diffusion. The not covered part of the area (the tail) can be considered to be due to diffusion.

2.4. Two dimensional approach

2.4.1. Possibilities for a two dimensional approach

The differential equation describing the two dimensional convective/dispersive transport is given by (CHENG et al, 1984):

$$\frac{\partial c}{\partial t} + u_x \frac{\partial c}{\partial x} + u_y \frac{\partial c}{\partial y} = D\left(\frac{\partial c^2}{\partial x^2} + \frac{\partial^2 c}{\partial y^2}\right) \qquad (35)$$

15

The velocity in x and y direction at a certain point is expressed by u_x and u_y. If the dispersion is not isotropic the second order term may be given by $D_x \frac{\partial^2 c}{\partial x^2} + D_y \frac{\partial^2 c}{\partial y^2}$.

A discrete form for the equation is:

$$\frac{c(x,y,t+\Delta t) - c(x,y,t)}{\Delta t} + u_x \frac{c(x,y,t) - c(x-\Delta x,y,t)}{\Delta x} +$$

$$+ u_y \frac{c(x,y,t) - c(x,y-\Delta y,t)}{\Delta y} = D\left[\frac{c(x+\Delta x,y,t) - 2c(x,y,t) + c(x-\Delta x,y,t)}{(\Delta x)^2} + \right.$$

$$\left. + \frac{c(x,y+\Delta y,t) - 2c(x,y,t) + c(x,y-\Delta y,t)}{(\Delta y)^2}\right] \tag{36}$$

Expressions for the discrete terms are obtained by the method of Taylor expansion:

$$\frac{c(x,y,t+\Delta t) - c(x,y,t)}{\Delta t} = \frac{\partial c}{\partial t} + \frac{\Delta t}{2!}\frac{\partial^2 c}{\partial t^2} + \frac{(\Delta t)^2}{3!}\frac{\partial^3 c}{\partial t^3} + \ldots \tag{37a}$$

$$\frac{c(x,y,t) - c(x-\Delta x,y,t)}{\Delta x} = \frac{\partial c}{\partial x} - \frac{\Delta x}{2!}\frac{\partial^2 c}{\partial x^2} + \frac{(\Delta x)^2}{3!}\frac{\partial^3 c}{\partial x^3} - \ldots \tag{37b}$$

$$\frac{c(x,y,t) - c(x,y-\Delta y,t)}{\Delta y} = \frac{\partial c}{\partial y} - \frac{\Delta y}{2!}\frac{\partial^2 c}{\partial y^2} + \frac{(\Delta y)^2}{3!}\frac{\partial^3 c}{\partial y^3} - \ldots \tag{37c}$$

$$\frac{c(x+\Delta x,y,t) - 2c(x,y,t) + c(x-\Delta x,y,t)}{(\Delta x)^2} = \frac{\partial^2 c}{\partial x^2} + 2\frac{(\Delta x)^2}{4!}\frac{\partial^4 c}{\partial x^4} + \ldots \tag{37d}$$

$$\frac{c(x,y+\Delta y,t) - 2c(x,y,t) + c(x,y-\Delta y,t)}{(\Delta y)^2} = \frac{\partial^2 c}{\partial y^2} + 2\frac{(\Delta y)^2}{4!}\frac{\partial^4 c}{\partial y^4} + \ldots \tag{37e}$$

The second order derivative to time $\frac{\partial^2 c}{\partial t^2}$ can expressed in derivatives to place:

$$\frac{\partial^2 c}{\partial t^2} = \frac{\partial}{\partial t}\left(- u_x \frac{\partial c}{\partial x} - u_y \frac{\partial c}{\partial y} + D \frac{\partial^2 c}{\partial x^2} + D \frac{\partial^2 c}{\partial y^2}\right) \tag{38a}$$

Neglection of the third and higher order terms when transport dominates over diffusion/dispersion:

$$\frac{\partial^2 c}{\partial t^2} = - u_x \frac{\partial}{\partial x}\left(\frac{\partial c}{\partial t}\right) - u_y \frac{\partial}{\partial y}\left(\frac{\partial c}{\partial t}\right) \qquad (38b)$$

$$= - u_x \frac{\partial}{\partial x}\left(- u_x \frac{\partial c}{\partial x} - u_y \frac{\partial c}{\partial y}\right) - u_y \frac{\partial}{\partial y}\left(- u_x \frac{\partial c}{\partial x} - u_y \frac{\partial c}{\partial y}\right) \qquad (38c)$$

$$= u_x^2 \frac{\partial^2 c}{\partial x^2} + 2 u_x u_y \frac{\partial c^2}{\partial x \partial y} + u_y^2 \frac{\partial^2 c}{\partial y^2} \qquad (38d)$$

Substitution of (37a), (37e) and (38d) into (36) yields:

$$\frac{\partial c}{\partial t} + u_x \frac{\partial c}{\partial x} + u_y \frac{\partial c}{\partial y} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2}\right) +$$
$$+ \frac{1}{2}\left[(u_x \Delta x - u_x^2 \Delta t) \frac{\partial^2 c}{\partial x^2} - 2 u_x u_y \Delta t \frac{\partial^2 c}{\partial x \partial y} + (u_y \Delta y - u_y^2 \Delta t) \frac{\partial^2 c}{\partial y^2}\right] + \ldots \qquad (39)$$

The last term of the right hand side expresses the numerical dispersion which is introduced by the finite differences. The effect of the numerical dispersion is a function of the velocity field and the coefficients in (39) are not constant. The use of the differences schedule given in (36) introduces an additional dispersion and the size of the dispersion can not be controlled.

CHENG et al (1984) gave a method that excludes the numerical dispersion and which is based on the interpolation of the surrounding grid points with second order Lagrange polynomials (fig. 4).
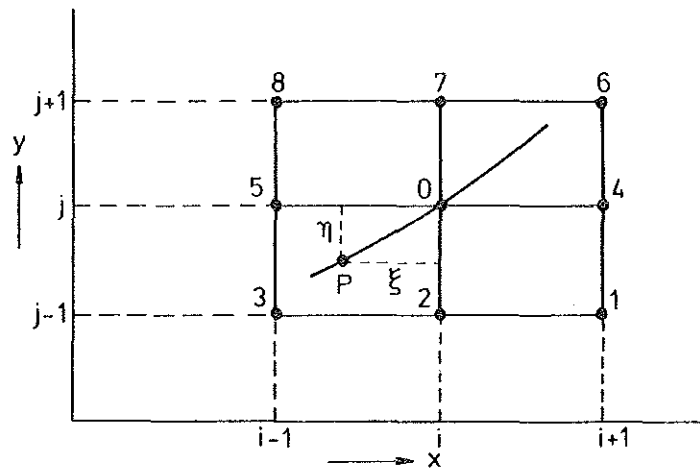

Fig. 4. Interpolation of the surrounding grid points

The finite difference approach for (35) in this method is given by:

$$\frac{c(x,y,t+\Delta t) - c(x-\xi\Delta x,y-\eta\Delta y,t)}{\Delta t} = D\left[\frac{c(x+\Delta x,y,t) - 2c(x,y,t) + c(x-\Delta x,y,t}{(\Delta x)^2} +\right.$$

$$\left.\frac{c(x,y+\Delta y,t) - 2c(x,y,t) + c(x,y-\Delta y,t)}{(\Delta y)^2}\right] \tag{40}$$

with $\xi = -v_x \frac{\Delta t}{\Delta x}$ and $\eta = -v_y \frac{\Delta t}{\Delta y}$

The concentration in point P $c(x-\xi\Delta x,y-\eta\Delta y,t)$ is composed of the concentrations in the surrounding grid points:

$$c(x-\xi\Delta x,y-\eta\Delta y,t) = a_0 c(x,y,t) + a_1 c(x+\Delta x,y-\Delta y,t) + a_2 c(x,y-\Delta y,t) +$$

$$+ a_3 c(x-\Delta x,y-\Delta y,t) + a_4 c(x+\Delta x,y,t) = a_5 c(x-\Delta x,y,t) +$$

$$+ a_6 c(x+\Delta x,y+\Delta y,t) + a_7 c(x,y+\Delta y,t) + a_8 c(x-\Delta x,y+\Delta y,t) \tag{41}$$

with
$$a_0 = (1-\xi^2)(1-\eta^2) \qquad a_5 = -\frac{1}{2}\xi(1-\xi)(1-\eta^2)$$

$$a_1 = -\frac{1}{4}\xi(1+\xi)\eta(1-\eta) \qquad a_6 = \frac{1}{4}\xi(1+\xi)\eta(1+\eta)$$

$$a_2 = -\frac{1}{2}(1-\xi^2)\eta(1-\eta) \qquad a_7 = \frac{1}{2}(1-\xi^2)\eta(1+\eta)$$

$$a_3 = \frac{1}{4}\xi(1-\xi)\eta(1-\eta) \qquad a_8 = -\frac{1}{4}\xi(1-\xi)\eta(1+\eta)$$

$$a_4 = \frac{1}{2}\xi(1+\xi)(1-\eta^2)$$

The cancelling of the numerical dispersion can be shown by the development of $c(x,y,t+\Delta t)$ and $c(x-\xi\Delta x,y-\eta\Delta y,t)$ in Taylor series:

$$c(x,y,t+\Delta t) = c(x,y,t) + \Delta t \frac{\partial c}{\partial t} + \frac{\Delta t^2}{2}\left[u_x^2 \frac{\partial^2 c}{\partial x^2} + 2u_x u_y \frac{\partial^2 c}{\partial x \partial y} + u_y^2 \frac{\partial^2 c}{\partial y^2}\right] + \ldots \tag{42a}$$

and

$$c(x-\xi\Delta x,y-\eta\Delta y,t) = c(x,y,t) - \xi\Delta x \frac{\partial c}{\partial x} - \eta\Delta y \frac{\partial c}{\partial y} + \xi^2 \frac{\Delta x^2}{2}\frac{\partial^2 c}{\partial x^2} +$$

$$\xi\eta\Delta x\Delta y \frac{\partial^2 c}{\partial x \partial y} + \eta^2 \frac{\Delta y^2}{2}\frac{\partial^2 c}{\partial y^2} + \ldots \tag{42b}$$

18

The substitution of the left hand side of (40) by the terms given in (42a) and (42b) yields:

$$\frac{\partial c}{\partial t} + u_x \frac{\partial c}{\partial x} + u_y \frac{\partial c}{\partial y} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2}\right) + \dots \tag{43}$$

The numerical dispersion introduced from temporal discretization in (42a) equals exactly the dispersion caused by the discretization of the space derivate in (42b).

2.4.2. Pseudo two dimensional approach

The mixing-cell concept contains the mixing ratio $\frac{u\Delta t}{\Delta x}$ which can be replaced by $\frac{\Delta t}{T}$:

$$c(x,t+\Delta t) = c(x,t) + \frac{\Delta t}{T}(c(x-\Delta x,t) - c(x,t)) \tag{44}$$

where the residence time of the solution in a compartment T is defined as:

$$T = \frac{\Delta x}{u} \tag{45}$$

The system can be extended to two or three dimensions by the introduction of T (VAN OMMEN, 1985).

The inflow and outflow in a cell, situated between two streamlines in a two dimensional section is constant and the area A_i of the compartments are equal (Fig. 5).
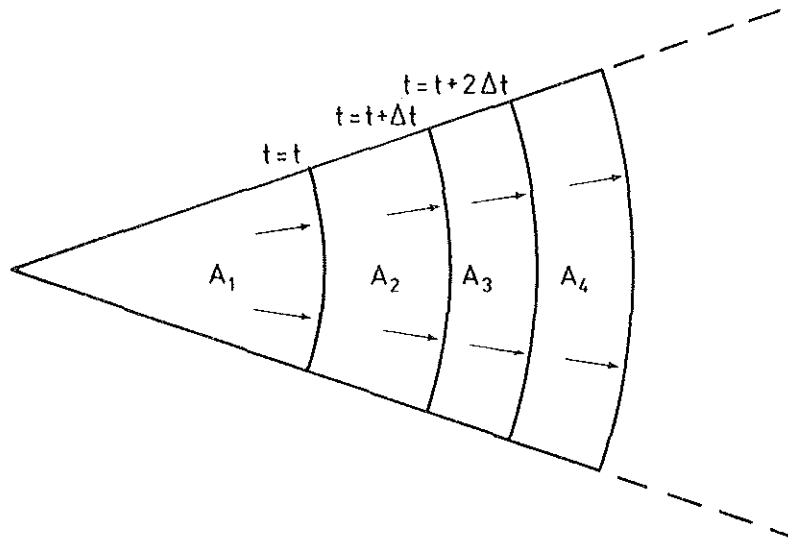
Fig. 5. Pseudo two dimensional approach with equal compartment areas
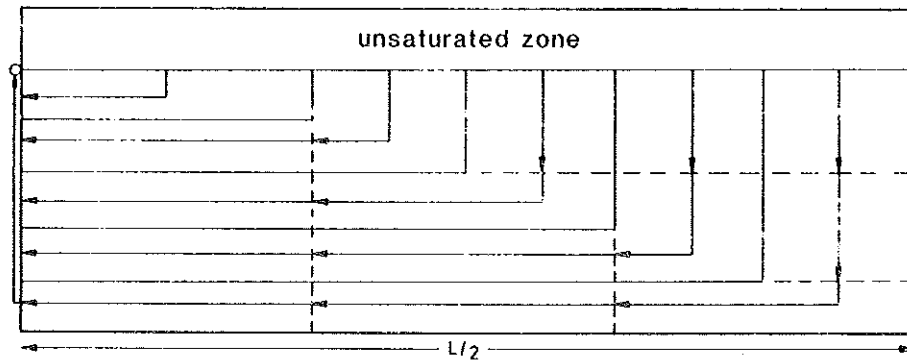
Fig. 6. Schematic representation of horizontal and vertical streamtubes

ROEST and RIJTEMA (1983) gave another formulation for a two dimensional approach. A schematization of the velocity field in a saturated aquifer is introduced by parallel columns (Fig. 6).

The assumption is made that no discharge from the unsaturated zone enters the drain directly and the feed of the aquifer is considered as a diffuse source. The effect of transversal dispersion is neglected and no other interactions between the streamtubes occurs.

Each streamtube is composed of a vertical and a horizontal part. The volume of a horizontal part equals to the volume of a vertical part and therefore, the compartments will generally have different sizes in order to satisfy the condition of equal volumes.

The length of a contributing section to a drain is L/2, where L is the drain distance. The effective depth is assumed to be L/4, when a physical drainage barrier does not exist.

ROEST and RIJTEMA (1983) gave the following relation for the resulting concentration of the drainage water in the TRADE model:

$$c_d(t) = \frac{1}{N} \sum_{i=1}^{N} c_{n,i}(t) \qquad (46)$$

Applied to the mixing cell concept, the concentration of the percolation water at a certain time can be obtained by the calculation of the average concentration of the longest streamtube.

Incorporation of phenomena such as seepage and percolation to a deeper aquifer is possible in this system.

3. EXCHANGE MODEL

3.1. Adsorption equilibrium

3.1.1. Three cation system

The complete content of cations in a soil compartment can be distinguished in a solid and a solute phase. The solid phase contains the precipitated fraction of the cation species and the fraction adsorbed to clay minerals and organic matter. The solute phase contains the free ions in solution and the ions which are incorporated in ligands The precipitated phase is not considered in this report.

Traditionally, the unity of the adsorption capacity of the solid phase is expressed in meq per 100 gr dry soil and the concentration of salt in the solute phase in eq liter^{-1} solution. One eq liter^{-1} of a ion in solution corresponds with $\frac{\theta_v}{\rho_d}$ meq per 100 gr adsorbed at the solid phase, where θ_v is the volumetric water content in % and ρ_d is the dry bulk density in gr cm^{-3}.

Different formulations are used to describe the exchange equilibrium of cations. The Kerr equation is used to describe the exchange between homovalent cations and the Gapon equation describes the exchange between mono and divalent cations.

Kerr equation:

$$\frac{\gamma_{Ca^{2+}}}{\gamma_{Mg}} = K_k \frac{A_{Ca^{2+}}}{A_{Mg^{2+}}} \qquad (47a)$$

Gapon equation:

$$\frac{\gamma_{Na^+}}{\gamma_{Ca^{2+}}} = K_G \frac{A_{Na^+}}{\sqrt{A_{Ca^{2+}}}/2} \qquad (47b)$$

where: γ_{Na^+} = adsorbed quantity of Na$^+$ (meq per 100 gr)

$\gamma_{Ca^{2+}}$ = adsorbed quantity of Ca^{2+} (meq per 100 gr)

$\gamma_{Mg^{2+}}$ = adsorbed quantity of Mg^{2+} (meq per 100 gr)

A_{Na^+} = Na$^+$ activity   (eq liter^{-1})

$A_{Ca^{2+}} = Ca^{2+}$ activity $\qquad$ (eq liter^{-1})

$A_{Mg^{2+}} = Mg^{2+}$ activity $\qquad$ (eq liter^{-1})

K_G = Gapon exchange coefficient $\quad$ (liter$^{\frac{1}{2}}$ eq$^{-\frac{1}{2}}$)

K_K = Kerr exchange coefficient

In the exchange equations the activities of the mentioned cations are used. The figures of the concentrations of the cations are needed to define the mass balance of each cation. Therefore activity coefficients are introduced according to:

$$A_k = f_k [K] \tag{48}$$

with: f_k = activity coefficients of a cation
$\quad$ $[K]$ = concentration of a cation K $\quad$ (eq liter^{-1})

The coefficients are calculated by means of the Debye-Hückel equation:

$$\log f_k = - \frac{A Z_k^2 \sqrt{I}}{1 + \overset{o}{a}_k B \sqrt{I}} \tag{49}$$

where I represents the ionic strength of the solution:

$$I = \frac{1}{2} \sum_k z_k^2 [K] \qquad (eq\ liter^{-1}) \tag{50}$$

Z_k = valency of cation K $\qquad \overset{o}{a}_{Na^+} = 4\ \overset{o}{A}$

$A = 0.51$ liter$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ $\qquad \overset{o}{a}_{Ca^{2+}} = 6\ \overset{o}{A}$

$B = 0.33$ liter$^{\frac{1}{2}}$ $\overset{o}{A}^{-1}$ mole$^{-\frac{1}{2}}$ $\qquad \overset{o}{a}_{Mg^{2+}} = 8\ \overset{o}{A}$

(after BOLT, 1978; Soil Chemistry, A. Basic Elements; p. 17, 18)

The activity coefficients can be introduced in the exchange equations by adjusting the exchange constants:

$$K_K^* = \frac{f_{Ca^{2+}}}{f_{Mg^{2+}}} K_K \tag{51a}$$

22

$$K_G^* = \frac{f_{Na^{2+}}}{\sqrt{f_{Ca^{2+}}}} K_G \qquad (52b)$$

Any change in the mass balance of a cation by transport processes causes a shift in the exchange equilibrium. Such a change in the soil solution concentration can be described by the introduction of an alteration term in the exchange formulations:

$$\frac{\gamma_{Ca^{2+}} + \frac{\theta_v}{\rho_d} \Delta Ca^{2+}}{\gamma_{Mg^{2+}} + \frac{\theta_v}{\rho_d} \Delta Mg^{2+}} = K_k^* \frac{[Ca^{2+}] - \Delta Ca^{2+}}{[Mg^{2+}] - \Delta Mg^{2+}} \qquad (52a)$$

$$\frac{\gamma_{Na^+} + \frac{\theta_v}{\rho_d} \Delta Na^+}{\gamma_{Ca^{2+}} + \frac{\theta_v}{\rho_d} \Delta Ca^{2+}} = K_G^* \frac{[Na^+] - \Delta Na^+}{\sqrt{([Ca^{2+}] - \Delta Ca^{2+})/2}} \qquad (52b)$$

with: ΔNa^+ = change in sodium concentrations (eq liter^{-1})

ΔCa^{2+} = change in calcium concentrations (eq liter^{-1})

ΔMg^{2+} = change in magnesium concentrations (eq liter^{-1})

The total quantity of adsorbed cations remains constant and the mass balance can be expressed by:

$$\Delta Na^+ + \Delta Ca^{2+} + \Delta Mg^{2+} = 0 \qquad (53)$$

The condition of electroneutrality yields:

$$\sum [K^{z+}] = \sum [K^{z-}] \qquad (54)$$

where: $[K^{z+}]$ = concentration of cation K having valency z (eq liter^{-1})

$[K^{z-}]$ = concentration of anion K having valency z (eq liter^{-1})

An expression for the change in sodium concentration can be obtained by the combination of (52a) and (53):

$$\Delta Na^+ = -\frac{u_1 + u_2 \Delta Ca^{2+} + u_3 (\Delta Ca^{2+})^2}{u_4 + u_3 \Delta Ca^{2+}} \qquad (55)$$

with:

$$u_1 = \gamma_{Ca^{2+}}[Mg^{2+}] - K_K^* \gamma_{Mg^{2+}}[Ca^{2+}] \tag{56a}$$

$$u_2 = \gamma_{Ca^{2+}} + \frac{\theta_v}{\rho_d}[Mg^{2+}] + K_K \gamma_{Mg^{2+}} + \frac{\theta_v}{\rho_d} K_K^*[Ca^{2+}] \tag{56b}$$

$$u_3 = \frac{\theta_v}{\rho_d}(1-K_K^*) \tag{56c}$$

$$u_4 = \gamma_{Ca^{2+}} + \frac{\rho v}{\rho_d} K_K^*[Ca^{2+}] \tag{56d}$$

The following expression for ΔCa^{2+} is found by substituting (55) into (52b):

$$g_1(\Delta Ca^{2+})^6 + g_2(\Delta Ca^{2+})^5 + g_3(\Delta Ca^{2+})^4 + g_4(\Delta Ca^{2+})^3 + g_5(\Delta Ca^{2+})^2 +$$

$$+ g_6\Delta Ca^{2+} + g_7 = 0 \tag{57}$$

with:

$$g_1 = u_3^2 u_5 \tag{57a}$$

$$g_2 = u_3^2(u_6-u_8) + 2u_2u_3u_5 \tag{57b}$$

$$g_3 = u_3^2(u_7-u_9+u_{11}) + u_2u_3(2u_6-u_8) + 2u_1u_3u_5 - u_3u_4u_8 + u_2^2u_5 \tag{57c}$$

$$g_4 = u_3^2(u_1+u_{12}) + u_1u_3(2u_6-u_8) + u_2u_3(2u_7-u_9) + u_3u_4(2u_{11}-u_9) +$$

$$+ u_2^2u_6 + 2u_1u_2u_5 - u_2u_4u_8 \tag{57d}$$

$$g_5 = u_1^2u_5 + u_2^2u_7 + u_3^2u_{13} + u_4^2u_4 + u_1u_3(2u_7-u_9) + u_3u_4(2u_{12}-u_{10}) +$$

$$+ 2u_1u_2u_6 - u_2u_3u_{10} - u_2u_4u_9 - u_1u_4u_8 \tag{57e}$$

$$g_6 = u_1^2u_6 + u_4^2u_{12} + u_1(2u_2u_7-u_4u_9-u_3u_{10}) + u_4(2u_3u_{13}-u_2u_{10}) \tag{57f}$$

$$g_7 = u_1^2u_7 - u_1u_4u_{10} + u_4^2u_{13} \tag{57g}$$

24

and:

$$u_5 = 2\left(\frac{\theta_v}{\rho_d} K_G^*\right)^2 \tag{56e}$$

$$u_6 = 4K_G^{*2} \frac{\theta_v}{\rho_d} \gamma_{Ca^{2+}} + \left(\frac{\theta_v}{\rho_d}\right)^2 \tag{56f}$$

$$u_7 = 2(K_G^* \gamma_{Ca^{2+}})^2 - \left(\frac{\theta_v}{\rho_d}\right)^2 [Ca^{2+}] \tag{56g}$$

$$u_8 = -4\left(K_G^* \frac{\theta_v}{\rho_d}\right)^2 [Na^+] \tag{56h}$$

$$u_9 = -8 K_G^* \frac{\theta_v}{\rho_d} \gamma_{Ca^{2+}}[Na^+] + 2 \frac{\theta_v}{\rho_d} \gamma_{Na^+} \tag{56i}$$

$$u_{10} = -4(K_G^* \gamma_{Ca^{2+}})^2 [Na^+] - 2 \frac{\theta_v}{\rho_d} \gamma_{Na^+}[Ca^{2+}] \tag{56j}$$

$$u_{11} = 2\left(K_G^* \frac{\theta_v}{\rho_d}[Na^+]\right)^2 \tag{56k}$$

$$u_{12} = 4(K_G^*[Na^+])^2 \frac{\theta_v}{\rho_d} \gamma_{Ca^{2+}} + \gamma_{Na^+}^2 \tag{56l}$$

$$u_{13} = 2(K_G^* \gamma_{Ca^{2+}}[Na^+])^2 - \gamma_{Na^+}^2 [Ca^{2+}] \tag{56m}$$

The equation obtained is a sixth degree function and principally may have six mathematical solutions. Only one solution suffices to the boundary conditions which can be defined by the consideration of the mass balance of each cation. Each numerator and denominator in the equations (52a) and (52b) must be greater than or equal to zero:

$$- \gamma_{Na^+} \cdot \frac{\rho_d}{\theta_v} \leq \Delta Na^+ \leq [Na^+] \tag{58a}$$

$$- \gamma_{Ca^{2+}} \cdot \frac{\rho_d}{\theta_v} < \Delta Ca^{2+} < [Ca^{2+}] \tag{58b}$$

$$- \gamma_{Mg^{2+}} \cdot \frac{\rho_d}{\theta_v} < \Delta Mg^{2+} < [Mg^{2+}] \tag{58c}$$

25

The original exchange equations can be formulated in terms of left hand side and right hand side expressions:

$$\text{lhs1} = \frac{\gamma_{Ca^{2+}}}{\gamma_{Mg^{2+}}} \tag{59a}$$

$$\text{rhs1} = K_k^* \frac{[Ca^{2+}]}{[Mg^{2+}]} \tag{59b}$$

$$\text{lhs2} = \frac{\gamma_{Na^+}}{\gamma_{Ca^{2+}}} \tag{59c}$$

$$\text{rhs2} = K_G^* \frac{[Na^+]}{\sqrt{[Ca^{2+}]/2}} \tag{59d}$$

These formulations can be used to obtain expressions for the minimum and maximum value of ΔCa^{2+}. The following conditions can be formulated (Table 1).

If these statements are combined with the conditions mentioned in – 58a, 58b, 58c – the minimum and maximum value of ΔCa^{2+} can be derived (Table 2).

Table 1. Conditions for the minimum and maximum value of ΔCa^{2+}

	lhs1 > rhs1	lhs1 $\leq$ rhs1
lhs2 > rhs2	$\Delta Na^+ < \Delta Ca^{2+} < \Delta Mg^{2+}$	$\Delta Ca^{2+} > \Delta Na^+$; $\Delta Ca^{2+} \geq Mg^{2+}$
lhs2 $\leq$ rhs2	$\Delta Ca^{2+} < \Delta Mg^{2+}$; $\Delta Ca^{2+} \leq \Delta Na^+$	$\Delta Mg^{2+} \leq \Delta Ca^{2+} \leq \Delta Na^+$

Table 2. Minimum and maximum values for ΔCa^{2+} with min = minimum value for ΔCa^{2+} (eq/l); max = maximum value for ΔCa^{2+} (eq/l)

	lhs1 > rhs1	lhs1 $\leq$ rhs1
lhs2 > rhs2	min = $\dfrac{\rho_d}{\theta_v}$ max$\left(-\gamma_{Ca^{2+}}, -\gamma_{Mg^{2+}}\right)$	min = 0.0
	max = min$([Na^+], [Ca^{2+}])$	max = $[Ca^{2+}]$
lhs2 $\leq$ rhs2	min = $-\dfrac{\rho_d}{\theta_v}\gamma_{Ca^{2+}}$	min = $\dfrac{\rho_d}{\theta_v}$ max$\left(-\gamma_{Na^+}, -\gamma_{Ca^{2+}}\right)$
	max = 0.0	max = min$([Ca^{2+}], [Mg^{2+}])$

Equation (57) can be solved by using the Newton Raphson iteration procedure. If F(X) it formulated as a function of X, similarly to the 6th degree function given in (57) the iteration schedule is given by:

$$X^{n+1} = X^n - \frac{F(X^n)}{F'(X^n)} \tag{60}$$

with: X^{n+1} = value of ΔCa^{2+} after n+1 iterations

X^n = value of ΔCa^{2+} after n iterations

$F(X^n)$ = value of the 6th degree function

$F'(X^n)$ = value of the first derivate of the 6th degree function

A satisfactory value of ΔCa^{2+} has been obtained if the convergence criterion has been met according to:

$$\left| X^{n+1} - X^n \right| < \delta \tag{61}$$

δ = convergence value

The start value for the iteration must be selected carefully for efficiency reasons. The result of the iteration procedure has to be checked against the conditions formulated in (58a), (58b) and (58c) and Table 2. If the result does not meet the conditions another start value has to be chosen and the procedure must be repeated.

In the programme SCMEX, the start value is set at the average of the minimum and maximum value for ΔCa^{2+}. When the iteration results in

an erroneous solution of the 6th degree function, another start value is estimated according to:

$$X' = ((j+10).Min + (10-j).Max)/20 \qquad (62)$$

and:

$$j = (-1)^{i+1}.INT\{(i+1)/2\} \quad i = 0, 1, \ldots, 20 \qquad (63)$$

with INT as a truncation function of a real number.

3.1.2. Absence of sodium of magnesium

The algebraic solution of the modified exchange equations can be simplified if the system contains no magnesium or sodium. When sodium is absent, the absolute change in calcium concentration equals the absolute change in magnesium.

Equation 52a can be formulated in alteration terms of calcium:

$$\frac{\gamma_{Ca^{2+}} + \dfrac{\theta_v}{\rho_d}\Delta Ca^{2+}}{\gamma_{Mg^{2+}} - \dfrac{\theta_v}{\rho_d}\Delta Ca^{2+}} = K_K^* \frac{[Ca^{2+}] - \Delta Ca^{2+}}{[Mg^{2+}] + \Delta Ca^{2+}} \qquad (64)$$

where: $\Delta Mg^{2+} = -\Delta Ca^{2+}$

and when it is written in coefficient form, the expression yields a second degree function of ΔCa^{2+}:

$$u_3(\Delta Ca^{2+})^2 + u_2 \Delta Ca^{2+} + u_1 = 0 \qquad (65)$$

with u_1, u_2 and u_3 as the coefficients given in (56a), (56b) and (56c). In case of absence of magnesium the adsorbed quantity of sodium is only replaced by calcium and vice versa.

For this case equation (52b) can be rewritten:

$$\frac{\gamma_{Na^+} \cdot - \dfrac{\theta_v}{\rho_d}\Delta Ca^{2+}}{\gamma_{Ca^{2+}} + \dfrac{\theta_v}{\rho_d}\Delta Ca^{2+}} = K_G^* \frac{[Na^+] + \Delta Ca^{2+}}{\sqrt{([Ca^{2+}]-\Delta Ca^{2+})/2}} \qquad (66)$$

where: $\Delta Na^+ = -\Delta Ca^{2+}$

This formulation can be written in coefficient form as a fourth degree function:

$$u_5(\Delta Ca^{2+})^4 + (u_6 - \tfrac{1}{2}u_8)(\Delta Ca^{2+})^3 + (u_7 - u_9 + u_{11})(\Delta Ca^{2+})^2 +$$

$$+ (u_{12} - u_{10}) \Delta Ca^{2+} + u_{13} = 0 \qquad (67)$$

with $u_5 - u_{13}$ as the coefficients given by (56e)-(56m).

3.2. Linear solution

A linear solution of the combined dispersion adsorption effect is given by REINIGER and BOLT (1972) by adjusting the velocity and dispersion coefficient (eq 4a):

$$D^* = D'/(r_D + 1) \varepsilon \qquad (68a)$$

and

$$v^* = v/(r_D + 1) \varepsilon \qquad (68b)$$

with r_D being the slope of the exchange isotherm at the concentration considered. In an exchange process, the concentration of a cation can alter and the slope of the chord of the exchange isotherm in the range under consideration may be taken for small values of Δc as:

$$r_D = \Delta q/\varepsilon\Delta c \qquad (69)$$

otherwise r_D may be defined as $r_D = q'(c)/\varepsilon$.

Relations for $q'(c)$ can be obtained from the Kerr and Gapon equations, f.e. (47a) and (47b), for systems with two relevant cations. For the favourable exchange situation (Sodium in a Na-Ca system and Calcium in a Ca-Mg system) the differential capacity of the exchange can be given by:

$$q'(c) = \frac{K_K c_o Q}{[c + K_K(c_o - c)]^2} \qquad (70a)$$

derived from the Kerr equation and:

$$q'(c) = \frac{K_G(c_o - \frac{1}{2}c)\ Q}{\sqrt{c_o - c}\ [\sqrt{c_o - c} + cK_G]^2} \qquad (70b)$$

from the Gapon equation with:

Q = cation exchange capacity   (meq/100 gr)

c_o = total concentration of cations or anions   (eq liter^{-1})

c = concentration of the favourable adsorbed cation (eq.liter^{-1})

A suitable solution can be obtained at once if only one value of $q'(c)$ has to be considered.

When (70a) or (70b) is used, a solution for (6) is reached iteratively. The relation given in (69) can be used for estimation of a start value for the procedure.

4. COLUMN EXPERIMENTS

The model formulation and the parameter estimation methods described have been tested with data of two quick column experiments performed in the ICW Laboratory.

The first experiment (A) has been done with a calcareous sandy loam soil from the polder near Lelystad and a feed solution containing NaCl and CaCl$_2$. The second experiment (B), reported by EL GUINDY and HARMSEN, (1985), has been performed with a mixture of Egyptian clay soil from the Nile Delta and sand. A three cation solute has been used for leaching.

4.1. Materials and methods

A High Performance Liquid Chromatography (HPLC) column of 25 cm length and 4.6 mm internal diameter has been used. The column has been filled completely with air dry soil. A schematization of the instruments used is presented in Fig. 7.

The flow rate was fixed at 0.1 ml.min^{-1} and has been pumped through the column by means of a Varian L.C. 500 pump. Assuming an effective porosity of 0.4 the water volume V_o of the soil column is replaced in about 17 minutes and the column is refreshed more than 80 times during one day. Generally, the sample volume obtained are small and depend on the frequency of sample collection. Advanced analysis instrumentation

Leaching Solution with defined Composition → HPLC Pump → Valve → HPLC Column with Soil Material → Detector → Fraction Collector → Chemical Analysis → Results of Interaction of Leaching Solution with Soil
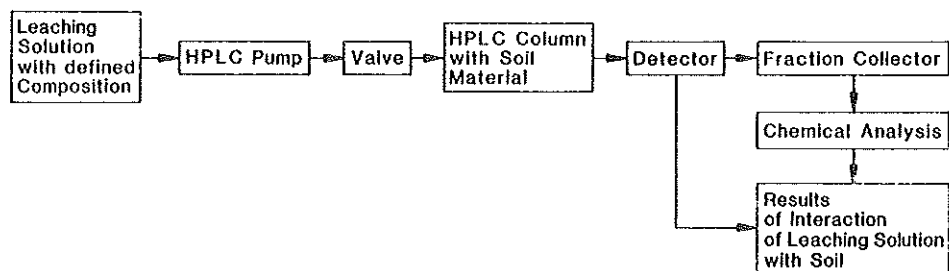
Fig. 7. Schematic illustration of the equipment for column experiments

must be available for the chemical analyses of the samples. For the experiment with the sandy loam soil, the samples have been collected by means of a fraction collector (ISCO 1200) at a frequency of 1 sample per 10 minutes. The Sodium and Calcium concentration has been determined with an Atomic Absorption Spectophotometer. A part of each sample has been diluted with a Cesium solution in order to suppress the ionization of Sodium and a part has been diluted with a Lanthanium solution to prevent disturbance caused by Calcium phosphate.

After reaching equilibrium, a small quantity of nitrate has been added to the feed solution and its concentration course was determined by means of an UV detector (Varichrom, Varian) measuring at a wave length of 210 nm. Nitrate proved to be non-reactive in quick column experiments and the advantage above other tracer ions such as chloride is the continuous determination utility.

The cation composition of the complex of the sandy loam soil has been measured with the BASCOMB method. Firstly, the cations of the complex are replaced by Barium and after separation of the phases, the residue is shaken with a Magnesium sulphate solution. Barium precipitates as $BaSO_4$ and the difference in Mg^{2+} concentration gives a value for the magnitude of the adsoption complex. The several ion species are determined in the first filtrate by means of an Inductively Coupled Plasma Instrument, I.L. 200 (ICP). The sandy loam used has a small exchange capacity and the adsorbed quantity of the considered cations was 2.07 meq per 100 gr dry soil only.

The concentration of the cations in the soil moisture of a saturated sample has been determined and a solute with the same concentration has been used to leach the column several times. The advantage of this method is that the initial concentration is exactly known.

Table 3 presents the figures of the concentrations and adsorbed quantities of Sodium and Calcium. No other relevant cations were present.

The cation composition and CEC of the Egyptian clay-soil has been determined by Dr. El Guindy at the DRI laboratory in Cairo and are presented in Table 4.

The particle size distribution of the soil is given in Table 5.

The clay soil has been mixed with pure sand in a ratio of 1:2 in order to prevent clogging and to reduce the exchange capacity of the soil. An extension part has been connected during the packing of the column (Fig. 8).

Table 3. Chemical data of the column experiment with sandy loam

	Na^+	Ca^{2+}	
Initital soil moisture	7.7	9.0	meq.liter^{-1}
Feed solution	101.5	4.7	meq.liter^{-1}
Complex composition	0.13	1.94	meq per 100 gr

Table 4. Complex composition of the Egyptian clay soil

Na^+	K^+	Ca^{2+}	Mg^{2+}	CEC	meq per 100 gr
6.5	0.7	37.8	9.4	56	

Table 5. Particle size distribution of the
soil sample from the Nile Delta in
Egypt

Sand	Silt	Clay
> 50 µm	2-50 µm	< 2 µm
7 %	45,5 %	47,5 %
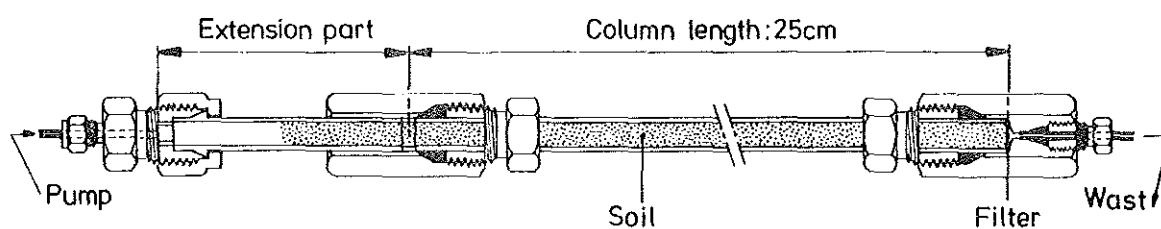
Fig. 8. The connection of the column with the extension part during the preparation of the column bed

The HPLC pump used, is able to deliver a constant flow of leaching solution even at high pressure, which may occur in case of swelling. The column was filled with dry soil up to halfway the extension part and a feed solution with a concentration of 65 meq liter^{-1} $CaCl_2$ was pumped through the soil. Due to the pressure, the wet soil reached a stable packing after some time. The extension part has been removed after 20 hours and the column closed. This method prevents an incomplete filled column due to shrinking or a too tightly packed column due to swelling.

Three breakthrough experiments with different feed solution have been performed. The concentration and compositions of the feed solutions are presented in Table 6.

Table 6. The composition of the leaching solutions

Solution	pH	Electric conductivity $25^{o}C$ (mS.cm^{-1})	NaCl (mM)	NaHCO$_3$ (mM)	MgSO$_4$ (mM)	CaCl$_2$ (mM)
I	7.8	6.4	45	5	2.5	5
II	7.8	5.8	30	5	5	7.5
III	7.8	6.2	0	0	0	32.5

Before the experiments with solution I and II started, the column was leached with the $CaCl_2$ solution in order to replace the cations adsorbed at the complex by Calcium. Samples have been collected in a similar way as in the former experiment, but at a frequency of 1 sample per 20 minutes. The total Inorganic Carbon content has been determined in all samples with the carbon analyser 915 of Beckman. The sample solution was diluted 10 times and Na^+, Ca^{2+} and Mg^{2+} has been measured with the ICP. Sulphate has been determined by means of the turbidemetric method described in the Standard Methods, using 5% of the recommended quantities.

4.2. Results and discussion

4.2.1. Experiment A

4.2.1.1. Nitrate breakthrough in experiment A. The parameters needed to simulate the experiment have been calculated from the first and second statistical moments and the expression for the dispersion length eq. (9). (Table 7)

A large number of theoretical layers are necessary for simulation. The effect of mechanical dispersion is small due to the homogeneity of the soil. The results of the pore space and average breakthrough time calculations from the nitrate curve are equal to the experimental figures which are based on air-dry soil. The curve has been simulated with two sets of parameters to get an impression of the influence of the dispersion length and the number of layers. The simulated and measured curves are presented in the Fig. 9a and 9b.

The computations mentioned have been performed with a mixing ratio of 0.2, 0.5 and 0.8 and 100 theoretical layers. The other curves are calculated with a fixed mixing ratio $\left(= \dfrac{u\Delta t}{\Delta x} \right)$ of 0.5 and 50, 100 and 200 layers. The effect of the mixing ratio and the number of layers is small when an extensive amount of layers is used.

Table 7. Parameters obtained from the nitrate
breakthrough curve

$\bar{t}$	20.54	min	α_L	eq. (9)	1,00	mm
σ_t^2	3,84	min^2	α_L	eq. (19)	1,14	mm
n	109		u		12,17	$mm.min^{-1}$
Δx	2,29	mm	ε_e		49,4	%
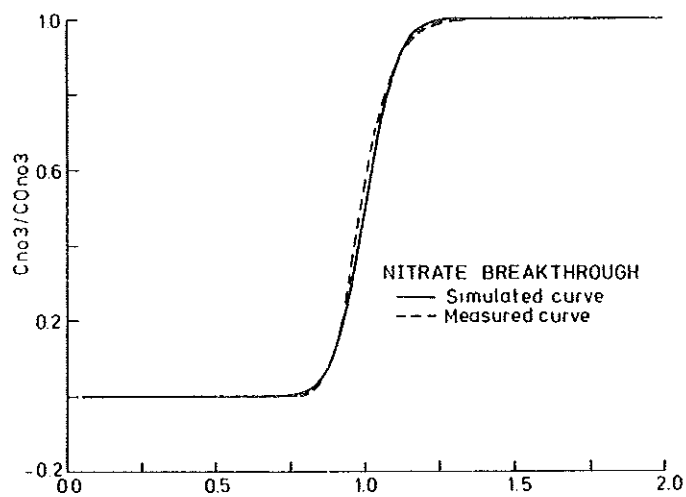
Fig. 9a. Measured simulated nitrate breakthrough curves
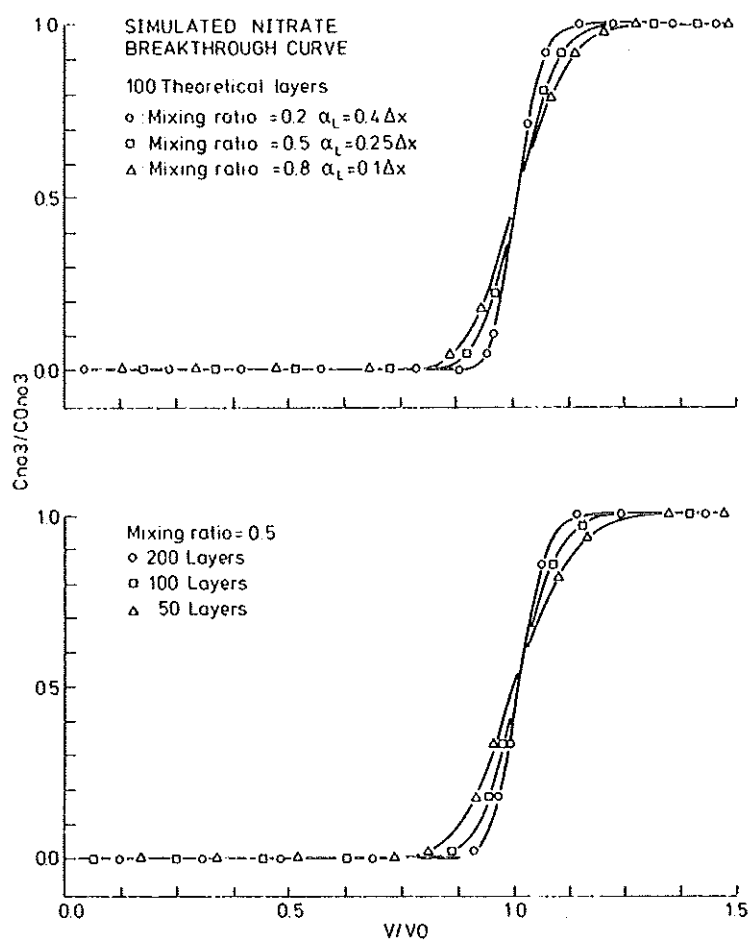
Fig. 9b. Simulated breakthrough curves with different sets of para-
meters

4.2.1.2. Behaviour of cations in experiment A.The effect of adsorption of cations with respect to retardation of the effluent. generally is much more important than the dispersion Phenomena. As a consequence the mixing ratio and number of theoretical layers parameters are of less importance for ion species involved in exchange processes.

The Sodium-Calcium exchange was almost completed after about 10 times replacing the water volume of the column. The low CEC and the high Sodium concentration are factorsthat speeded up the process. The results are presented in Fig. 10a and b. The concentrations are taken relative
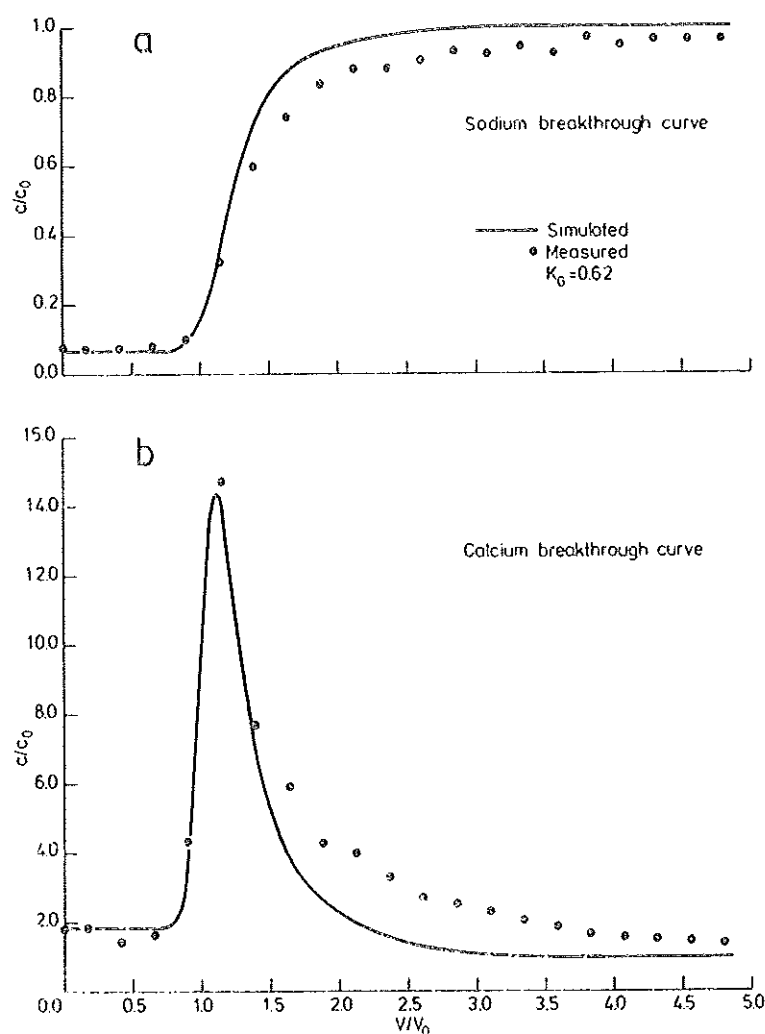
Fig. 10. Measured and simulated concentration course. a: Na^+; b: Ca^{2+}

to the feed solution in these figures and plotted against the number of pore volumes of the column.

Fig. 11 shows the simulated adsorption of cations at the complex. The ESP reaches a value above 55%, but the high Sodium content did not cause permeability problems, most probably due to a high stability of the soil.

The experimental derived Sodium and Calcium concentrations reached the final values slower than the computed results. An extra quantity of Calcium might come into solution by dissolution of precipitated $CaCO_3$. The soil is calcareous in its original composition and it should be noted that the feed solution was very agressive with respect to the carbonate and bi-carbonate ions (see Table 3). Table 8 presents the balances of the two cations.

The peak of the computed Calcium breakthrough curve fits well with the curve experimentally derived. The Gapon exchange constant has been adjusted with one general correction factor due to activity effects and set at $K_G^* = 0.62$. The correction factor has been calculated as an average for the whole experiment according to eq. (49), presented Fig. 12.
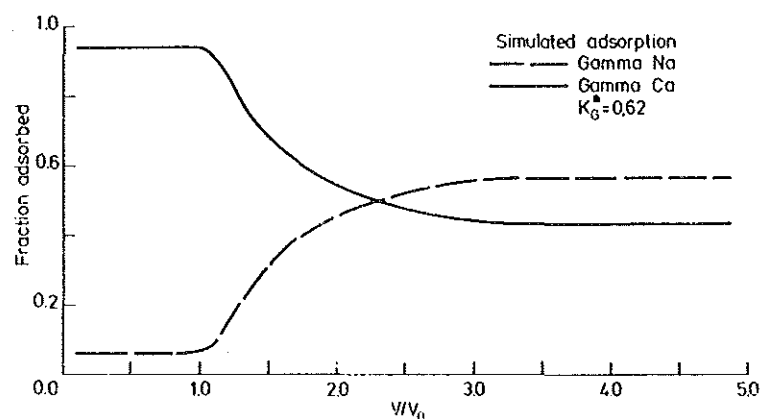
Fig. 11. Simulated adsorption during the column experiment

Table 8. Balances of Sodium and Calcium in meq $(100 \text{ gr})^{-1}$

	Na^+	Ca^{2+}	$Na^+ + Ca^{2+}$
Initial situation:			
adsorbed to the complex	0.13	1.94	2.07
in solution	0.28	0.31	0.59
total	0.41	2.25	2.66
Final situation:			
adsorbed to the complex	1.17	0.90	2.07
in solution	3.73	0.17	3.90
total	4.90	1.07	5.97
Liberated cations experimental		2.07	
calculated		1.18	
Adsorbed cations experimental	2.94		
calculated	4.49		
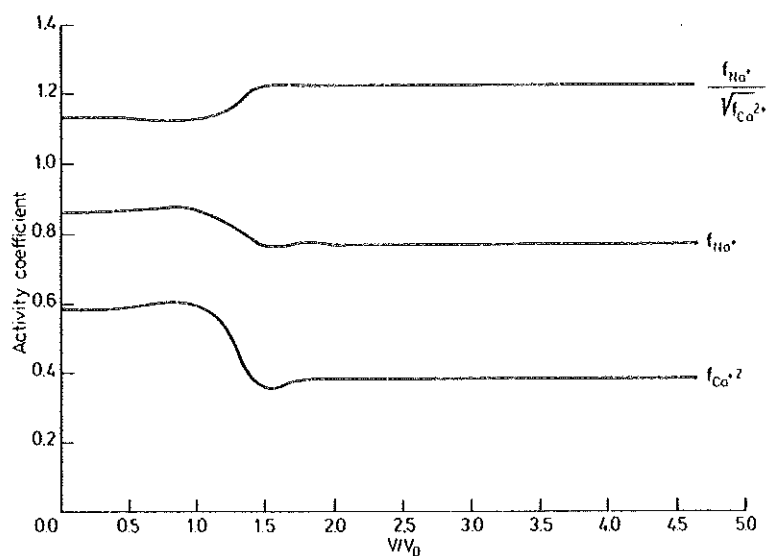
Fig. 12. Activity coefficients calculated with the Debye-Hückel
equation

4.2.2. Experiment B

4.2.2.1. Nitrate breakthrough in experiment B. The nitrate curve has been determined in a similar way as in the former experiment. The curve shows an assymetry which may be explained by a non-uniform pore size distribution. The parameters have been calculated by the method given in Section 2.3 and are presented in Table 9.

Table 9. Parameters obtained from the nitrate
breakthrough

$\bar{t}$	16.90	min	α_L	eq. (9)	7.30	mm
σ_t^2	32.94	min^2	α_L	eq. (19)	14.42	mm
n	8		u		14.79	$mm.min^{-1}$
Δx	31.25	mm	ε_e		40.9	%

These parameters have been tested by the simulation of the curve using the mixing cell algorithm (fig. 13).

The tangent curve has been divided into two and three subcurves representing columns of a more column system. The parameters of the column systems can be derived from the data presented in Tables 10a and 10b.
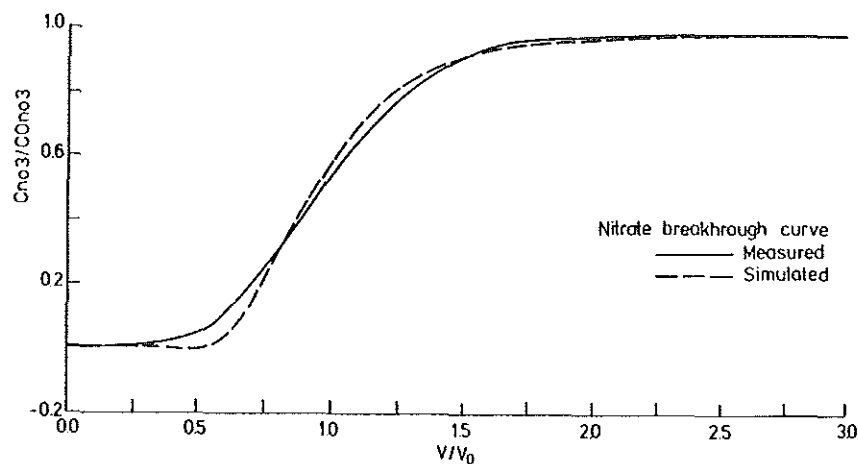
Fig. 13. Measured and simulated relative concentration course

Table 10a. Statistical data of the
two column system

	Column 1	Column 2	
$\bar{t}$	14.00	23.71	min
σ_t^2	6.16	28.32	min^2
ϕ_j	69.9	30.1	%

Table 10b. Statistical data of the three
column system

	Column 1	Column 2	Column 3	
$\bar{t}$	13.50	18.00	24.94	min
σ_t^2	5.26	2.08	29.70	min^2
ϕ_j	60.9	15.5	23.6	%

The simulation of the curve with 2 and 3 parallel columns and the alternative difference schedule given in eq. (25) yields better results. The diffusion coefficient is estimated by the subtraction of the adjusted apparent diffusion, given by the area beneath the tangent curve of column 1, and the total apparent diffusion, given by the area of the total tangent curve, as $D_{diff} = 145 \ mm^2.min^{-1}$.

The Peclet number has also been calculated on the basis of the main separated tangent curve with the same assumption that the tail was due to diffusion as $Pe = 0.5$.

In reality, the tail is caused by the combined effect of diffusion and non-uniform distributed mechanical dispersion.

The tangent curve of the 3 column system and the simulated breakthrough curves are given in Fig. 14a, b and c.
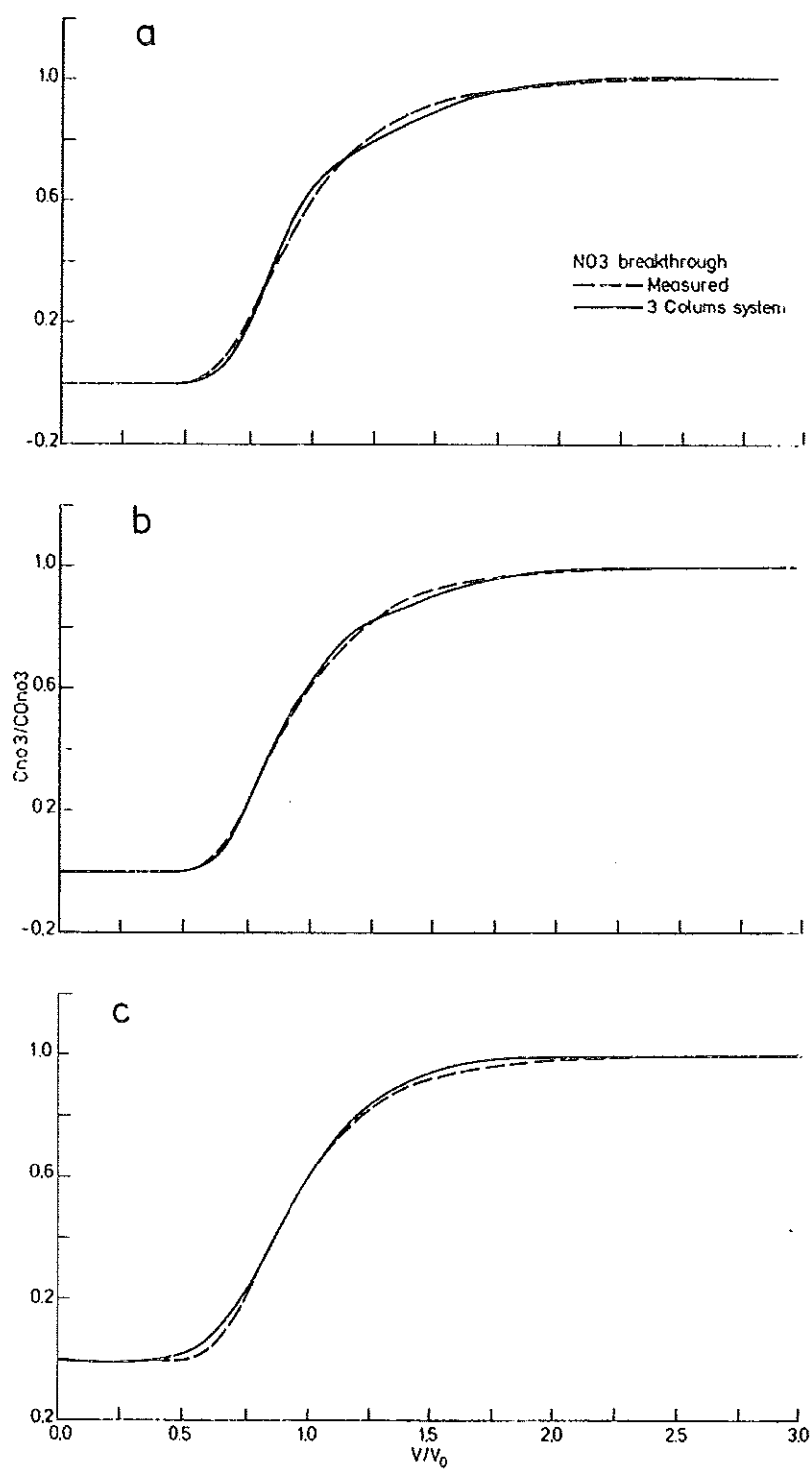
Fig. 14. Measured and simulated breakthrough curves. a: 2 column
system; b: 3 column system; c: equation 25
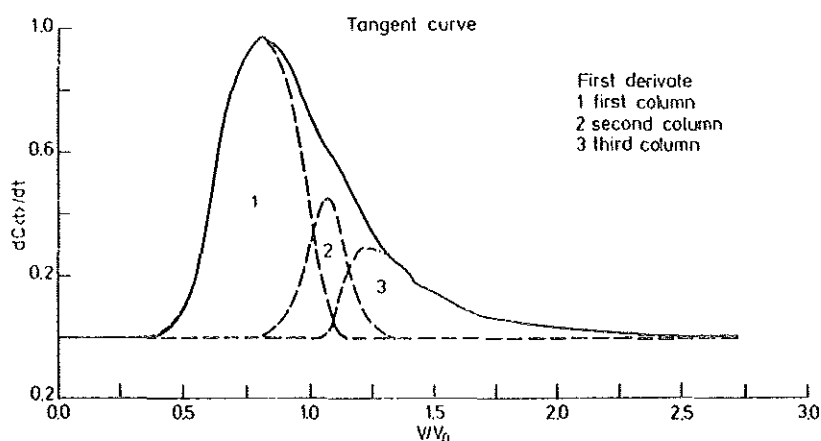
Fig. 14d. First derivate curve and separated three column curves

4.2.2.2. Behaviour of anions in experiment B. The concentrations of the effluent are calculated relative to the feed solution. The effluent concentrations in the return experiment with $CaCl_2$ as feed solution have been calculated relative to the initial concentration because the feed influent solution does not contain Na^+ and Mg^{2+}. The Sulphate and Total Inorganic Carbon concentrations have been measured because of the possibility of precipitation with Calcium and Magnesium. The results of the normalized curves are presented in Fig. 15a, b and c.

The nitrate breakthrough curve has also been plotted in order to compare the behaviour of the anions mentioned compared to a non-reactive anion.

It can be concluded that Sulphate has almost no interaction with the soil because the measured points fits the nitrate curve quite well. The differences can not be explained by precipitation because the solubility of $CaSO_4$ was not exceeded. A possible explanation may be found in the measuring technique.

The Total Inorganic Carbon concentration shows a different behaviour. The breakthrough occurs at about 2 pore volumes passed and it did not reach equilibrium during the experiment.

For the first part of the curve, the deviation from the nitrate curve may be caused by precipitation of Calcium carbonate. The Calcium carbonate solubility product is exceeded due to the high Calcium concentration. The product is calculated taking into account activities and ion pairs (ABDEL KHALIK and BLÖMER, 1984) and a solubility product of

42
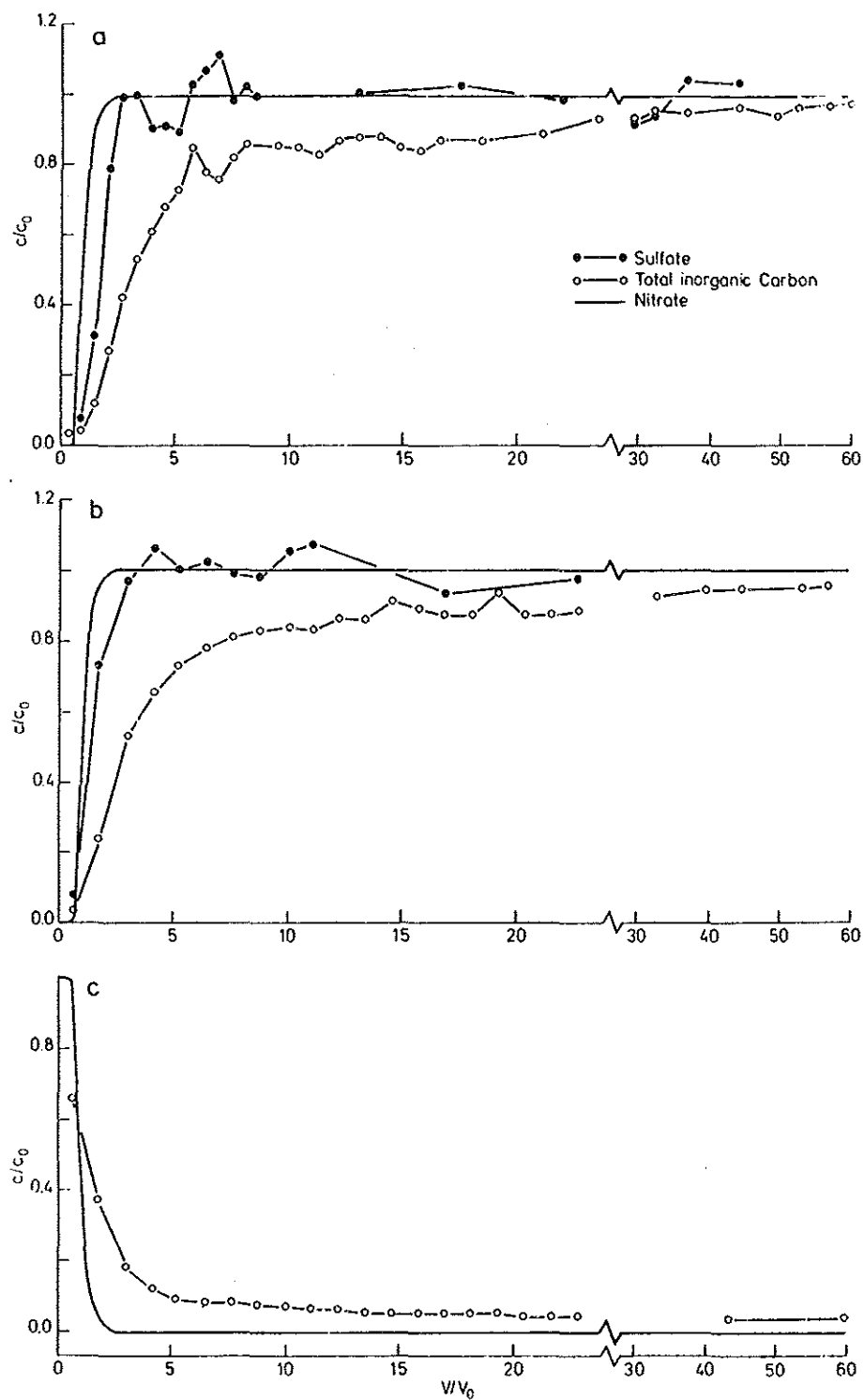
Fig. 15. Anion breakthrough curves. a: solution I; b: solution II;
c. solution III, after reaching equilibrium with solution II

ikaite $CaCO_3 \cdot H_2O$: pK = 7.9. Later on, the solubility product is exceeded due to an increase of the pH (pH = 8.3).

The weight of the Inorganic Carbon quantity is small with regard to the total weight of the soil. From the mass balance it can be calculated that the weight of precipitated carbonate equals 45 mg per 100 gr dry soil for solution II. The leaching influent of solution III ($CaCl_2$) contains no carbonate, while the concentration reaches slowly to zero in the effluent.

4.2.2.3. Behaviour of cations in experiment B. The concentration courses of the cations of the three experiments and the results computed by the programme SCMEX are presented in Fig. 16. The simulated adsorption is given in Fig. 17.

The exchange coefficients were set at $K_G^* = 0.6$ and $K_K^* = 1.1$, calculated on the basis of the average activity coefficients, calculated with the Debye-Hückel equation (eq. 37).

The mass balance of the exchanged ions is given in Table 11. The exchange between Sodium and Calcium and reversed is a relatively fast process. Within 10 times of replacement of the pore water content, the Sodium concentration reaches the final value. The simulation with the model yields nearly the same results as the experimental figures.

The replacement of Calcium by Magnesium and reversed was much slower. The Mg^{2+}/Ca^{2+} ratio of solution I was lower than the ratio of solution II and therefore a slower exchange between these cations could be expected in the experiment with Solution I. The computed curve does not fit completely with the experimental figures. The model calculates with a constant selectivity coefficient. It can be expected, however, that not all exchange places do have the same features. Preferential adsorption should be taken into account to produce better results. Some places are more selective for Calcium than others. The places with a higher selectivity for Calcium results in a delayed breakthrough of Magnesium.

An other reason may be the transport system showing an asymmetry which has been discussed in Section 4.2.2.1. It seems logical that a small deviation in the breakthrough of a non-reactive component will result in a greater deviation of the breakthrough of retarded cations. The figures presented in Table 11 show a difference in the mass balance of Sodium and Magnesium that does not equal the quantity of Calcium. Each figure has been composed of the summation of about 60 small
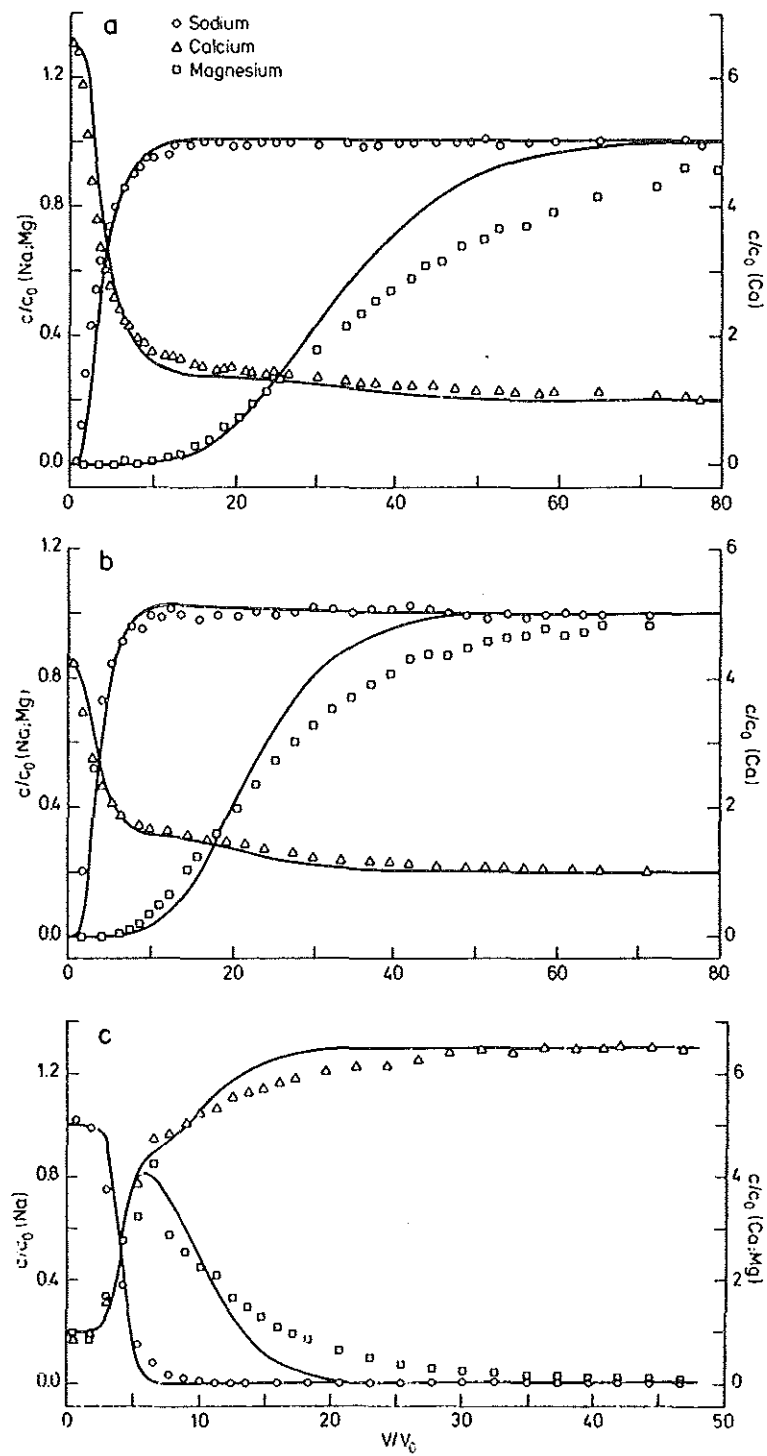
Fig. 16. Measured and simulated concentration course. a: feed solution
I; b: feed solution II; c: feed solution III ($CaCl_2$)
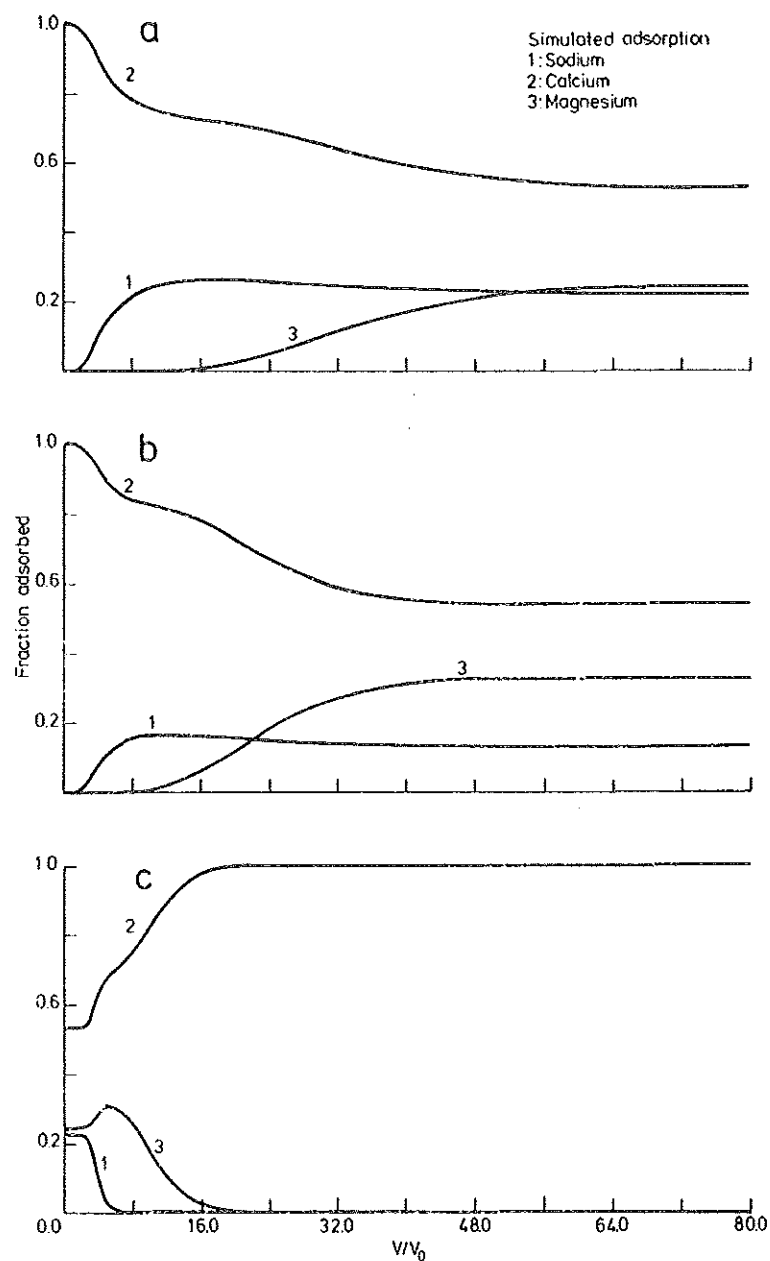
Fig. 17. Simulated relative complex composition. a: feed solution I; b: feed solution II; c: (CaCl$_2$) feed solution III

Fig. 11. Quantity of exchanged cations during the three column experiments performed

Exchanged ion meq $(100\ gr)^{-1}$	Solution I	Solution II	Solution III
Na^+	+12.2	+ 7.1	-13.0
Ca^{2+}	+14.9	+21.9	-17.0
Mg^{2+}	-28.9	-30.7	+30.3

figures. Another explanation may be found in the precipitation or dissolvation of Magnesium and Calcium salts.

5. APPLICATION TO THE WATER QUALITY OF THE NILE DELTA

5.1. Data and assumptions

The mixing cell model has been applied to the water quality of some locations in the Nile Delta.

Effects are forecasted under several assumptions, derived from data that became available from recently performed research.

The cropping pattern is based on the growth of a summer and a winter crop. Two crops per year are grown: rice, maize, cotton and vegetables during the summer, wheat and fodder in wintertime.

The Nile Delta has been divided in four areas according to the density of rice cultivation. This distinction is based on water balance studies presented by RIJTEMA (1981) and in the Workshop on the Reuse of drainage water (1984).

For this study, three locations have been selected and are assumed to be representative for the 33, 50, 67 percent rice cultivation areas. Fig. 18 presents the water balance model used in the computations. The application water losses from the irrigation system feed the collector drain directly. Seepage is considered as an independent contributing subsystem, which does not influence the water quality within the aquifer.

A part of the irrigated water percolates from the rootzone into the aquifer. The two dimensional approach given by ROEST and RIJTEMA (1983) has been used to calculate the concentration of the water
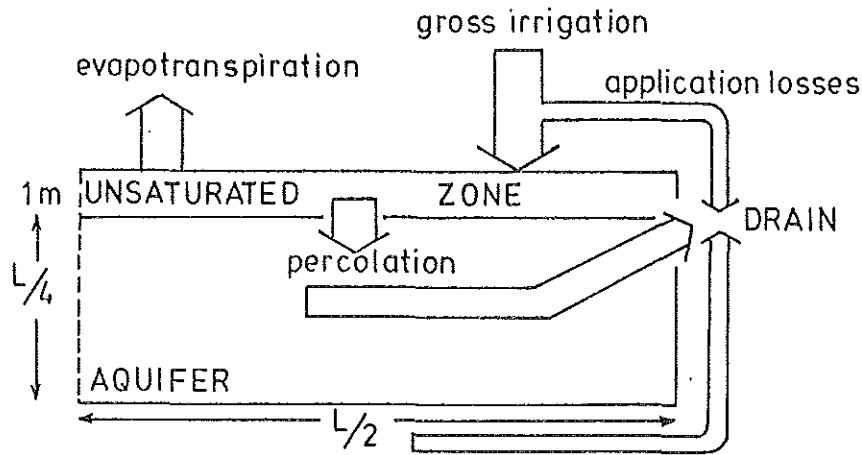
Fig. 18. Simple water flow model

contributed to the collector drain by the aquifer. The concentration
of the drainage water can be calculated according to:

$$c_{dr}(t) = \frac{D_{aq} \cdot c_{aq}(t) + D_{ap} \cdot c_{ap} + D_{seep} \cdot c_{seep}}{D_{aq} + D_{ap} + D_{seep}}$$ (71)

with: $c_{dr}(t)$ = concentration of the drainage water   (meq liter^{-1})

     $c_{aq}(t)$ = concentration of the contributing aquifer   (meq liter^{-1})

     c_{ap} = concentration of the irrigation water   (meq liter^{-1})

     c_{seep} = concentration of the seepage water   (meq liter^{-1})

     D_{aq} = quantity of water, contributed by the aquifer (mm day^{-1})

     D_{ap} = application losses   (mm day^{-1})

     D_{seep} = quantity of water, contributed by seepage   (mm day^{-1})

The volumetric water content of the satured aquifer has been set
at 50%, on the basis of a pF-curve of a heavy clay soil. Table 12 pre-
sents the data used in the calculations for the aquifer subsystem. The
drain distance and water balance data are obtained from the 'WORKSHOP'
(1984). The number of cells and the dispersion length are unknown para-
meters. The number of cells has been set at 10 and the dispersion
length a 1/4 of the length of the vertical compartments.

The cation exchange capacity of the soils has been assessed at
50 meq (100 gr)$^{-1}$. The drainage water quality data of the locations
selected are used in the water and salt balance calculations. The

Table 12. Physical data used in calculations

Location	Nizam	Saft	Main Qassabi	
density of rise cultivation	33	50	67	percent
drain distance	40	30	20	m
depth of aquifer	10	7.5	5	m
gross irrigation	6.60	7.25	8.33	$mm.day^{-1}$
nett ittigation	5.29	5.82	6.66	$mm.day^{-1}$
evapotranspiration	3.85	3.95	4.30	$mm.day^{-1}$
drainage	2.75	3.30	4.63	$mm.day^{-1}$
seepage	0.23	0.40	0.78	$mm.day^{-1}$
average stream velocity	1050	1365	1725	$mm.year^{-1}$
volume of a compartment	3.64	2.05	0.91	$m^3.m^{-1}$
length of compartment	1.0	0.75	0.5	m
dispersion length	0.25	0.19	0.13	m
dry bulk density	1.33	1.33	1.33	$gr.cm^{-3}$

present situation within the aquifer is supposed to be in equilibrium with the concentrated irrigation water obtained from the present inlet to the area (Table 13). The irrigation water quality figures have to be multiplied by the nett irrigation/percolation ratio because of the water consumption in the rootzone.

The drainage water to be reused in the locations mentioned, is delivered by the output of the area upstreams with less rice cultivation.

Table 13. Stations of which the water quality data are used in the calculations

Location	Present inlet	Drainage water to be reused
Nizam	Bahr Mous before mixing	Bahar Baqar Wadi P.S.
Saft	Mit Yazied Canal	Nizam
Main Qassabi	Bahr Sajhier ar Gamalia	Saft

The chemical data used in the computation are presented in Table 14. Seepage concentrations and figures have been slightly adapted from those mentioned in the 'WORKSHOP' (1984) in order to meet the water and salt balance. The seepage concentrations have been calculated from the salt balance.

Table 14. Chemical data used in the calculations

	$Na^+ + K^+$	$Ca^{2+} + Mg^{2+}$	
Location: Nizam			
adsorbed to the complex	0.83	49.17	meq $(100\ gr)^{-1}$
initial soil moisture concentration	2.72	13.00	meq.liter^{-1}
seepage concentration	96.2	52.0	meq.liter^{-1}
reuse water concentration	4.73	6.47	meq.liter^{-1}
concentrated reuse water	17.36	23.74	meq.liter^{-1}
Location: Saft			
adsorbed to the complex	0.78	49.22	meq $(100\ gr)^{-1}$
initial soil moisture concentration	2.53	12.85	meq.liter^{-1}
seepage concentration	96.8	18.4	meq.liter^{-1}
reuse water concentration	6.97	6.86	meq.liter^{-1}
concentrated reuse water	21.68	21.33	meq.liter^{-1}
Location: Main Qassabi			
adsorbed to the complex	2.51	47.49	meq $(100\ gr)^{-1}$
initial soil moisture concentration	7.88	11.15	meq.liter^{-1}
seepage concentration	154.3	86.8	meq.liter^{-1}
reuse water concentration	17.42	12.04	meq.liter^{-1}
concentrated reuse water	49.12	33.95	meq.liter^{-1}

5.2. Results and discussion

Most likely the drainage water will be pumped into the existing irrigation canals and the use of 100 percent drainage water at a certain location without mixing with the original irrigation water is an extreme assumption.

The figures given express the forecasting of this extreme case. The results of the simulations are given in the Fig. 17a, b and c.

Table 15 presents the final concentration of the drainage water and the percolation water contributed by the aquifer.

Table 16 gives the Sodium adsorption ratios values applied to the situation of 100% reuse. The SAR is defined as:

$$SAR = \frac{c_o^+}{\sqrt{\left(c_o^{2+}\right)/2}} \qquad (mmole^{\frac{1}{2}}.liter^{-\frac{1}{2}}) \qquad (72)$$

with c_o^+ and c_o^{2+} as the concentration of mono- and divalent cations in meq.liter^{-1}.

Table 17 presents the initial and final exchangeable sodium percentage figures of the soil. The ESP is given by:

$$ESP = 100 \frac{\gamma_{Na^+}}{CEC} \qquad (73)$$

The permeability of the soil decreases when the amount of adsorbed sodium relative to the cation exchange capacity increases. BOLT (1978) states 15 as a critical value. This value is rather arbitrary, because the physical reaction of the soil to the quantity of adsorbed sodium depends on the salt content, humus content, types and amounts of clay minerals, etc.

An important conclusion is the decreasing time of completion of the breakthrough with a decreasing drain distance.

The quality levels of the 1/3 rice area will be stabilised after 80-90 years, for the 1/2 rice area it will take to 60 years and 20-30 years for the 2/3 rice area.

A change in the irrigation water quality will have long term effects.
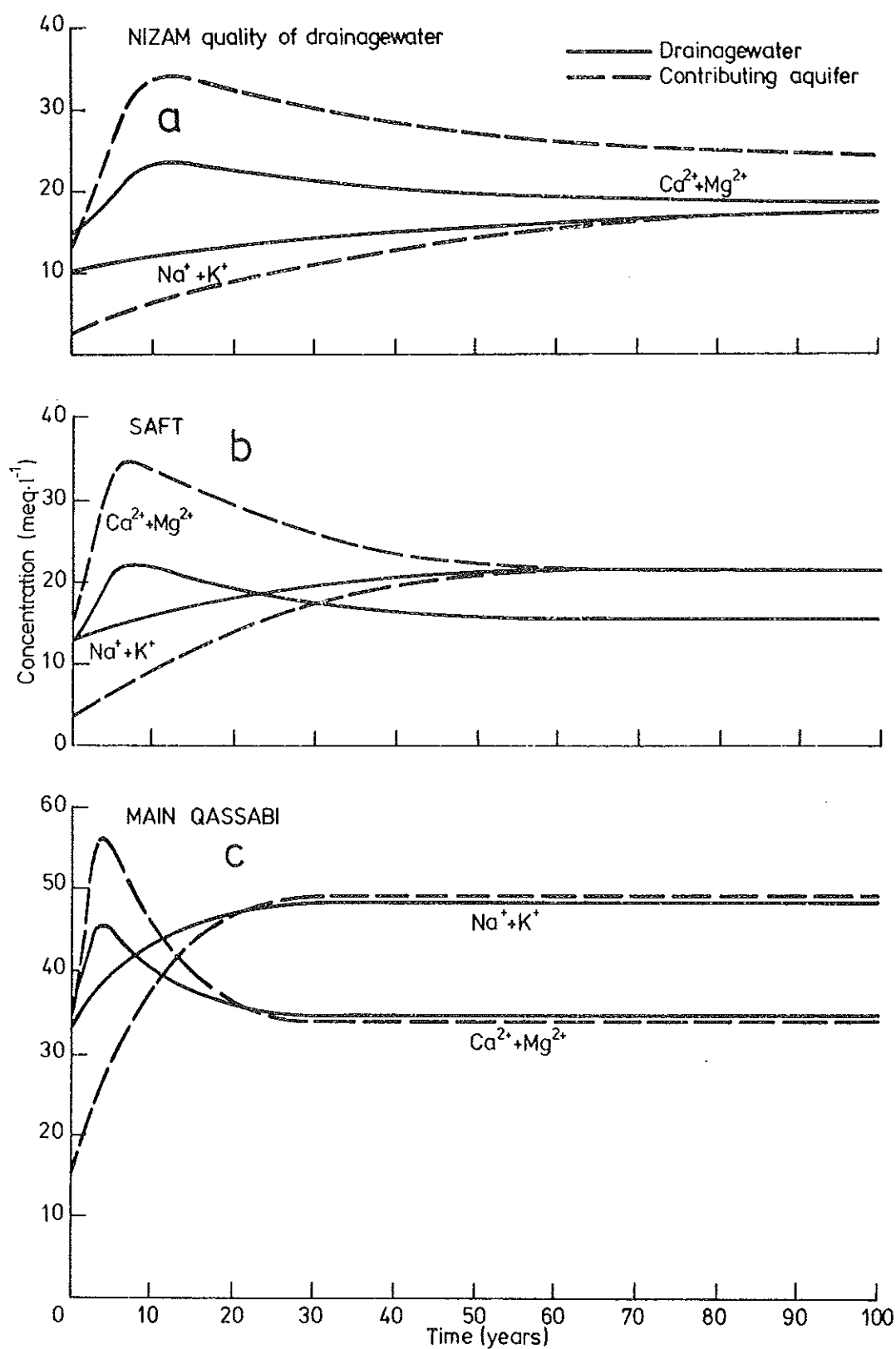
Fig. 19. Quality of drainage water. a: Nizam PS (1/3 rice); b: Saft PS
(1/2 rice); c: Main Qassabi PS (2/3 rice)

Tabel 15. Final water quality figures in meq.liter^{-1}

| | Drainage water | | Contributing aquifer | |
	$Na^+ + K^+$	$Ca^{2+} + Mg^{2+}$	$Na^+ + K^+$	$Ca^{2+} + Mg^{2+}$
Nizam	17.0	18.5	17.4	23.7
Saft	21.6	15.4	21.7	21.3
Main Qassabi	48.2	35.0	49.1	34.0

Table 16. SAR values in mmole$^{\frac{1}{2}}$.liter$^{-\frac{1}{2}}$ at 100% reuse

| | Initial soil moisture | Irrigation water | Seepage | Drainage quality | |
				initial	final
Nizam	0.75	1.86	13.3	2.7	4.0
Saft	0.70	2.66	22.5	5.0	5.5
Main Qassabi	2.36	5.02	16.6	6.2	8.1

Table 17. ESP values in the aquifer profile

	Initial	Final
Nizam	1.6	7.4
Saft	1.6	9.5
Main Qassabi	5.0	15.9

The SAR value of the drainage water at Nizam will decrease in the first ten years, due to the increasing relative content of $Ca^{2+} + Mg^{2+}$ and afterwards, the SAR increases slightly to the final value.

The period of decrease for Saft is 6 years and at Main Qassabi the SAR value increases slightly to the final value.

The input quality data of the three locations, obtained from one station in each area, are taken to be constant. However, these data are based on the figures of 1 year and no estimation could be made about the development of the quality in the future. A constant SAR

value at the present does not guarantee the prevention of problems in the future when drainage water is reused. Precipitation of Calcium and Magnesium salts can not be proved due to the present lack of relevant data, but a trend of increase in the $Na^+/(Ca^{2+}+Mg^{2+})$ ratio is visible in the original and final drainage water quality data.

The situation at Saft is an exceptional one because of the high SAR value of the seepage water. From a comparison of the $Na^+/(Ca^{2+}+Mg^{2+})$ ratios of the seepage and drainage water of Nizam and Main Qassabi, it may be concluded that some Calcium and Magnesium do vanish from the solvent system. When the drainage water of the 1/3 and 1/2 rice areas will be used down streams in the first 5-10 years after the start of the drainage water reuse, the temporary lower SAR value will lead to a delay of the breakthrough of Sodium in those areas.

The reuse of the resulting drainage water of the whole breakthrough period causes also a delay of the breakthrough, but the final ESP and SAR values and absolute concentrations will be higher.

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FLOWCHART OF THE TRANSPORT MODEL SODIC
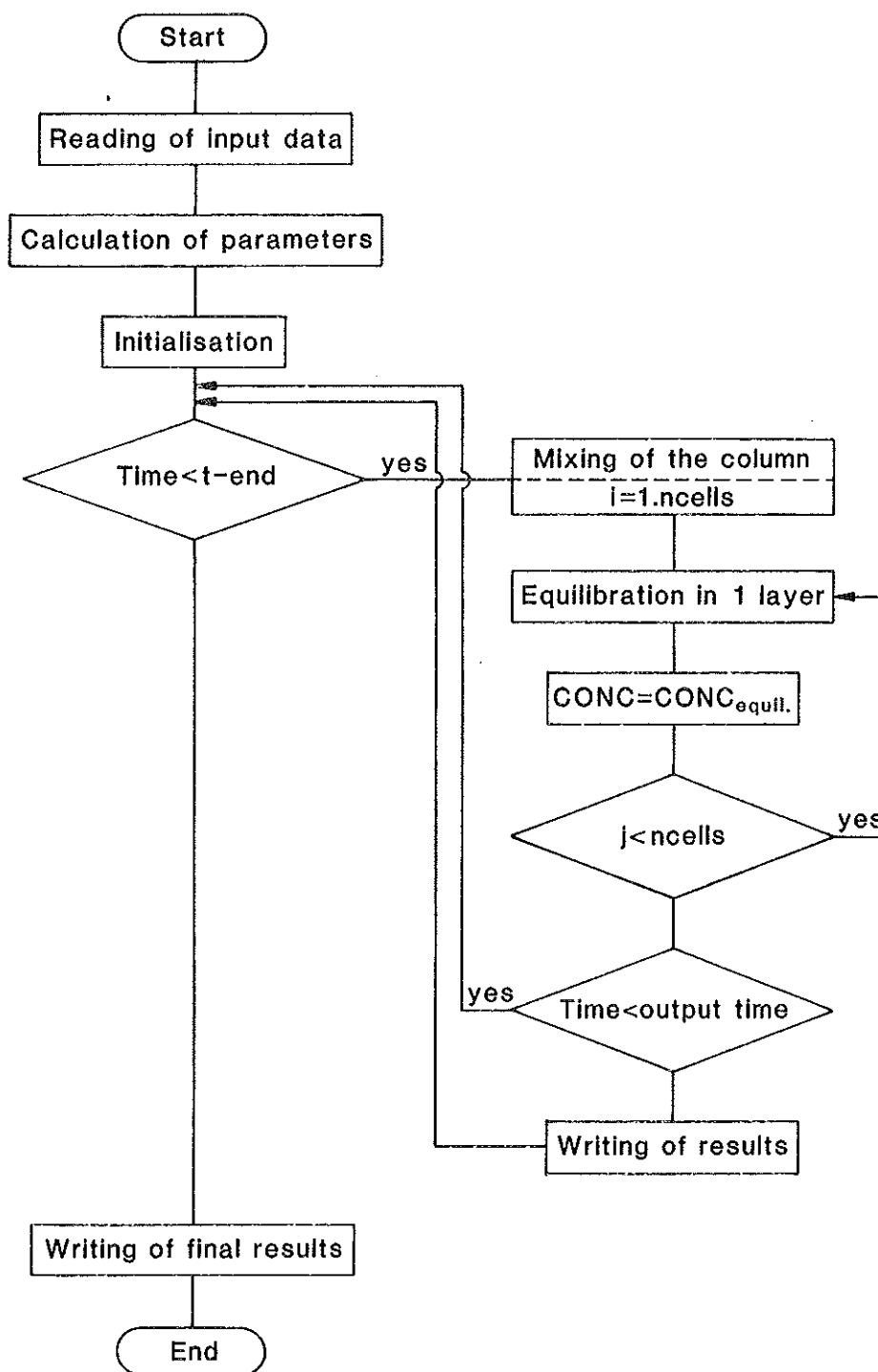
LISTING OF THE 'SODIC' PROGRAMME FOR A HP 41-CV POCKET CALCULATOR

```
♦LBL "SODIC"
"HCELLS" PROMPT STO 00
"DELZ?" PROMPT STO 78
"DISPL" PROMPT STO 77
"V" PROMPT STO 79
"TEND" PROMPT STO 80
"Ca0" PROMPT STO 71
"Na0" PROMPT STO 72
"CaIN" PROMPT STO 73
"NaIN" PROMPT STO 74
"AdCaIN" PROMPT STO 75
"AdNaIN" PROMPT STO 76
"ALFA" PROMPT STO 81
"KG" PROMPT STO 85
"ITMAX" PROMPT STO 86
1 STO 94 11 STO 95
21 STO 96 31 STO 97

♦LBL 01
RCL 73 STO IND 94
RCL 74 STO IND 95
RCL 75 STO IND 96
RCL 76 STO IND 97 1
ST+ 94 ST+ 95 ST+ 96
ST+ 97 RCL 00 RCL 94
X<=Y? GTO 01 RCL 78
RCL 77 2 * CHS +
RCL 79 / STO 41
RCL 80 RCL 41 / ,5 +
INT STO 84 RCL 41
RCL 78 / RCL 79 *
STO 87 "BETA" PROMPT
STO 83 RCL 71 STO 77
RCL 72 STO 78 1
STO 82 51 STO 43
XEQ "TIME"

♦LBL 02
1 RCL 83 - RCL 71 *
RCL 77 RCL 83 * +
STO 77 1 RCL 83 -
RCL 72 * RCL 78
RCL 83 * + STO 78
XEQ "MIX" 1 STO 94 11
STO 95 21 STO 96 31
STO 97 0 STO 75
STO 76

♦LBL 03
XEQ "EQ" RCL IND 94
ST+ 75 RCL IND 95
ST+ 76 1 ST+ 94
ST+ 95 ST+ 96 ST+ 97
RCL 00 RCL 94 X<=Y?
GTO 03 RCL 82 ENTER↑
RCL IND 43 RCL 41 /
X<=Y? GTO "DR"
```

```
♦LBL A
RCL 75 RCL 00 /
STO 77 RCL 76 RCL 00
/ STO 78 1 ST+ 82
RCL 84 RCL 82 X<=Y?
GTO 02 1 STO 94 11
STO 95 21 STO 96 31
STO 97

♦LBL 04
"Ca<" RCL 94 FIX 0
ARCL X "+)="
RCL IND 94 SCI 4
ARCL X AVIEW "Na<"
RCL 95 10 - FIX 0
ARCL X "+)="
RCL IND 95 SCI 4
ARCL X AVIEW "ACa<"
RCL 96 20 - FIX 0
ARCL X "+)="
RCL IND 96 SCI 4
ARCL X AVIEW "ANa<"
RCL 97 30 - FIX 0
ARCL X "+)="
RCL IND 97 SCI 4
ARCL X AVIEW 1 ST+ 94
ST+ 95 ST+ 96 ST+ 97
RCL 00 RCL 94 X<=Y?
GTO 04 RTN

♦LBL "TIME"
"NTIMES" PROMPT STO 42

♦LBL 00
"T=" PROMPT STO IND 43
1 ST+ 43 RCL 42
RCL 43 50 - X<=Y?
GTO 00 "CONCLAYER"
PROMPT STO 79 51
STO 43 RTN

♦LBL "DR"
RCL 79 STO 94 10 +
STO 95 "TIME="
RCL IND 43 FIX 0
ARCL X AVIEW "Ca<L"
RCL 79 ARCL X "+)="
RCL IND 94 SCI 4
ARCL X AVIEW "Na<L"
RCL 79 FIX 0 ARCL X
"+)=" RCL IND 95 SCI 4
ARCL X AVIEW 1 STO 94
11 STO 95 0 STO 73
STO 74
```

```
♦LBL 25
RCL IND 94 ST+ 73
RCL IND 95 ST+ 74 1
ST+ 94 ST+ 95 RCL 00
RCL 94 X<=Y? GTO 25
"Ca<T" RCL IND 43
FIX 0 ARCL X "+)="
RCL 73 RCL 00 / SCI 4
ARCL X AVIEW "Na<T"
RCL IND 43 FIX 0
ARCL X "+)=" RCL 74
RCL 00 / SCI 4 ARCL X
AVIEW 1 ST+ 43 GTO A
RTN

♦LBL "MIX"
1 STO 94 11 STO 95
RCL 77 RCL IND 94
STO 88 - RCL 87 *
RCL IND 94 +
STO IND 94 RCL 78
RCL IND 95 STO 89 -
RCL 87 * RCL IND 95 -
STO IND 95

♦LBL 09
1 ST+ 94 ST+ 95
RCL 89 RCL IND 94 -
RCL 87 * RCL IND 94
STO 88 + STO IND 94
RCL 89 RCL IND 95 -
RCL 87 * RCL IND 95
STO 89 + STO IND 95
RCL 00 RCL 94 X<=Y?
GTO 09 RTN

♦LBL "EQ"
RCL 85 X↑2 RCL 81 X↑2
* 2 * STO 61 RCL 81
RCL 85 X↑2 *
RCL IND 95 * 2
RCL IND 96 * RCL 85
X↑2 * + RCL 81 2 /
+ RCL 81 * 2 *
STO 62 RCL IND 96 X↑2
2 * RCL IND 95 X↑2
RCL 81 X↑2 * 2 * +
8 RCL 81 * RCL IND 96
* RCL IND 95 * +
RCL 85 X↑2 * RCL 81
CHS RCL IND 94 * 2
RCL IND 97 * - RCL 81
* + STO 63 RCL IND 96
X↑2 RCL IND 95 * 4 *
4 RCL 81 * RCL IND 97
* RCL IND 95 X↑2 * -
```

```
RCL 85  Xf2  *  2
RCL 81  *  RCL IND 94  *
RCL IND 97  +
RCL IND 97  *  +  STO 64
2  RCL IND 96  Xf2  *
RCL 85  Xf2  *
RCL IND 85  Xf2  *
RCL IND 94  RCL IND 97
Xf2  *  -  STO 65
XEQ "XST"  :  STO 66

♦LBL 10
RCL 90  4  YfX  RCL 61
*  RCL 90  3  YfX
RCL 62  *  +  RCL 90
Xf2  RCL 63  *  +
RCL 90  RCL 64  *  +
RCL 65  +  STO 69
RCL 90  3  YfX  RCL 61
*  4  *  RCL 90  Xf2
RCL 62  *  3  *  +
RCL 90  RCL 63  *  2  *
+  RCL 64  +  STO 70
X=0?  GTO 22  RCL 69
RCL 70  /  STO 91
RCL 91  RCL 90  /  ABS
1,0 E-03  X>Y?  GTO 20
RCL 91  ABS  1,0 E-08
X>Y?  GTO 20  RCL 90
RCL 91  -  STO 90  1
ST+ 68  RCL 86  RCL 68
X<=Y?  GTO 10

♦LBL 20
RCL 66  RCL 67  X>Y?
GTO 17  RCL 90  RCL 92
X>Y?  GTO 18  RCL 92
0,0  X>Y?  GTO 22
RCL 92  STO 90  GTO 21

♦LBL 18
RCL 90  0,0  X>Y?
GTO 22  GTO 21

♦LBL 17
RCL 93  RCL 90  X>Y?
GTO 19  0,0  RCL 93
X>Y?  GTO 22  RCL 93
STO 90  GTO 21

♦LBL 19
0,0  RCL 90  X>Y?
GTO 22  GTO 21

♦LBL 22
0,0  STO 90  GTO 21
```

```
♦LBL 21
RCL IND 94  RCL 90  -
STO IND 94  RCL IND 95
RCL 90  +  STO IND 95
RCL 90  RCL 81  *
RCL IND 96  +
STO IND 96  RCL 90
RCL 81  *  CHS
RCL IND 97  +
STO IND 97  RTN

♦LBL "XST"
RCL IND 97  RCL IND 96
/  STO 66  RCL IND 94  2
/  SQRT  1/X  RCL IND 95
*  RCL 85  *  STO 67
RCL 67  RCL 66  X>Y?
GTO 12  GTO 11

♦LBL 12
RCL IND 97  RCL 81  /
ENTER↑  RCL IND 94  X<Y?
GTO 13  GTO 14

♦LBL 11
RCL IND 99  CHS  ENTER↑
RCL IND 96  CHS  RCL 81
/  X<Y?  GTO 15  GTO 16

♦LBL 13
RCL IND 94  STO 92  0,5
*  STO 90  RTN

>LBL 14
RCL IND 97  RCL 81  /
STO 92  0,5  *  STO 90
RTN

♦LBL 15
RCL IND 95  CHS  STO 93
0,5  *  STO 90  RTN

♦LBL 16
RCL IND 96  CHS  RCL 81
/  STO 93  0,5  *
STO 90  RTN  END
```

SYMBOLS OF INPUT DATA

NCELLS   : number of layers

DELZ   : layer thickness

DISPL   : dispersion length

V   : stream velocity

TEND   : end of execution time

CaO   : Calcium concentration of
            feed solution (eq/1)

NaO   : Sodium concentration of
            feed solution (eq/1)

CaIN   : initial calcium concentration
            of the soil moisture (eq/1)

NaIN   : quantity of adsorbed calcium
            (meq/100 gr)

AdNaIN   : quantity of adsorbed sodium
            (meq/100 gr)

ALFA   : soil moisture content (%)
            divided by dry bulk density (gr/cm^3)

KG   : Gapon exchange coefficient $(eq/1)^{-\frac{1}{2}}$

ITMAX   : maximum number of iterations

BETA   : Reuse ratio
            CaO' = CaO + BETA (Ca(NCELLS) − CaO)
            NaO' = NaO + BETA (Na(NCELLS) − NaO)

NTIMES   : number of output times

T   : time of output

CONCLAYER: layer of which the output concentration is given each time

REMARKS   : SIZE   : 100
            MAXIMUM NUMBER OF LAYERS: 10

```
      program scmex

c****************************************************************c
c                                                              c
c      Program scmex simulates the sodium,calcium and magnesium c
c      breakthrough of a column experiment.                    c
c      The transport process is described by the 'mixing-cell' c
c      concept and the exchange process is formulated by a modified c
c      Gapon and Kerr equation.                                c
c      More information about the theoretical background is given c
c      in NOTA 1578, I.C.W., Wageningen.                       c
c      The names of the input and outputfiles are read in indexfiles c
c                                                              c
c      S Y M B O L S   I N D E X                               c
c      ------------------------                                c
c      scmex1.ndx  : indexfile for input datafiles            c
c      scmex2.ndx  : indexfile for output resultfiles         c
c                                                              c
c      tend    : end of execution time                        c
c      ncells  : number of layers                             c
c      tetav   : volume moisture content              (%)     c
c      rho     : dry bulk density                     (gr/cm3) c
c      delz    : layer thickness                      (mm)    c
c      displ   : dispersion length                    (mm)    c
c      v       : velocity                             (mm/min) c
c      diff    : diffusion coefficient                (mm2/min) c
c      kg      : Gapon exchange coefficient           (eq/l)-0.5 c
c      kcm     : Kerr exchange coefficient            ( - )   c
c      cnain   : initial sodium soil moisture concentration   (eq/l) c
c      ccain   : initial calcium soil moisture concentration  (eq/l) c
c      cmgin   : initial magnesium soil moisture concentration (eq/l) c
c      cna0    : sodium concentration of the feed solution    (eq/l) c
c      cca0    : calcium concentration of the feed solution   (eq/l) c
c      cmg0    : magnesium concentration of the feed solution (eq/l) c
c      adnain  : initial sodium adsorption            (meq/100gr)c
c      adcain  : initial calcium adsorption           (meq/100gr)c
c      admgin  : initial magnesium adsorption         (meq/100gr)c
c      cec     : cation exchange capacity             (meq/100gr)c
c      nsteps  : number of calculation steps                  c
c      delt    : size of time interval                (min)   c
c      alfa    : liquid / solid phase ratio           (cm3/gr) c
c      num     : measure for interval results writing         c
c      number  : cumulated measure for interval results writing c
c                                                              c
c      author  : Piet Groenendijk                             c
c      date    : november 1984                                c
c                                                              c
c****************************************************************c

c
c***   declarations
c
      integer*4 tend,ncells
      real*4 number,num,kg,kcm
      real*4 adna(100),adca(100),admg(100),cna(100),cca(100),cmg(100)
      real*4 cnamix(100),ccamix(100),cmgmix(100)
      character*40 name1,name2
c
c***   opening of index file and final result file
c
      open(unit=3,name='scmex1.ndx',status='old')
      open(unit=4,name='scmex2.ndx',status='old')
      open(unit=20,name='scmex.res',status='new')
c
c***   reading of index files
c
 700  read(3,11,err=1000,end=900)name1
      read(4,11,err=800)name2
c
c***   opening of datafiles
c
      open(unit=1,name=name1,status='old')
      open(unit=2,name=name2,status='new')
c
c***   reading of data
c
 600  read(1,22,err=1000,end=800)cnain,ccain,cmgin,cna0,cca0,cmg0,
     1     adnain,adcain,admgin,delz,displ,v,tetav,rho,num,diff,kg,
     2     kcm,ncells,tend

      cec = adnain + adcain + admgin
```

```
c
c***   initialisation
c
      do 100 i=1,ncells
         cna(i) = cnain
         cca(i) = ccain
         cmg(i) = cmgin
         adna(i) = adnain
         adca(i) = adcain
         admg(i) = admgin
  100 continue
c
c***   calculation of parameters
c
      delt = (delz-2.0*displ)/v
      nsteps = ifix(tend/delt)
      alfa = tetav/rho
      a1 = delt*diff/(delz**2)
      a2 = 1 - v*delt/delz - 2.*a1
      a3 = v*delt/delz + a1
      cmin = (cnain + ccain + cmgin)/1000.
      admin = (adnain + adcain + admgin)/1000.
c
c***   mixing of layers
c
      number = num
      do 200 i=1,nsteps
         if (floatj(i).ge.number) then
            time = floatj(i)*delt
            write(2,33)time
         end if
         call mixing(cna,cca,cmg,ncells,cna0,cca0,cmg0,
     1                a1,a2,a3,cnamix,ccamix,cmgmix)
c
c***   exchange of cations in 1 layer
c
         do 300 j=1,ncells
           if (cnamix(j).lt.cmin .and. adna(j).lt.admin) then
             if ( cmgmix(j).lt.cmin .and. admg(j).lt.admin) then
               goto 310
             else
               call camg(ccamix(j),cmgmix(j),adca(j),admg(j),kcm,alfa)
               goto 310
             end if
           else if (cmgmix(j).lt.cmin .and. admg(j).lt.admin)then
             if (ccamix(j).lt.cmin .and. adca(j).lt.admin) then
               goto 310
             else
               call soca(cnamix(j),ccamix(j),adna(j),adca(j),kg,alfa)
               goto 310
             end if
           else if (ccamix(j).lt.cmin .and. adca(j).lt.admin) then
             if (cnamix(j).lt.cmin .and. adna(j).lt.admin) then
               goto 310
             else
               kgcm = kg*sqrt(kcm)
               call soca(cnamix(j),cmgmix(j),adna(j),adca(j),kgcm,alfa)
               goto 310
             end if
           else
             call equil(cnamix(j),ccamix(j),cmgmix(j),adna(j),adca(j),
     &                  admg(j),kg,kcm,alfa)
           end if
  310      cna(j) = cnamix(j)
           cca(j) = ccamix(j)
           cmg(j) = cmgmix(j)
           if (cna(j).lt.0.0 .or. cca(j).lt.0.0 .or.
     &         cmg(j).lt.0.0 .or. adna(j).lt.0.0 .or.
     &         adca(j).lt.0.0 .or. admg(j).lt.0.0) then
               time = floatj(i)*delt
               write(20,33)time
               write(20,333)i,j,cna(j),cca(j),cmg(j),adna(j),
     &           adca(j),admg(j)
               goto 800
           end if
  300    continue
c
c***   writing of c/c0 and v/v0 in result file
c
```

```fortran
              if (floatj(i).ge.number) then
                 xx = time*v/(floatj(ncells)*delz)
                 xd= adna(ncells)/cec
                 xe= adca(ncells)/cec
                 xf= admg(ncells)/cec
                 if (cna0.eq.0.0.or.cca0.eq.0.0.or.cmg0.eq.0.0) then
                    xa= cna(ncells)
                    xb= cca(ncells)
                    xc= cmg(ncells)
                 else
                    xa= cna(ncells)/cna0
                    xb= cca(ncells)/cca0
                    xc= cmg(ncells)/cmg0
                 end if
                 write(2,44)xx,xa,xb,xc,xd,xe,xf
                 number = number + num
              end if
 200      continue
c
c***   writing of original data and final results in file
c
          write(20,54)name1
          write(20,55)cna0,cca0,cmg0,cnain,ccain,cmgin,
     1               adnain,adcain,admgin
          write(20,66)delz,displ,v,tetav,rho,diff
          write(20,76)
          do 400 i=1,ncells
             if (cna(i).le.1.0e-08) then
                cna(i) = 0.0
             end if
             if (cca(i).le.1.0e-08) then
                cca(i) = 0.0
             end if
             if (cmg(i).le.1.0e-08) then
                cmg(i) = 0.0
             end if
             write(20,77)cna(i),cca(i),cmg(i),adna(i),adca(i),admg(i)
 400      continue
c
c***
c
          goto 600

 800      close(unit=1)
          close(unit=2)
          goto 700

 900      close(unit=3)
          close(unit=4)
          stop ' end of program scmex'

 1000     write(2,88)
          close(unit=3)
          close(unit=4)
          stop ' error during reading'
c
c***   format statements
c
 11       format(a)
 22       format(18(25x,f10.4/),25x,i5/,25x,i5)
 33       format(' time = 'f10.4)
 44       format(7f8.4)
 54       format(//' datafile used: 'a/)
 55       format(' sodium concentration feed-solution: ',2x,f10.4,2x,' eq/l'/
     1           ' calcium concentration feed-solution: ',x,f10.4,2x,' eq/l'/
     2           ' magnesium concentration feed-solution: ',f9.4,2x,' eq/l'/
     3           ' initial sodium concentration:      ',4x,f10.4,2x,' eq/l'/,
     4           ' initial calcium concentration:     ',4x,f10.4,2x,' eq/l'/,
     5           ' initial magnesium concentration: ',4x,f10.4,2x,' eq/l'/,
     6           ' initial sodium adsorbed:      ',9x,f10.4,2x,' meq/100gr'/,
     7           ' initial calcium adsorbed:     ',9x,f10.4,2x,' meq/100gr'/,
     8           ' initial magnesium adsorbed: ',9x,f10.4,2x,' meq/100gr')
 66       format(' layer thickness:             ',2x,f10.4,2x,' mm'/,
     1           ' dispersionlength:            ',2x,f10.4,2x,' mm'/,
     2           ' flux/porosity:               ',9x,f10.4,2x,' mm/min'/,
     3           ' volume moisture content:     ',9x,f10.4,2x,' %'/,
     4           ' dry bulk density:            ',9x,f10.4,2x,' gr/cm3'/,
     5           ' diffusion coefficient:       ',9x,f10.4,2x,' mm2/min'/)
 76       format(//' final concentrations and adsorbed quantities of',
     1           ' cations'//,'    Na-conc.   Ca-conc.   Mg-conc. ',
     2           '   Ads.na ',x,'  Ads.Ca ',x,'  Ads.Mg ')
 77       format(6(f10.4))
 88       format(' file not found or format type mismatch')
 333      format(' E R R O R in calculation'//,' timestep : ',
```

63

```fortran
     &           i5,'layer no.:',i5,'cna :',g12.4,'cca :',
     &           g12.4,'cmg :',g12.4/,' adna :',g12.4,
     &           ' adca :',g12.4,' admg :',g12.4)
      end


      subroutine camg(cca,cmg,adca,admg,kcm,alfa)

C***********************************************************************C
c                                                                      c
c     Subroutine C A M G calculates the exchange between Calcium and   c
c     Magnesium when Sodium is absent.                                 c
c                                                                      c
C***********************************************************************C

      real*4 kcm
      g1 = alfa - alfa*kcm
      g2 = alfa*cmg+adca+kcm*admg+kcm*alfa*cca
      g3 = cmg*adca-kcm*admg*cca
      if (abs(g1) .lt. 1.0e-10) then
         y = -g3/g2
      else
         y1 = (-g2+sqrt(g2**2-4.*g1*g3))/(2.*g1)
         y2 = (-g2-sqrt(g2**2-4.*g1*g3))/(2.*g1)
         if ((adca+alfa*y1).lt. 0.0 .or. (cca-y1).lt. 0.0
     &      .or. (admg-alfa*y1).lt.0.0 .or. (cmg+y1).lt.0.0) then
            y = y2
         else
            y = y1
         end if
      end if
      z = -y
      cca = cca - y
      cmg = cmg - z
      adca = adca + alfa*y
      admg = admg + alfa*z

      return
      end


      subroutine soca(cna,cca,adna,adca,kg,alfa)

C***********************************************************************C
c                                                                      c
c     Subroutine S O C A determines the equilibrium between            c
c     Sodium and Calcium when Magnesium is absent.                     c
c                                                                      c
C***********************************************************************C

      real*4 kg,lhs,noemy
      data   eps/1.0e-03/,itmax/10/
      g1 = 2.*alfa*alfa*kg*kg
      g2 = 2.*alfa*(alfa*kg*kg*cna+2.*adca*kg*kg+alfa*kg/2.0)
      g3 = kg*kg*(2.*adca*adca+2.*alfa*alfa*cna*cna+8.*alfa
     1      adca*cna)+alfa*(-alfa*cca-2.*adna)
      g4 = kg*kg*(4.*adca*adca*cna+4.*alfa*adca*cna*cna) +
     1      adna*(2.*alfa*cca+adna)
      g5 = 2.*adca*adca*kg*kg*cna*cna-cca*adna*adna
      lhs = adna/adca
      rhs = kg*cna/(sqrt(cca/2.))
      if (lhs.gt.rhs) then

         ymax=amin1(adna/alfa,cca)
         y = 0.5*ymax
      else
         ymin=amax1(-cna,-adca/alfa)
         y = 0.5*ymin
      end if
      do i=1,itmax
         tely = g1*y**4+g2*y**3+g3*y*y+g4*y+g5
         noemy= 4.*g1*y**3+3.*g2*y*y+2.*g3*y+g4
         if (abs(noemy) .le. 1.0e-20) then
            y = 0.0
            goto 320
         end if
         dely = tely/noemy
         if (abs(dely/y).lt.eps .or. abs(dely).lt.
     1       1.0e-08) then
            goto 320
         end if
      end do
  320 if (lhs.gt.rhs) then
         y = amax1(amin1(ymax,y),0.0)
      else
         y = amin1(amax1(ymin,y),0.0)
      end if
      x = -y
```

64

```fortran
      cna = cna - x
      cca = cca - y
      adna = adna + alfa*x
      adca = adca + alfa*y
      return
      end

      subroutine equil(cna,cca,cmg,adna,adca,admg,kg,kcm,alfa)

c*******************************************************************c
c                                                                  c
c     Subroutine E Q U I L determines the exchange equilibrium between c
c     Sodium, Calcium and Magnesium within one timestep in one layer.  c
c                                                                  c
c*******************************************************************c

      real*4 kg,kcm
      data eps/1.0e-03/,itmax/15/
      u1=adca*cmg-kcm*admg*cca
      u2=adca+alfa*cmg+kcm*admg+alfa*kcm*cca
      u3=alfa-alfa*kcm
      u4=adca+alfa*kcm*cca
      u5=2.*kg*kg*alfa*alfa
      u6=4.*kg*kg*alfa*adca+alfa*alfa
      u7=2.*kg*kg*adca*adca-alfa*alfa*cca
      u8=-4.*kg*kg*alfa*alfa*cna
      u9=-(8.*kg*kg*alfa*adca*cna-2.*alfa*adna)
      u10=-(4.*kg*kg*adca*adca*cna+2.*alfa*adna*cca)
      u11=2.*kg*kg*alfa*alfa*cna*cna
      u12=4.*kg*kg*alfa*adca*cna*cna+adna*adna
      u13=2.*kg*kg*adca*adca*cna*cna-adna*adna*cca
      g1=u3*u3*u5
      g2=u3*u3*(u6-u8)+2.*u2*u3*u5
      g3=u3*u3*(u7-u9+u11)+u2*u3*(2.*u6-u8)+2.*u1*u3*u5-u3*u4*u8+u2*u2*u5
      g4=u3*u3*(u1+u12)+u1*u3*(2.*u6-u8)+u2*u3*(2.*u7-u9)+u3*u4*
     1    (-u9+2.*u11)+u2*u2*u6-u2*u4*u8+2.*u1*u2*u5

      g5=u1*u1*u5+u2*u2*u7+u3*u3*u13+u4*u4*u11+u1*u3*(2.*u7-u9)+u3*u4*
     1    (-u10+2.*u12)+2.*u1*u2*u6-u2*u3*u10-u2*u4*u9-u1*u4*u8
      g6=u1*u1*u6+u4*u4*u12+u1*(2.*u2*u7-u4*u9-u3*u10)+
     1    u4*(-u2*u10+2.*u3*u13)
      g7=u1*u1*u7-u1*u4*u10+u4*u4*u13

      call start(cna,adna,cca,adca,cmg,admg,alfa,kg,kcm,y,ymin,ymax)

      do 600 k=0,20
         j = (-1)**(k+1)*(jint((k+1)/2.))
         y = (floatj(j+10)*ymin+floatj(10-j)*ymax)/20.
         ystart = y
         do 500 i=1,itmax
            ytel=g1*y**6+g2*y**5+g3*y**4+g4*y**3+g5*y**2+g6*y+g7
            ynoem=6.*g1*y**5+5.*g2*y**4+4.*g3*y**3+3*g4*y**2+2.*g5*y+g6
            if(abs(ynoem).le.1.0e-20) then
               y = 0.0
               goto 525
            end if
            dely=ytel/ynoem
            if (abs(y).lt.1.0e-08.and.abs(dely).gt.1.0e-08) then
               goto 475
            else if (abs(y).lt.1.0e-08.and.abs(dely).le.1.0e-08) then
               goto 525
            else if (abs(dely/y).lt.eps.or.abs(dely).lt.1.0e-08) then
               goto 525
            end if
475         y = y - dely
500      continue

525      x = - (u1+u2*y+u3*y*y)/(u4+u3*y)
         z = - x - y
         if (x.ge.-adna/alfa .and. x.le.cna.and.
     &       y.ge.ymin .and. y.le.ymax .and.
     &       z.ge.-admg/alfa .and. z.le.cmg) then
            goto 510
         end if
600   continue
```

```
510   continue
      cna = cna - x
      cca = cca - y
      cmg = cmg - z
      adna = adna + alfa*x
      adca = adca + alfa*y
      admg = admg + alfa*z
      return
      end

      subroutine mixing(cna,cca,cmg,ncells,cna0,cca0,cmg0,
     1                  a1,a2,a3,cnamix,ccamix,cmgmix)

c*******************************************************************c
c                                                                 c
c     Subroutine M I X I N G determines the mixing of the the soil-  c
c     moisture with the feed solution and makes use of the finite  c
c     difference approach. The parameters are derived from the    c
c     nitrate breakthrough curve.                                 c
c                                                                 c
c*******************************************************************c

      integer*4 ncells
      real*4 cna0,cca0,cmg0,ratio
      real*4 cna(100),cca(100),cmg(100),cnamix(100),ccamix(100)
      real*4 cmgmix(100)

      cnamix(1) = a1*cna(2)+a2*cna(1)+a3*cna0
      ccamix(1) = a1*cca(2)+a2*cca(1)+a3*cca0
      cmgmix(1) = a1*cmg(2)+a2*cmg(1)+a3*cmg0
      do i=2,ncells-1
         cnamix(i) = a1*cna(i+1)+a2*cna(i)+a3*cna(i-1)
         ccamix(i) = a1*cca(i+1)+a2*cca(i)+a3*cca(i-1)
         cmgmix(i) = a1*cmg(i+1)+a2*cmg(i)+a3*cmg(i-1)
      end do
      cnamix(ncells) = (a1+a2)*cna(ncells)+a3*cna(ncells-1)
      ccamix(ncells) = (a1+a2)*cca(ncells)+a3*cca(ncells-1)
      cmgmix(ncells) = (a1+a2)*cmg(ncells)+a3*cmg(ncells-1)

      return
      end

      subroutine start(cna,adna,cca,adca,cmg,admg,alfa,kg,kcm,
     1                 y,ymin,ymax)

c*******************************************************************c
c                                                                 c
c     Subroutine S T A R T determines the start value for the Newton-  c
c     Raphson iteration procedure and is based on the side-conditions  c
c     which can be derived from the mass balances of the cations.  c
c                                                                 c
c*******************************************************************c

      real*4 lhs1,lhs2,kcm,kg

      if (adca.le.1.0e-20 .or. cca.le.1.0e-20) then
         ymin = 0.0
         ymax = 0.0
      else
         lhs1 = adna/adca
         rhs1 = kg*cna/(sqrt(cca/2.))
         lhs2 = admg/adca
         rhs2 = cmg/(kcm*cca)
         if (lhs1.gt.rhs1 .and. lhs2.le.rhs2) then
            ymin = amax1(-admg/alfa,-adca/alfa)
            ymax = amin1(cna,cca)
         else if (lhs1.gt.rhs1 .and. lhs2.gt.rhs2) then
            ymin = 0.0
            ymax = cca
         else if (lhs1.le.rhs1 .and. lhs2.le.rhs2) then
            ymin = -adca/alfa
            ymax = 0.0
         else
            ymin = amax1(-adca/alfa,-adna/alfa)
            ymax = amin1(cca,cmg)
         end if
      end if

      return
      end
```