[2]

# Flushing factors and a sharp front solution for solute transport with multicomponent ion exchange

## C.A.J. Appelo[a], J.A. Hendriks[a,b] and M. van Veldhuizen[b]

[a]*Institute for Earth Sciences, Free University, De Boelelaan 1085, 1081 HV Amsterdam, Netherlands*
[b]*Department of Mathematics, Free University, De Boelelaan 1083, 1081 HV Amsterdam, Netherlands*

## ABSTRACT

Appelo. C. A. J., Hendriks, J. A. and van Veldhuizen, M., 1993. Flushing factors and a sharp front solution for solute transport with multicomponent ion exchange. J. Hydrol., 146: 89–113.

Three cation exchange equations due to Vanselow, Gapon, and Gaines and Thomas are often used in transport models of ions subject to ion exchange with the solid aquifer matrix. The equations differ in the convention for the activity of adsorbed ions, and give different isotherm slopes for binary ion exchange pairs which influence calculated transport. In the binary case, the velocity of a composition is inversely related to the slope of the isotherm. The term 'flushing factor' is introduced as an inverse velocity that permits the easy construction of elution curves. In the multicomponent case, the flushing factors are found as eigenvalues. An analytical solution is obtained for multicomponent (heterovalent) transport with shock fronts that can be validated with the flushing factor theory. This analytical solution is applied to the freshwater injection in a brackish water aquifer presented by Valocchi and coworkers. The results indicate that the Gaines and Thomas, and Vanselow conventions can adequately describe observed data with constant exchange coefficients for the binary exchange reaction pairs. The Gapon convention gives an S-shaped isotherm for multivalent ions that can easily lead to selectivity reversals; such selectivity reversal has not been observed.

## INTRODUCTION

Multicomponent ion exchange is an important aspect of modeling of transport in aquifers and soils (Valocchi et al., 1981; Appelo et al., 1990; cf. Grove and Stollenwerk, 1987, and Mangold and Tsang, 1991, for reviews). Ion exchange is of importance where groundwater quality changes, as a result of saltwater intrusion, water injection or pollution. Different conventions

Correspondence to: C. A. J. Appelo, Institute for Earth Sciences, Free University, De Boelelaan 1085, 1081 HV Amsterdam, Netherlands.

have been proposed to describe the cation exchange process, the three most commonly used being due to Vanselow (1932), Gapon (1933), and Gaines and Thomas (1953). The three conventions have also been applied to model transport with cation exchange. For example, the data of Valocchi et al. (1981) have been modeled with the Gaines and Thomas convention by Valocchi et al. (1981), with the Vanselow convention by Miller and Benson (1983), and with the Gapon equation by Van Ommen (1985). Data fit appears to be equally good for all three. However, for soil scientists the choice among these conventions is often determined by the different fit they provide for experimental data (Vanselow, 1932; Van der Molen, 1958; Evangelou and Phillips, 1988), and the three conventions are known to yield different isotherms for binary, heterovalent, ion pairs (Bolt, 1967).

   The shape of the isotherm is of importance, since chromatographic theory has demonstrated that transport of solutes is profoundly influenced by this parameter (Sillén, 1951; Helfferich and Klein, 1970; Charbeneau, 1981; Rhee et al., 1989). It is therefore of interest to study the effects of the three exchange conventions, and we use chromatographic theory to obtain analytical solutions to describe transport of (heterovalent) ions, subject to ion exchange. First, the formulae to calculate multicomponent equilibria for the three conventions mentioned are presented. Then, we illustrate the importance of the slope of the isotherm in the calculation of transport. An analytical solution for shock fronts allows an easy comparison of the three conventions, and is used to examine the classical field injection experiment described by Valocchi et al. (1981).

## Conventions for ion-exchange equations

   The equations for calculating binary ion exchange can be found in textbooks by Sposito (1981) and Bolt (1982). Consider the ion-exchange reaction

$$0.5Ca^{2+} + Na\text{-}X \leftrightarrow Ca_{0.5}\text{-}X + Na^+ \tag{1}$$

for which a mass-action equation can be written (Gapon, 1933)

$$K^G{}_{Ca\backslash Na} = \frac{[Na^+][Ca_{0.5}\text{-}X]}{[Ca^{2+}]^{0.5}[Na\text{-}X]} \tag{2}$$

where $[i]$ is the activity in solution, $[i\text{-}X]$ is the activity on the exchanger surface, and $K^G{}_{Ca\backslash Na}$ is the equilibrium coefficient. An alternative description

of the exchange reaction is

$$0.5Ca^{2+} + Na\text{-}X \leftrightarrow 0.5Ca\text{-}X_2 + Na^+ \tag{1a}$$

for which the mass-action equation is (Kerr, 1928; Vanselow, 1932; Gaines and Thomas, 1953)

$$K^{GT}_{Ca\backslash Na} = \frac{[Na^+][Ca\text{-}X_2]^{0.5}}{[Ca^{2+}]^{0.5}[Na\text{-}X]} \tag{2a}$$

Reaction (1) uses the exchange sites filled with a given cation as the basis for calculating the activity of the exchangeable cation (Gapon convention). Reaction (1a) uses the exchangeable cations as the basis for their activity (Gaines and Thomas or Vanselow convention). Activities on the exchanger are expressed as fractions, which can be calculated on a mole or an equivalent basis. Normally the exchangeable fractions will not be equal to activities, and activity coefficients are used as correction terms

$$[i\text{-}X_{z_i}] = \beta_i \phi_i \tag{3}$$

where $\beta_i$ is the fraction on exchanger, $\phi_i$ is the activity coefficient, used as a non-ideality correction term, and $z_i$ is the charge of ion $i$. From measured quantities (usually in mEq. $(100\ g)^{-1}$), the amounts of exchangeable cations are more conveniently expressed in units of equivalents per decimeter cubed of porewater by multiplying mEq. $(100g)^{-1}$ with $\rho_b/(100\ \epsilon)$, where $\rho_b$ is the bulk density (kg dm$^{-3}$) and $\epsilon$ is the porosity (a fraction).

In a multicomponent system the exchangeable fractions are calculated, for the Gapon, and the Gaines and Thomas equation

$$\beta_i = \frac{(i\text{-}X_{z_i})}{CEC} \tag{4}$$

and for the Vanselow equation

$$\beta_i^M = \frac{(i\text{-}X_{z_i})/z_i}{\sum\limits_{i,j,k,...} (i\text{-}X_{z_i})/z_i} \tag{5}$$

where $(i\text{-}X_{z_i})$ or $(i_{1/z_i}\text{-}X)$ is exchangeable $i$ (Eq. dm$^{-3}$), $z_i$ is the charge of $i$, CEC is the cation exchange capacity (Eq. dm$^{-3}$), $\beta_i$ is the equivalent fraction of $i$, $\beta_i^M$ is the mole fraction of $i$ and $i, j, k, ...$ are exchangeable cations.

   The equivalent fraction used in the Gapon, and Gaines and Thomas equation is identical. The sum of the fractions equals 1

$$\sum \beta_i = 1 \text{ and } \sum \beta_i^M = 1 \tag{6}$$

Combination of eqns. (4) and (5) gives

$$\beta_i^M = \frac{\beta_i/z_i}{\beta_i/z_i + \beta_j/z_j + \beta_k/z_k + \ldots} \tag{7a}$$

and

$$\beta_i = \frac{\beta_i^M z_i}{\beta_i^M z_i + \beta_j^M z_j + \beta_k^M z_k + \ldots} \tag{7b}$$

   Table 1 gives the formulae to calculate exchanger compositions for a given set of solution activities and exchange coefficients. For example, to obtain $\beta_i$, the exchangeable fractions $\beta_j$, $\beta_k$, ... are expressed as $\beta_i$ with mass action eqns. (8) or (10). The resulting expressions are entered in the sum $\sum \beta = 1$, eqn. (6), to yield $\beta_i$. The reverse situation, of calculating the solute concentrations for an exchanger composition, proceeds along the same line, but now all solute concentrations are expressed as a function of one ion, and subsequently entered in the sum $\sum z_i m_i = A_0$.

   The three formulations each give different results, when the exchanger composition is calculated for a mixture of heterovalent ions, with constant $K$ and activity coefficient $\phi_G$, $\phi_{GT}$ or $\phi_V$ set to 1 (i.e. for the ideal exchanger). Figure 1 illustrates this statement for Ca/Na exchange for two different normalities in solution. The solute activities have also been expressed as equivalent fractions for this figure

$$[i] = \alpha_i = z_i m_i / A_0 \tag{13}$$

where $\alpha_i$ is the equivalent fraction in solution, $m_i$ is the solute concentration (mol dm$^{-3}$), $A_0$ is the total cationic concentration (Eq. dm$^{-3}$), and the aqueous activity coefficient is assumed to be 1.

   It may be noted from the formulae in Table 1, that the Gapon equation allows for the easiest calculation of exchangeable cations from solution data. The other equations become quadratic or higher order in a multicomponent, heterovalent solution. A peculiarity with the Gapon convention arises for multivalent cations (Appelo et al., 1990). The exchange reaction for $Ca^{2+}$ and $Mg^{2+}$ is

TABLE 1

Calculation of exchanger composition ($i$-$X_{z_i}$) from activities in a multicomponent solution

Notation:

$z_i$ is the charge of $i$;
[$i$] is the solute activity and [$i$-$X$] is the exchangeable activity;
$\beta_i$, $\beta_i^M$ are the equivalent and mole fraction on exchanger, respectively;
$\phi_i$ is the activity coefficient for exchangeable $i$;
$K_{ij} = (K_{ji})^{-1}$ is the exchange coefficient;
($i_{1/z_i}$-$X$) = ($i$-$X_{z_i}$) is exchangeable $i$ (Eq. dm$^{-3}$);

Gapon convention

$$1/z_i \cdot i + j_{1/z_j}\text{-}X \leftrightarrow i_{1/z_i}\text{-}X + 1/z_j \cdot j$$
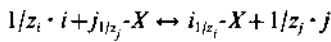
$$K_{ij}^G = \frac{[i_{1/z_i}\text{-}X][j]^{1/z_j}}{[j_{1/z_j}\text{-}X][i]^{1/z_i}} = \frac{\beta_i \phi_i [j]^{1/z_j}}{\beta_j \phi_j [i]^{1/z_i}} \tag{8}$$

$$\beta_i = \frac{[i]^{1/z_i}}{[i]^{1/z_i} + K_{ji}^G \cdot \phi_i/\phi_j \cdot [j]^{1/z_j} + K_{ki}^G \cdot \phi_i/\phi_k \cdot [k]^{1/z_k} + \cdots} \tag{9}$$

($i_{1/z_i}$-$X$) = $\beta_i$ CEC (Eq. dm$^{-3}$).

Gaines and Thomas convention

$$1/z_i \cdot i + 1/z_j \cdot j\text{-}X_{z_j} \leftrightarrow 1/z_i \cdot i\text{-}X_{z_i} + 1/z_j \cdot j$$

$$K_{ij}^{GT} = \frac{[i\text{-}X_{1/z_i}]^{1/z_i}[j]^{1/z_j}}{[j\text{-}X_{1/z_j}]^{1/z_j}[i]^{1/z_i}} = \frac{(\beta_i \phi_i)^{1/z_i} \cdot [j]^{1/z_j}}{(\beta_j \phi_j)^{1/z_j}[i]^{1/z_i}} \tag{10}$$

$$\sum_{j=i,j,k,\ldots} \frac{(\beta_i \phi_i)^{z_j/z_i} [j] (K_{ji}^{GT})^{z_j}}{\phi_j [i]^{z_j/z_i}} = 1 \tag{11}$$

($i$-$X_{z_i}$) = $\beta_i$ CEC (Eq. dm$^{-3}$)

Vanselow convention

Calculation of $\beta$ identical to Gaines and Thomas, with exchange constant $K_{ij}^V$, but gives mole fraction $\beta^M$

$$(i\text{-}X_{z_i}) = \frac{\beta_i^M z_i}{\sum_j \beta_j^M z_j} \text{ CEC} \tag{12}$$
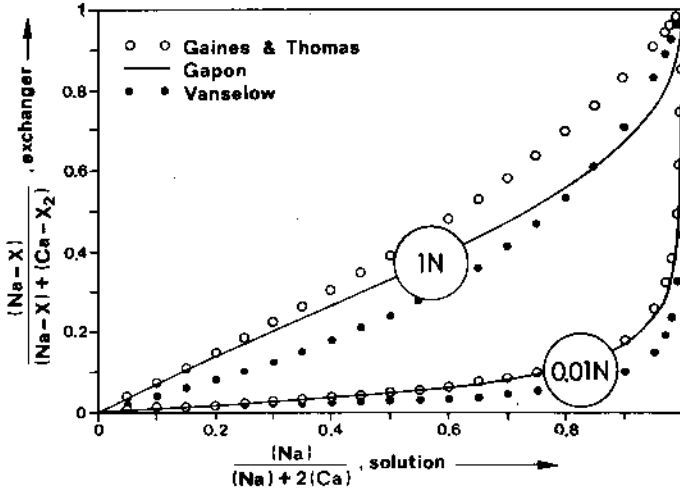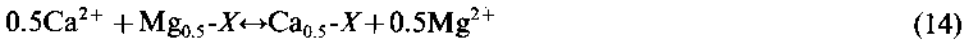
(in Eq. dm$^{-3}$)

Fig. 1. Three options to calculate the exchanger composition from solution concentrations give different results. $K_{Ca:Na} = 2$; two solution normalities, $1N$, and $0.01N$.

$$0.5Ca^{2+} + Mg_{0.5}\text{-}X \leftrightarrow Ca_{0.5}\text{-}X + 0.5Mg^{2+} \tag{14}$$

which gives

$$K^G_{Ca\backslash Mg} = \frac{[Ca_{0.5}\text{-}X][Mg^{2+}]^{0.5}}{[Mg_{0.5}\text{-}X][Ca^{2+}]^{0.5}} \tag{15}$$

Thus, a linear relation on the exchanger is combined with a square root relationship in solution. The result is an S-shaped isotherm, that gives a selectivity reversal since the ion with lower concentration is always favored even when the exchange coefficient is 1 (Fig. 2). As such, it is an extreme form of the Kielland equation (Kielland, 1935) that was recently used by Mansell et al. (1988) to model the column experiments of Lai et al. (1978). An example of the effect of the isotherm slope for reaction (14) on column elution has been reported by Appelo et al. (1990).

EXCHANGE ISOTHERM EFFECTS IN TRANSPORT MODELS

We now discuss the influence of the isotherm slope on transport of ions, subject to ion exchange. Analytical solutions have been derived for column elutions in which dispersion and diffusion are neglected, but in which the isotherm effects are explicitly accounted for, and these are therefore relevant
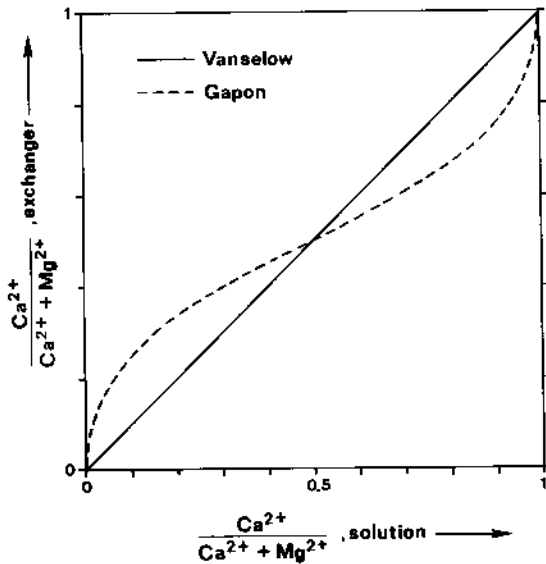
Fig. 2. Isotherm for Ca/Mg exchange with strict application of the Gapon convention gives an S-shaped isotherm for the double charged ions, also when $K_{Ca,Mg} = 1$. Linear behavior of Vanselow (or Gaines and Thomas) convention shown for comparison.

to the discussion. The basic theory was developed in the early days of ion chromatography for binary exchange (DeVault, 1943; Weiss, 1943), and was subsequently expanded for multicomponent exchange (Sillén, 1951; Klein et al., 1967; Tondeur, 1969; Helfferich and Klein, 1970; Charbeneau, 1988; Rhee et al., 1989).

*Flushing factors from isotherm slopes*

Consider binary ion exchange in a column of length $L$, one ion $i$ having equivalent fractions of, respectively, $\alpha_i$ in solution and $\beta_i$ on the exchanger. Total concentrations are, respectively, $A_0$ in solution, and CEC on the exchanger, both expressed in equivalents per decimeter cubed as noted before. The column initially has a uniform concentration along the length. Conservation of matter requires

$$A_0\left(\frac{\partial \alpha_i}{\partial t}\right)_x = -u_{H_2O} A_0\left(\frac{\partial \alpha_i}{\partial x}\right)_t - \text{CEC}\left(\frac{\partial \beta_i}{\partial t}\right)_x \tag{16}$$

where $u_{H_2O}$ is the pore water flow velocity (m s$^{-1}$). We can write the change in exchangeable fraction as a differential relation between (exchangeable) $\beta_i$

and (solute) $\alpha_i$

$$\left(\frac{\partial \beta_i}{\partial t}\right)_x = \frac{d\beta_i}{d\alpha_i}\left(\frac{\partial \alpha_i}{\partial t}\right)_x \tag{17}$$

which gives in eqn. (16)

$$\left(1 + \frac{CEC}{A_0}\frac{d\beta_i}{d\alpha_i}\right)\left(\frac{\partial \alpha_i}{\partial t}\right)_x = -u_{H_2O}\left(\frac{\partial \alpha_i}{\partial x}\right)_t \tag{18}$$

Implicit differentiation of $\alpha_i(x, t) =$ constant gives

$$\left(\frac{\partial \alpha_i}{\partial t}\right)_x = -\left(\frac{\partial \alpha_i}{\partial x}\right)_t\left(\frac{\partial x}{\partial t}\right)_{\alpha_i} \tag{19}$$

When this relation is inserted in eqn. (18), and both sides of the resulting equation are divided by $(\partial \alpha_i/\partial x)$, the transport velocity $u_{\alpha_i} = (\partial x/\partial t)_{\alpha_i}$ of a concentration $\alpha_i$ is obtained as

$$u_{\alpha_i} = \frac{u_{H_2O}}{1 + \dfrac{CEC}{A_0}\dfrac{d\beta_i}{d\alpha_i}} \tag{20}$$

The equation closely resembles the retardation equation, except that the slope of the isotherm enters the equation as a variable instead of the (invariant) distribution coefficient. The retardation can thus be expressed as relative velocity $u_{\alpha_i}/u_{H_2O}$. Or, with $V_0$ the pore volume of the column (m$^3$), it can be stated in terms of pore volumes

$$V_{\alpha_i}/V_0 = u_{H_2O}/u_{\alpha_i} \tag{21}$$

which must flush a column (or flowtube) before a given concentration arrives at the column outlet

$$V^* = \frac{V_{\alpha_i}}{V_0} - 1 = \frac{CEC}{A_0}\frac{d\beta_i}{d\alpha_i} \tag{22}$$

Equation (22) can be used to construct elution curves when an ion is displaced by a less tightly bound ion, as illustrated in Fig. 3. The ion A has
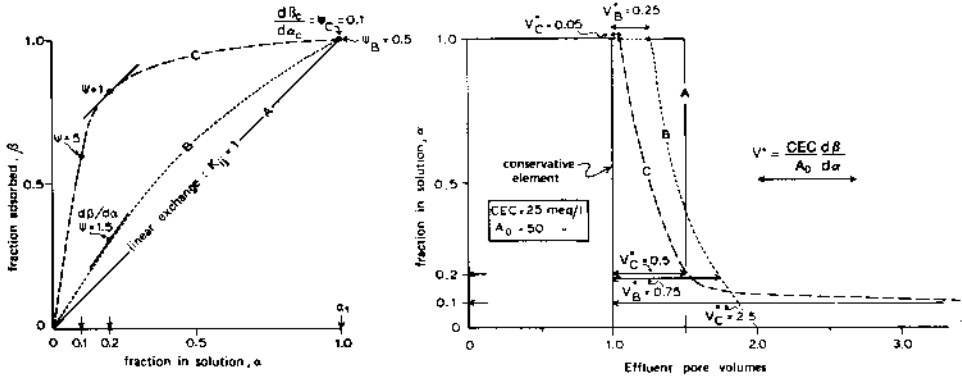
Fig. 3. Effect of exchange isotherm on elution curve: (left) ions A, B and C have given exchange isotherm with ion j; (right) elution of A, B or C with j can be constructed from the exchange isotherm.

a linear exchange isotherm with the ion j, and the retardation is independent of concentration (constant) when j is used to elute A from the column. The slope of the isotherm of the ions B and C (also with respect to j) increases for smaller fractions of B and C, and the elution of smaller fractions of B or C with j requires more and more pore volumes $V^*$. The elution curves for these two ions are hyperboles with a shape dictated by the isotherm slope.

When the eluting ion is more tightly held than the resident cation in the column, the slope of the isotherm becomes smaller with higher solute fraction of the eluting ion (the isotherms shown in Fig. 3, left, are mirrored around a center of symmetry). This implies that higher concentrations of the eluting ion would need less pore volumes to arrive at the column outlet than lower concentrations. An impossible situation, of course, and a sharp front develops according to the integral mass balance

$$V^s = \frac{CEC}{A_0} \frac{\Delta\beta}{\Delta\alpha} \tag{23}$$

where $V^s$ is the number of pore volumes that the sharp front needs for traveling down the column.

The integral mass balance can be illustrated for the case where ion j is eluted with ion B or C. The fronts and their appearance at a column outlet are shown in Fig. 4. It is assumed that the initial solution in the column contains fractions of 0.8 j and 0.2 of either A, B or C, and that the column is eluted with a solution that has only A, B or C. The ion C has the most strongly curved isotherm with j, so that only small amounts of j are initially adsorbed when C is the complementary ion. $\Delta\beta/\Delta\alpha$ is therefore smallest with C, and C appears most rapidly in the effluent of the column (Fig. 4).
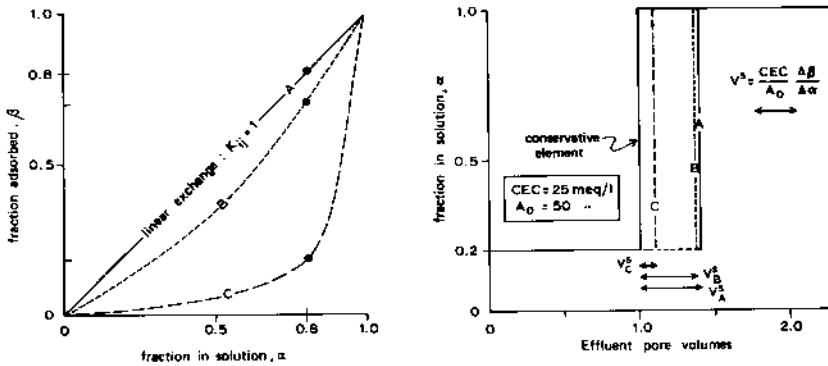
Fig. 4. The conditions of Fig. 3 are inverted, and j is eluted with A, B or C: (left) ion j has given exchange isotherm with ions A, B and C; note that the axes give $\alpha_j$ and $\beta_j$; (right) initial solution containing 80% of j and 20% of A, B or C, is eluted with 100% A, B or C: with B and C shock fronts develop, while with A just linear retardation occurs.

In eqns. (22) and (23), $V^*$ or $V^s$ when multiplied with $A_0/\text{CEC}$, are akin to the '$\Psi$-condition' of Sillén (1951), or to the 'throughput parameter $T'''$ (Vermeulen et al., 1984). However, it is easier to consider it a 'flushing factor' indicating the number of pore volumes which must flush through the column to reach a given solute fraction in the effluent. Any change in adsorbed quantity ($\text{CEC}d\beta$), that must occur because of a change in solution concentration, requires that this quantity be transported in solution, i.e. $V^*$ pore volumes must carry the difference in solute concentration $A_0 d\alpha$. The flushing factor is also similar to the distribution coefficient used in the retardation factor, i.e. $R = 1 + V^*$ for one, given concentration. However, the term 'flushing factor' is useful for several reasons. First, it embraces a wider field of application, including differential changes of solid over solute concentrations. Second, it is appropriate for extension to multicomponent interactions as shown in the next section. Third, the term is suitable for indicating the number of pore volumes which can flush an aquifer pollutant down to a given concentration.

## Multicomponent ion exchange

The same theory applied to multicomponent ion exchange requires that the flushing factor be equal for all components simultaneously. This condition is known as 'coherence' (Helfferich and Klein, 1970). For the differential eqn. (22), it leads to an eigenvalue problem, hinted at already by DeVault (1943),

but first noted by Mangelsdorf (1966)

$$\det.(F - V^*I) = 0 \tag{24}$$

where $F$ is the Jacobian matrix for the exchanging ions, and $I$ is the identity matrix. We use the standard chemical conventions for solute ions as in Table 1, so that the Jacobian matrix for a multicomponent solution is written as

$$F = \text{CEC} \begin{bmatrix} \dfrac{\partial \beta_a}{z_a \partial m_a} & \dfrac{\partial \beta_a}{z_b \partial m_b} & \cdots & \dfrac{\partial \beta_a}{z_{n-1} \partial m_{n-1}} \\[2mm] \dfrac{\partial \beta_b}{z_a \partial m_a} & \ddots & & \vdots \\[2mm] \vdots & & \ddots & \vdots \\[2mm] \dfrac{\partial \beta_{n-1}}{z_a \partial m_a} & \dfrac{\partial \beta_{n-1}}{z_b \partial m_b} & \cdots & \dfrac{\partial \beta_{n-1}}{z_{n-1} \partial m_{n-1}} \end{bmatrix} \tag{25}$$

with $m_a, m_b, ..., m_{n-1}$ the molar concentration of the first, second, ..., $n-1$th ion in solution. Note that the $n$th ion is implicitly known if cation exchange capacity and total solute concentration are fixed via eqns. (6) and (13).

The matrix $F$ given by eqn. (25) has $(n-1)$ real eigenvalues if only homovalent ions are present (Helfferich and Klein, 1970), and also in the heterovalent case it can be proved that the eigenvalues are real and different. These eigenvalues correspond to $(n-1)$ flushing factors for a single solution composition. In other words, coherence is possible with $(n-1)$ different velocities. When along a flowline a uniform composition exists initially, and water of a constant, but different composition is injected, an ordered sequence in the effluent compositions develops. There will be $n$ plateau zones where composition is invariant for some time (the initial and injected water compositions are the first and the last plateau), and $(n-1)$ composition paths which lead to the plateaux. The existence of the plateaux and connecting paths is derived in the theory of coherence (Helfferich and Klein, 1970), as well as in the theory of hyperbolic systems (Lax, 1973; Rhee et al., 1989). A path may entail a gradual change of composition (also called 'broadening' or a 'non-sharpening front', or a 'wave'), or it may be abrupt (called a 'shock' or a 'sharp front'), similar to the case of binary exchange.

The plateaux appear in sequential order in the effluent. The $k$th plateau has a $k$th eigenvalue that is larger than the $(k-1)$th eigenvalue of the preceding, $(k-1)$th plateau. This follows logically from the fact that a larger eigenvalue

implies a larger flushing factor, or alternatively, a lower velocity of the composition. The problem is that, except in the case of homovalent exchange (Helfferich and Klein, 1970), one does not know the plateau composition, nor the length of a plateau, i.e. where to step off on the path to the next plateau. For three ions there is only one intermediate plateau, and in that case a combined integration along the two eigenvectors (which represent the paths) from the upstream and the downstream end, can provide a solution as shown by Charbeneau (1988).

*Sharp fronts with multicomponent ion exchange*

However, when all paths are shocks, a set of equations can be obtained that allows the calculation of plateau composition as well as plateau length, irrespective of the number of ions or their charge. Coherence simply implies that the change in adsorbed ions $CEC\Delta\beta$ in the $k$th shock is transported by $V_k^s$ pore volumes. It requires the mass balance

$$CEC\Delta\beta_i = V_k^s z_i \Delta m_i$$

to be fulfilled for all exchanging ions, for each shock. Rewriting eqn. (23) gives for $(n-1)$ components in the $k$th plateau

$$V_k^s = \frac{CEC[(\beta_i)_{k+1} - (\beta_i)_k]}{z_i[(m_i)_{k+1} - (m_i)_k]} \tag{26a}$$

and so on for $(p-1)$ plateaux. Furthermore for $(p-2)$ intermediate plateaux

$(n-1)$ equilibrium relations from Table 1                              (26b)

and electroneutrality in solution and on the exchanger

$$\sum z_i m_i = A_0, \qquad \sum(\beta_i) = 1 \tag{26c}$$

so that $(n-1)(p-1)+(n-1)(p-2)+2(p-2) = 2np-3n-1$ equations are obtained.

Initial and final compositions of solution and exchanger (first and last plateau) are known. Thus, $2n(p-2)$ concentrations, and $(p-1)$ flushing factors add up to $2np-4n+p-1$ unknowns. Since the number of plateaux equals the number of components $(p = n)$ (Helfferich and Klein, 1970; Lax, 1973), it makes sense to look for a solution. Klein et al. (1967) derived a

similar set of equations, but did not apply these in an example with sharp fronts, and did not consider how the sharpness of the fronts could be proved.

One problem is that only chemically intuitive arguments can be given to deduce whether sharp fronts will develop in a given situation with multicomponent, heterovalent ion exchange. However, if initial and final solution compositions are known, the exchange complex can be calculated for these compositions, and compared with exchange isotherms for pairs of ions. Shock fronts will develop when the concentration of the ion that is favored most strongly by the exchanger increases (cf. Fig. 4). The assumption of sharpness can be checked, by comparing eigenvalues at both sides of each shock obtained from eqn. (24) (Lax, 1973). The criteria are easily understood by noting that the eigenvalues are flushing factors. The flushing factor of the plateau after a shock must be smaller than of the foregoing plateau, so that the latter is pushed ahead, i.e.

$$(V_k^*)_{k+1} < V_k^s < (V_k^*)_k \tag{27a}$$

Also, the sequence of shocks must show, in an upstream direction, increasing sharp front flushing factors $V_k^s$, which results in

$$(V_{k+1}^*)_{k+1} > V_k^s > (V_{k-1}^*)_k \tag{27b}$$

where $(V_k^*)_{k+1}$ is the $k$th flushing factor, of the $(k+1)$th plateau composition, with flushing factors ordered from small to large. (The sequence is illustrated in Fig. 7).

The procedure thus involves: (1) calculation of amounts of exchangeable ions that need to be displaced from the sediment, or must enter the exchange complex for equilibration with the entering water; (2) inspection of the exchange isotherm to predict whether front sharpening or broadening will occur; (3) apparently sharp fronts allow the calculation of plateau concentrations and lengths; (4) the assumption of sharpness is checked, by comparison with flushing factors of the plateau concentrations.

## APPLICATION: SHARP FRONTS IN THE VALOCCHI CASE

It is of interest to reconsider the injection experiment by Valocchi et al. (1981), which has provided a starting point for many studies and simulations on aquifer transport with ion-exchange reactions. Valocchi et al. (1981) injected fresh water in a brackish-water aquifer, and noted a curious pattern in observation wells of, e.g. Ca concentrations becoming lower than in groundwater, but also lower than in injection water. The concentration

TABLE 2

Mass balance calculations for exchanging ions in the injection experiment by Valocchi et al. (1981): observation well S23

| Ion | $K_{A\backslash Na}^{GT}$ | Water | | Sediment | | |
|-----|------|--------|------|---------|-----|------|
|     |      | Native | Inj. | Initial | End | DIF |
| Na  | 1.0  | 86.5   | 9.4  | 160     | 56  | +104 |
| Mg  | 1.84 | 18.2   | 0.5  | 142     | 41  | +101 |
| Ca  | 2.45 | 11.1   | 2.13 | 153     | 306 | −153 |

Gaines and Thomas convention, assuming concentration equals activity.
Concentrations in mmoles per decimeter cubed; sediment CEC = 750 mEq. dm$^{3}$

changes could be explained by chromatographic separation through ion exchange, with Na and Mg being exchanged for Ca from the injected water.

Computer simulations of the field data by several authors proved very successful, despite the use of different ion-exchange equations and conventions. Valocchi et al. used the Gaines and Thomas equation, without considering activity coefficients in solution or on the exchanger surface. Miller and Benson (1983) used the Vanselow convention; Van Ommen (1985) could model the data equally well with the Gapon equation and activity coefficient corrections for solute concentrations. Cederberg et al. (1985) and recently Charbeneau (1988) returned to the Gaines and Thomas equations as used by Valocchi et al. (1981).

A direct comparison of differences imposed by different exchange equations has not yet been made, perhaps because an analytical solution was considered formally impossible (Valocchi, 1984). It will be shown that the sharp front analytical solution proposed in the preceding section can be applied.

*Mass balance of exchanging ions*

Use of eqns. (9), (11) and (12) from Table 1 allows the calculation of the amounts which need to be exchanged to equilibrate the aquifer sediment with injected water (step 1 of our procedure). Table 2 shows the results for the Gaines and Thomas equation as used by Valocchi et al. (1981), however with their Eq. dm$^{-3}$ based constant recalculated to mol dm$^{-3}$ for the solute ions (eqn. (10) in Table 1)

$$K_{Ca\backslash Na}^{GT} = \sqrt{2} K_{Ca\backslash Na} \text{ (Valocchi et al.)}$$

Table 2 shows that the major adaption of the exchangeable ions in the sediment is an increase of Ca, in return for a loss of Na and Mg. Selected

results for the three exchange conventions are given in Appendix A, where for each equation the value of the exchange constant has been chosen to comply with the same observed exchange complex in equilibrium with (native) brackish water. Data in Appendix A show that inclusion of solute activity corrections (calculated here with the Davies equation) has a small (10%) effect on relative amounts with the Gaines and Thomas convention. Use of activities or concentrations has not much effect with the other equations either. The Vanselow equation gives practically identical results as the Gaines and Thomas convention here, in contrast to the Gapon equation which gives marked deviations for Mg and Ca.

With all equations the binding strength of the exchanger for the ions is for $Ca > Mg > Na$. The adaption of the exchanger complex thus takes a step form here, with Ca sweeping Mg, which in turn displaces Na. The sharp front approximation seems valid, with development of three different plateaux.

*Plateau concentrations and lengths*

Table 2 indicates that considerably more cations are exchangeable in the sediment (on a mmol $dm^{-3}$ porewater basis) than are present in the injected water. The implication is that composition of injection water after a short flowlength is adapted to the exchanger composition (which is still in equilibrium with brackish water). Initially only dilution takes place and the exchangeable ions have not changed; the composition can be calculated with the formulae from Table 1, and the electroneutrality

$$m_{Na^+} + 2(m_{Mg^{2+}} + m_{Ca^{2+}}) = A_0$$

where $A_0 = 0.01466$ Eq. $dm^{-3}$ in the injected water. All ions can be expressed in terms of the $Ca^{2+}$ concentration with the appropriate equilibrium relation from Table 1

$$[i] = [i\text{-}X](K_{Ca\backslash i}[Ca]^{0.5}/[Ca\text{-}X_2]^{0.5})^{z_i}$$

where $[i\text{-}X]$ and $[Ca\text{-}X_2]$ are known from the brackish water composition (Table 2 and Appendix A). Hence, with the Gaines and Thomas equation, assuming activity $[i]$ identical to solute concentration

$$0.818 \sqrt{Ca} + 2Ca(1.64 + 1) = 0.01466 \tag{28}$$

The result is identical for all exchange formulae (all exchange constants have been adapted to obtain the same exchanger composition in equilibrium
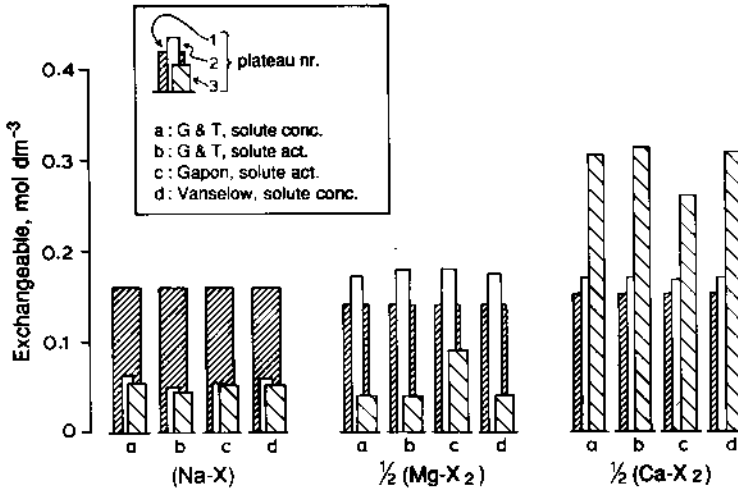
Fig. 5. Exchangeable cations in the injection experiment of Valocchi et al. (1981), using different exchange formulations. The three plateaux correspond to: (1) native brackish water; (2) intermediate plateau; (3) final injection water equilibrium.

with brackish water); the result only depends on the square root of the dilution, which appears in the $[Na]/\sqrt{[Ca]}^2$ exchange equilibrium. Including a solute activity correction will affect this ratio, and gives, therefore, other concentrations in the dilution plateau as well.

The lengths of the first and second plateaux, as well as second plateau concentrations in water and sediment give eight unknowns, for which eight equations (26) are available. These equations have been simplified as shown in Appendix B, and solved by Newton–Raphson iteration. The calculated adaption of the exchange complex is visualized in Fig. 5 (actual numbers are given in Appendix A). It can be seen that the exchangeable Mg concentration increases from the first to the second plateau, even though the end stage of equilibrium with the injected fresh water (the third plateau) requires a decrease. The decrease takes place in the second plateau, where solute concentrations of Mg are higher in the effluent than in the influent. The figure also shows that the Gapon convention gives marked deviations for exchangeable $Mg-X_2$ and $Ca-X_2$ in the last plateau.

Calculated $Ca^{2+}$ and $Mg^{2+}$ concentrations for the Gaines and Thomas convention were added to the original data presented by Valocchi et al. (1981) for well S23 (Fig. 6). Breakthrough of $Cl^-$ in this well occurred after 260 $m^3$ was injected, which means that successive shocks arrive after injection of 260 $V^s$ $m^3$. The sharp front solution simulates the measured data and the computer model of Valocchi et al. (1981) remarkably well, although the
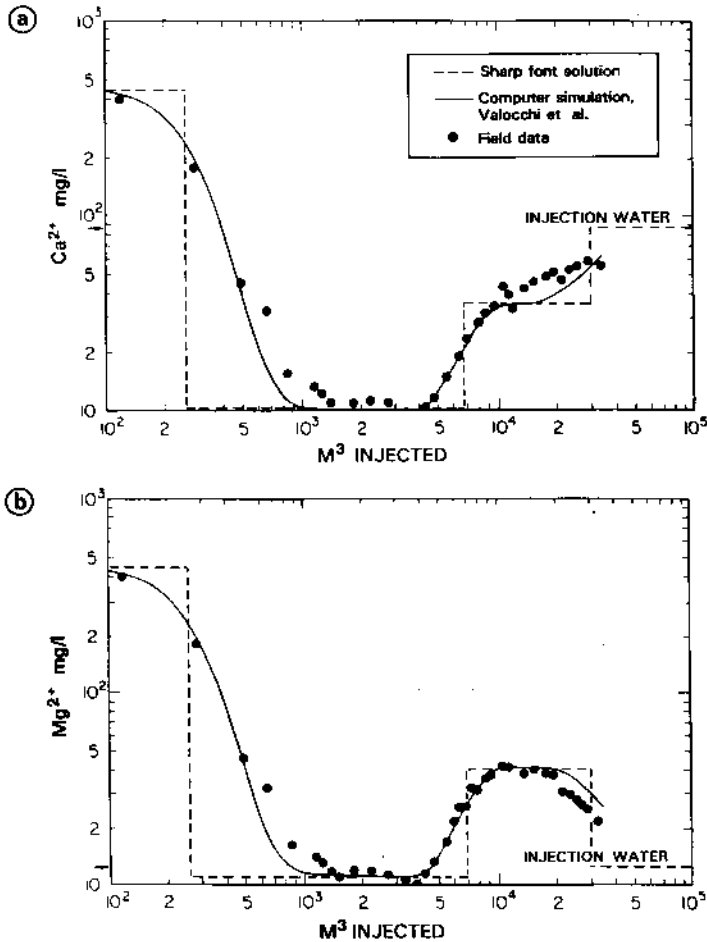
Fig. 6. Concentrations of Ca and Mg in water from observation well S23 during injection of fresh water (Valocchi et al., 1981). The results of the sharp front approximation are also shown.

observed fronts are more diffuse because we neglect the effect of dispersion in our calculation.

*Flushing factors of shocks and plateaux*

Calculation of the flushing factors (step 4 of our procedure) provides proof of the validity of the sharp front assumption. Flushing factors (eigenvalues) for plateau compositions were determined with an analytical formula for the Gapon, and Gaines and Thomas convention (cf. Appendix C), and for the Vanselow convention by numerical differentiation (values are reported in Appendix A). The results are illustrated in Fig. 7 for the Gaines and Thomas
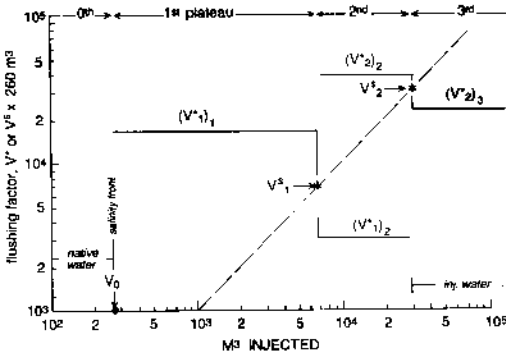
Fig. 7. Flushing factors for plateaux and sharp fronts for the Valocchi case (Fig. 6), Gaines and Thomas convention. With $(V_1^*)_2 < V_1^s < (V_1^*)_1$, similar for the second sharp front $V_2^s$, and $V_2^s > V_1^s$, the criteria for shock fronts given by Lax (1973) are met.

convention, showing that the sharp front conditions expressed in eqn. (27) are valid in this case. Similar results were calculated for the other conventions, and corroborate the good results of the researchers who used these ion-exchange equilibria in numerical models. However, one notable exception is formed by the Gapon equation. Figure 8 indicates that with this equation the last front has a lower flushing factor than the last plateau, which violates the sharp front condition that a plateau composition must be able to push the foregoing sharp front. The reason is related to the selectivity reversal, whereby Mg, relatively unfavored at a high concentration in the second plateau, is becoming more and more favored (with respect to Ca) at the low concentrations of the last plateau (i.e. the injection water composition).

The various ion-exchange conventions give plateau concentrations which
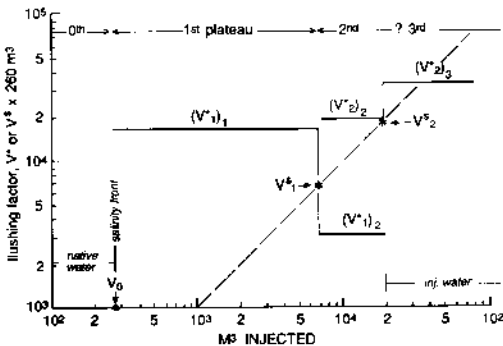


Fig. 8. Flushing factors for plateaux and sharp fronts for the Valocchi case (Fig. 6), Gapon convention. The criteria for shock fronts are violated in the second front, where $(V_2^*)_3 > (V_2^*)_2 > V_2^s$. Also note that the length of the second plateau is far too short.

can be considered equal within the experimental error of cation analysis in a field experiment, estimated here to be about 10%. The Gaines and Thomas, and Vanselow formulae give even closer agreement, whether or not solution activity corrections are included. The differences in mass balance (Fig. 5) are thus equalized in the ion chromatographic displacement. This supports the fine agreement found by Miller and Benson (1983), using the Vanselow convention, with the computer simulation by Valocchi et al. (1981) using the Gaines and Thomas equation. Although the concentrations calculated with the Gapon equation agree with those observed, the sharp front approximation is not valid, and $(V^s)_2$ of the second plateau is much too small. Van Ommen (1985) in his numerical model employed a hybrid form of the Gapon and Kerr equations, with exchange among Ca and Mg according to the convention of Kerr (1928). He also used different water compositions near the injection well, and observation well S23, in agreement with the data presented by Valocchi et al. (1981). However, these water compositions lead to initially greater amounts of exchangeable Mg than in other simulations, and this may have balanced the particular effect of selectivity reversal associated with the Gapon convention.

CONCLUSIONS

It was shown that the form of the exchange isotherm can influence the transport of ions affected by ion-exchange processes. The different conventions for ion exchange which are commonly employed, lead to different isotherm slopes for binary exchange pairs, and thus bear upon transport calculations as well. The effects should be duly considered when ion exchange is incorporated in transport models. This conclusion is especially valid for non-sharpening (broadening) fronts, whereas for sharp fronts dissimilar plateau lengths may be found. A flushing factor was defined that indicates the number of pore volumes that must flush a column or a flowline before a given concentration arrives at the column end. The flushing factor can be used to construct elution curves with binary exchange. Flushing factors similarly indicate number of pore volumes that must flush a column before different compositions arrive in the multicomponent case. An analytical solution for sharp fronts has been derived that allows for an easy intercomparison of the exchange equations for a multicomponent, heterovalent system. It can accurately describe the concentration changes in the injection experiment of Valocchi et al. (1981). It appears that the Gaines and Thomas, and the Vanselow conventions give near-identical results. When several multivalent ions are present, the Gapon equation easily leads to selectivity reversal, whereas the experimental data do not show this phenomenon. The application

of solute activity corrections has marginal effects on the relative amounts that need to be displaced from the sediment.

REFERENCES

Appelo, C.A.J., Willemsen, A., Beekman, H.E. and Griffioen, J., 1990. Geochemical calculations and observations on salt water intrusions. II Validation of a geochemical transport model with column experiments. J. Hydrol., 120: 225–250.
Bolt, G.H., 1967. Cation exchange equations used in soil science. A review. Neth. J. Agric. Sci., 15: 81–103.
Bolt, G.H. (Editor), 1982. Soil Chemistry B. Physico-chemical Models. Elsevier, Amsterdam, 527 pp.
Cederberg, G.A., Street, R.L. and Leckie, J.O., 1985. A groundwater mass transport and equilibrium chemistry model for multicomponent systems. Water Resour. Res., 21: 1095–1104.
Charbeneau, R.J., 1981. Groundwater contaminant transport with adsorption and ion exchange chemistry: method of characteristics for the case without dispersion. Water Resour. Res., 17: 705–713.
Charbeneau, R.J., 1988. Multicomponent exchange and subsurface transport: characteristics, coherence and the Riemann problem. Water Resour. Res., 24: 57–64.
DeVault, D., 1943. The theory of chromatography. J. Am. Chem. Soc., 65: 532–540.
Evangelou, V.P. and Phillips, R.E., 1988. Comparison between the Gapon and Vanselow exchange selectivity coefficients. Soil Sci. Soc. Am. J., 52: 379–382.
Gaines, G.L. and Thomas, H.C., 1953. Adsorption studies on clay minerals. II. A formulation of the thermodynamics of exchange adsorption. J. Chem. Phys., 21: 714–718.
Gapon, E.N., 1933. Theory of exchange adsorption V. J. Gen. Chem. (USSR), 3: 667–669 (Chem. Abstr., 28: 4516, 1934).
Grove, D.B. and Stollenwerk, K.G., 1987. Chemical reactions simulated by groundwater quality models. Water Resour. Bull., 23: 601–615.
Helfferich, F. and Klein, G., 1970. Multicomponent Chromatography; Theory of Interference. M. Dekker, New York, 419pp.
Kerr, H.W., 1928. The nature of base exchange and soil acidity. J. Am. Soc. Agron., 20: 309–335.
Kielland, J., 1935. Thermodynamics of base-exchange equilibria of some different kinds of clays. J. Soc. Chem. Ind., 54: 232–234T.
Klein, G., Tondeur, D. and Vermeulen, Th., 1967. Multicomponent ion exchange in fixed beds. Ind. Eng. Chem. Fund., 6: 339–351.

Lai, S.-H., Jurinak, J.J. and Wagenet, R.J., 1978. Multicomponent cation adsorption during convective–dispersive flow through soils: experimental study. Soil Sci. Soc. Am. J., 42: 240–243.

Lax, P.D., 1973. Hyperbolic systems of conservation laws and the mathematical theory of shock waves. SIAM, Philadelphia, PA, 48 pp.

Mangelsdorf, P.C., 1966. Difference chromatography. Anal. Chem., 38: 1540–1544.

Mangold, D.C. and Tsang, C.-F., 1991. A summary of subsurface hydrological and hydrochemical models. Rev. Geophys., 29: 51–79.

Mansell, R.S., Bloom, S.A., Selim, H.M. and Rhue, R.D., 1988. Simulated transport of multiple cations in soil using varible selectivity coefficients. Soil Sci. Soc. Am. J., 52: 1533–1540.

Miller, C.W. and Benson, L.V., 1983. Simulation of solute transport in a chemically reactive heterogeneous system: model development and application. Water Resour. Res., 19: 381–391.

Pope, G.A., Lake, L.W. and Helfferich, F.G., 1978. Cation exchange in chemical flooding: Part 1 · basic theory without dispersion. Soc. Pet. Eng. J., 418–433.

Rhee, H.-K., Aris, R. and Amundson, N.R., 1989. First Order Partial Differential Equations, Vol. II. Prentice Hall, Englewood Cliffs, NJ, 548 pp.

Sillén, L.G., 1951. On filtration through a sorbent layer. IV. The $\Psi$-condition, a simple approach to the theory of sorption columns. Ark. Kemi, 2: 477–498.

Sposito, G., 1981. The Thermodynamics of Soil Solutions. Clarendon Press, Oxford, 223 pp.

Tondeur, D., 1969. Théorie des colonnes d'échange d'ions. PhD Thesis, Univ. de Nancy.

Valocchi, A.J., 1984. Describing the transport of ion-exchanging contaminants using an effective $K_d$ approach. Water Resour. Res., 20: 499–503.

Valocchi, A.J., Street, R.L. and Roberts, P.V., 1981. Transport of ion-exchanging solutes in groundwater: chromatographic theory and field simulation. Water Resour. Res., 17: 1517–1527.

Van der Molen, W.H., 1958. The Exchangeable Cations in Soils Flooded with Seawater. Staatsdrukkerij, The Hague, 167pp.

Van Ommen, H.C., 1985. The 'mixing cell' concept applied to transport of non-reactive and reactive components in soils and groundwater. J. Hydrol., 78: 201–213.

Vanselow, A.P., 1932. Equilibria of the base-exchange reactions of bentonites, permutites, soil colloids, and zeolites. Soil Sci., 33: 95–113.

Vermeulen, Th., LeVan, M.D., Hiester, N.K. and Klein, G., 1984. Adsorption and ion exchange. In: Perry's Chemical Engineer's Handbook, 6th edn. McGraw-Hill, New York, pp. 16-1–16-48.

Weiss, J., 1943. On the theory of chromatography. J. Chem. Soc., 297–303.

## APPENDIX A

Plateau concentrations and lengths, fresh water injected in brackish water aquifer (Valocchi et al., 1981). Observation well S23. Concentrations in mmol $dm^{-3}$ in porewater

| Plateau | | Concentrations | | | Sharp $(V^s)$ | $(\Sigma\ m^3\ inj.)$ | Differential $(V^*)$ |
|---|---|---|---|---|---|---|---|
| | | Na | Mg | Ca | | | |
| (a) *Gaines and Thomas convention (solute activity = concentration); used by Valocchi et al., 1981; Cederberg et al., 1985; Charbeneau, 1988* | | | | | | | |
| 0, | Water | 86.5 | 18.2 | 11.1 | | | 10.8/2.8 |
| | sediment | 160.60 | 141.59 | 153.11 | | | |
| | | | | | 1 | (260) | |
| 1, | Water | 13.28 | 0.43 | 0.26 | | | 459/61.2 |
| | sediment | 160.60 | 141.59 | 153.11 | | | |
| | | | | | 25.3 | (6843) | |
| 2, | Water | 9.47 | 1.67 | 0.92 | | | 145/12.3 |
| | sediment | 64.18 | 173.00 | 169.91 | | | |
| | | | | | 113.2 | (29432) | |
| 3, | Water | 9.4 | 0.5 | 2.13 | | | 88.6/10.9 |
| | sediment | 56.35 | 40.55 | 306.27 | | | |
| (b) *Gaines and Thomas convention (solute activity calculated with Davies equation from ionic strength $I = \Sigma m_i \cdot (z_i^2 + z_i)/2$)* | | | | | | | |
| 1, | Water | 13.60 | 0.33 | 0.20 | | | 599/76.5 |
| | sediment | 160.60 | 141.59 | 153.11 | | | |
| | | | | | 25.4 | (6864) | |
| 2, | Water | 9.46 | 1.68 | 0.92 | | | 146/10.7 |
| | sediment | 55.42 | 175.83 | 171.46 | | | |
| | | | | | 114.5 | (29770) | |
| 3, | Water | 9.4 | 0.5 | 2.13 | | | 89.6/9.5 |
| (c) *Gapon convention (solute activity calculated with Davies equation); used by Van Ommen, 1985* | | | | | | | |
| 1, | Water | 13.60 | 0.33 | 0.20 | | | 302/67.6 |
| | sediment | 160.60 | 141.59 | 153.11 | | | |
| | | | | | 24.1 | (6526) | |
| 2, | Water | 9.44 | 1.77 | 0.84 | | | 76.4/11.1 |
| | sediment | 55.73 | 180.00 | 167.13 | | | |
| | | | | | 68.3 | (17758) | |
| 3, | Water | 9.4 | 0.5 | 2.13 | | | 82.3/10.7 |

APPENDIX A (continued)

| Plateau | | Concentrations | | | Sharp $(V^s)$ | ($\Sigma$ m³ inj.) | Differential $(V^*)$ |
|---------|-----|------|------|-----|------|------|------|
| | | Na | Mg | Ca | | | |
| (d) *Vanselow convention (solute activity = concentration); used by Miller and Benson (1983)* | | | | | | | |
| 1, | Water | 13.28 | 0.43 | 0.26 | | | 459/66.4 |
| | sediment | 160.60 | 141.59 | 153.11 | | | |
| | | | | | 26.2 | (7075) | |
| 2, | Water | 9.47 | 1.67 | 0.92 | | | 146/12.2 |
| | sediment | 60.71 | 174.19 | 170.46 | | | |
| | | | | | 113.8 | (29588) | |
| 3, | Water | 9.4 | 0.5 | 2.13 | | | 88.5/10.6 |

APPENDIX B: SHARP FRONT SOLUTION FOR FRESH WATER INJECTED IN BRACKISH WATER AQUIFER

For six unknown concentrations in the second plateau, and for two plateau lengths, there are eight equations obtained from eqn. (26)

$$V_n^s = \frac{\text{CEC}\,[(\beta_i)_{n+1} - (\beta_i)_n]}{z_i[(m_i)_{n+1} - (m_i)_n]} = \frac{(i\text{-}X_{z_i})_{n+1} - (i\text{-}X_{z_i})_n}{z_i[(m_i)_{n+1} - (m_i)_n]} \tag{26(a)}$$

where $i = \text{Na, Mg}$, and $n = 1, 2$. Furthermore (assuming $[i] = m_i$, Gaines and Thomas convention)

$$i\text{-}X_{z_i} = \text{CEC}^{(1-z_i/2)} m_i \left\{ K_{i\backslash\text{Ca}} \left[ \frac{(\text{Ca-}X_2)}{m_{\text{Ca}}} \right]^{0.5} \right\}^{z_i} \tag{26(b)}$$

where $i = \text{Na, Mg}$; and electroneutrality in solution and on the exchanger

$$\sum z_i m_i = A_0 \quad \text{and} \quad \sum (i\text{-}X_{z_i}) = \text{CEC} \tag{26(c)}$$

where $i = \text{Na, Mg, Ca}$.

The concentrations in the dilution plateau and in the injected water are known, i.e. $(m_i)$ and $(i\text{-}X)_n$, where $i = \text{Na, Mg, Ca}$, and $n = 1, 3$. We have $K_{\text{Mg}\backslash\text{Na}} = 1.84$, and $K_{\text{Ca}\backslash\text{Na}} = 2.45$, and combine to eliminate Na and Mg concentrations in the second plateau

$$[(V^s)_2 (m_{\text{Na}})_3 - (\text{Na-}X)_3] \times [2.45(m_{\text{Ca}})_2^{1/2}(V^s)_1 - (0.75(\text{Ca-}X_2)_2)^{1/2}] =$$

$$[(V^s)_1 (m_{\text{Na}})_1 - (\text{Na-}X)_1] \times [2.45(m_{\text{Ca}})_2^{1/2}(V^s)_2 - (0.75(\text{Ca-}X_2)_2)^{1/2}]$$

$$\tag{B1}$$

$$[(V^s)_2 2(m_{Mg})_3 - (Mg\text{-}X_2)_3] \times [2(m_{Ca})_2(V^s)_1 - (1.84/2.45)^2(Ca\text{-}X_2)_2] =$$

$$[(V^s)_1 2(m_{Mg})_1 - (Mg\text{-}X_2)_1] \times [2(m_{Ca})_2(V^s)_2 - (1.84/2.45)^2(Ca\text{-}X_2)_2]$$

$$\text{(B2)}$$

$$(V^s)_1 2[(m_{Ca})_1 - (m_{Ca})_2] = (Ca\text{-}X_2)_1 - (Ca\text{-}X_2)_2 \tag{B3}$$

$$(V^s)_2 2[(m_{Ca})_2 - (m_{Ca})_3] = (Ca\text{-}X_2)_2 - (Ca\text{-}X_2)_3 \tag{B4}$$

The four equations have been solved with Newton–Raphson iteration; the additional iteration for solute activity corrections can be introduced straight-forwardly.

APPENDIX C: EQUATIONS FOR CALCULATING THE PLATEAU FLUSHING FACTOR

The differential plateau flushing factors $V^*$, can be calculated from eqn. (4) by numerical differentiation. However, for a system of three cations having either Gapon or Gaines-Thomas exchange-relationship, a simpler procedure is available as shown by Pope et al. (1978). The Gaines and Thomas formula (eqn. (10)) is written in logarithmic form:

$$\frac{1}{z_i}\ln[i\text{-}X_{z_i}] - \frac{1}{z_i}\ln[i] = \ln(K_{ij}^{GT}) + \frac{1}{z_j}\ln[j\text{-}X_{z_j}] - \frac{1}{z_j}\ln[j] \tag{C1}$$

It is assumed that the activity-coefficients in solution ($\gamma_{i,j}$) and on exchanger ($\phi_{i,j}$) are constant, and are incorporated in the exchange constant $K'$. Then $[i] = m_i$, $[i\text{-}X_{z_i}] = \beta_i$, ($i = i,j$), and $K' = K_{ij}^{GT}(\phi_j/\gamma_j)^{1/z_j}(\gamma_i/\phi_i)^{1/z_i}$. These terms are replaced in (C1), which is differentiated to obtain

$$\left(\frac{d\beta_i}{\beta_i z_i \times dm_i} - \frac{1}{z_i m_i}\right)dm_i = \left(\frac{d\beta_j}{\beta_j z_j \times dm_j} - \frac{1}{z_j m_j}\right)dm_j \tag{C2}$$

With $z_i dm_i = A_0 d\alpha_i$, and eqn. (22), we can replace $d\beta_i/(z_i dm_i)$ by $V^*/\text{CEC}$, ($i = i,j,k,\ldots$), and solve for $dm_i$

$$dm_i = \frac{\dfrac{V^*}{\beta_j \text{CEC}} - \dfrac{1}{z_j m_j}}{\dfrac{V^*}{\beta_i \text{CEC}} - \dfrac{1}{z_i m_i}} dm_j \qquad i = i,j,k,\ldots \tag{C3}$$

Electroneutrality and a constant normality $A_0$ of the solution require $\sum z_i dm_i = 0$, which according to (C3) is true when

$$\sum_i \left(\frac{V^*}{\beta_i z_i \text{CEC}} - \frac{1}{z_i^2 m_i}\right)^{-1} = 0 \tag{C4}$$