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GEOCHEMICAL CALCULATIONS AND OBSERVATIONS ON SALT WATER INTRUSIONS. II. VALIDATION OF A GEOCHEMICAL MODEL WITH LABORATORY EXPERIMENTS

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ABSTRACT

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Column experiments with aquifer sediments have been performed. A description is given of procedures and equipment which can maintain the anaerobic status of the sediments from sampling in the field to subsequent experimentation in the laboratory. From two sediments native pore solutions were displaced with $SrCl_2$ solutions; another was percolated alternately with groundwater and once diluted seawater.

The chromatographic pattern which develops when exchangeable cations are eluted, was modelled with the earlier presented geochemical (multicomponent) transport model. Proper description of the $SrCl_2$-elution required reformulation of the cation exchange reaction for one sediment; the other sediment showed proton buffering and calcite dissolution with slow kinetics. These elutions could be modelled with constant exchange coefficients, but during fresh/saltwater displacements the selectivity for Ca/Mg exchange was variable.

INTRODUCTION

A preceding communication reported on a geochemical transport model which was used to simulate cation exchange during salt water intrusions in aquifers (Appelo and Willemsen, 1987). The present authors have since been experimenting with aquifer sediments in laboratory columns, in part to obtain experimental data which could be used to validate the transport model. Most modellers of transport by groundwater have relied on the classical field data obtained by Valocchi et al. 1981 (Cederberg et al., 1985; Van Ommen, 1985; Charbeneau, 1988). Valocchi et al. (1981) injected tertiary treated sewage water into a brackish water aquifer, and followed the changes in water concentrations in nearby observation wells. Calcium was dominant in the injected water, and Mg and Na were dominant cations in the native groundwater. The chromatographic separation which developed during transport, with Ca replacing Mg and Na from the aquifer sediment, could be satisfactorily modelled by all

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(Valocchi et al., 1981; Cederberg et al., 1985; Van Ommen, 1985; Charbeneau, 1988).

Other injection tests (or operational activities) in aquifers have been described (Ragone and Vecchioli, 1975; Stuyfzand, 1984; Van Beek and Van Puffelen, 1987), but results have not been modelled to the extent of the Valocchi et al. (1981) data. The other injection tests give little attention to ion exchange phenomena, but rather focus on quality changes as a result of oxidation/reduction reactions (e.g. Ragone and Vecchioli, 1975; Van Beek and Van Puffelen, 1987), adsorption and retardation of pollutants (Roberts et al., 1986), or clogging as a result of chemical precipitation (e.g. of calcite or Mg-silicate with Aquifer Thermal Energy Storage (ATES): Willemsen and Appelo, 1985; Holm et al., 1987). From an operational point of view this is understandable, since cation exchange is mostly not detrimental for a water injection and withdrawal scheme (although examples to the contrary are known, e.g. of clogging through clay-swelling, Brown and Signor, 1974). However, for groundwater transport modelling, which embraces a broad spectrum of environmental pollutants such as heavy metals and organics, cation exchange and other reactions with the solid aquifer material must be included. Also, modelling of cation exchange during salinisation and desalinisation, needs a proper description of cation exchange reactions.

Column experiments with soils and sediments which had as a major goal the acquisition of data for transport modelling have mostly been confined to binary exchange (Persaud and Wierenga, 1982; Robin and Elrick, 1985). An exception is the work by Schweich and Sardin who have modelled and experimented on multicomponent transport (Schweich and Sardin, 1985; Sardin et al., 1985; Schweich et al., 1988).

In order to obtain more experimental data on cation exchange in aquifer sediments, a laboratory setup (column) was devised. Special attention was given to the maintenance of sediment anaerobic status during sampling and experiments. The following describes the procedures needed to obtain sediment cores and to transfer them to a gas-tight laboratory column. Results are presented for fresh water/salt water displacements, and displacements of native pore water from sediment cores with oxygen- and CO_2-free $SrCl_2$ solutions. The results are compared with compositions which were modelled using the Appelo and Willemsen (1987) approach.

EXPERIMENTAL PROCEDURES

Sediment coring

A primary requirement for chemical experiments with anaerobic aquifer sediments is to prevent oxidation of labile sulphides and ferrous iron by oxygen from the air. Oxidation of the sulphides gives sulphate acid, which completely alters the sediment properties: the pore solution becomes a sulphate-rich, acid water, in which Al from clay minerals or Ca from calcite dissolves. Oxidation

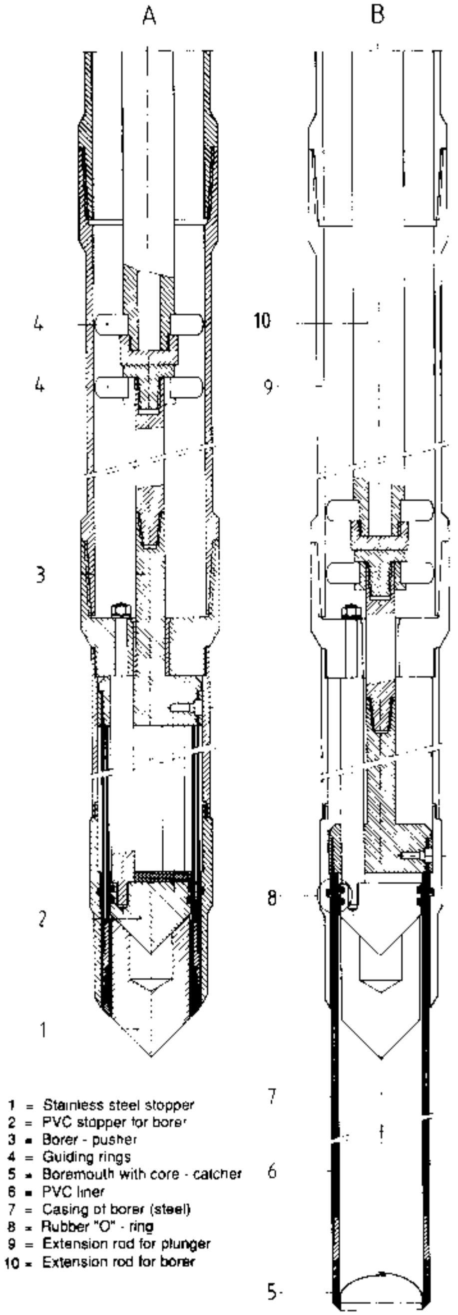

Fig. 1. Construction details of the corer used for anaerobic sampling of aquifer sediments (courtesy of Delft Geotechnics).

of ferrous iron leads to a similar acidification of the pore solution. A possible way to stop oxidation is to deep-freeze the sediment before contact with air takes place.

A core pushing device was constructed by Delft Geotechnics, which enabled the required anaerobic sampling. The corer (Fig. 1) consists of closed, stainless steel tubing which is pushed downwards using a 20-t truck. When the tubing reaches the desired depth, a 1-m long internal corer is pushed further downward out of the stainless steel tubing. The corer has a sediment catcher at its front, and is internally lined with a cleaned PVC tube. The assemblage is then withdrawn and dismantled. The front end of the corer including the core catcher, is removed and pieces of cotton rag are pushed against the sediment in the PVC liner. This part is closed off from atmospheric oxygen with molten stearine. The whole corer is then removed from the stainless steel tubing, the PVC liner is withdrawn, cotton rags are pushed in the still open end, and molten stearine further seals the sediment from atmospheric oxygen. The cotton rags prevent an unwanted flow of sediment, which is often in a near fluid state. The PVC liner containing the sample is then laid down in an isolation box, and liquid nitrogen is poured over to freeze the sample. The whole procedure of core removal to freezing takes 3 min. The samples are kept frozen by regular addition of liquid nitrogen and are transported to the laboratory to be stored at $-20°C$.

The maximal depth of sampling is ~ 20 m with 20 t pushing power, but may be less when sandy or gravelly layers obstruct the stainless steel tubing. A larger depth can be obtained in bailer borings, hammering down the corer. The sediment recovery (i.e. the amount of sediment recovered at the surface, compared with the depth of core-pushing) can be 100% in clayey and peaty sediments, and is less in sandy sediments, but generally not less than 70%. The loss can be attributed to malfunction of the core catcher and shows up in slip and shear faces in the sand when the core is dried and cut along its length. However, it is presumed that even with an incomplete recovery, the chemical properties remain intact. Proof of this is that analysis of pore water from the core gives the same composition as water sampled from a filter at the same spot.

Laboratory column

A laboratory column has been constructed as a receptacle for the sediment core. The column (Fig. 2) is constructed of stainless steel, internally lined with teflon. Teflon base and top plates with a spiral groove ensure an even distribution of inlet and outlet water. The groove is covered with a stainless steel filter (double, of 160 μm mesh) which prevents the sediment from entering and blocking the groove. The column is closed with a piston of stainless steel to which the top plate of teflon is fixed. Viton rings in the teflon section act as a barrier, but complete gas-tightness (tested to 10 atm) is obtained with viton rings in the stainless steel compartment of the piston which touch stainless steel of the column. The column is 5.8 cm in diameter, closely fitting the

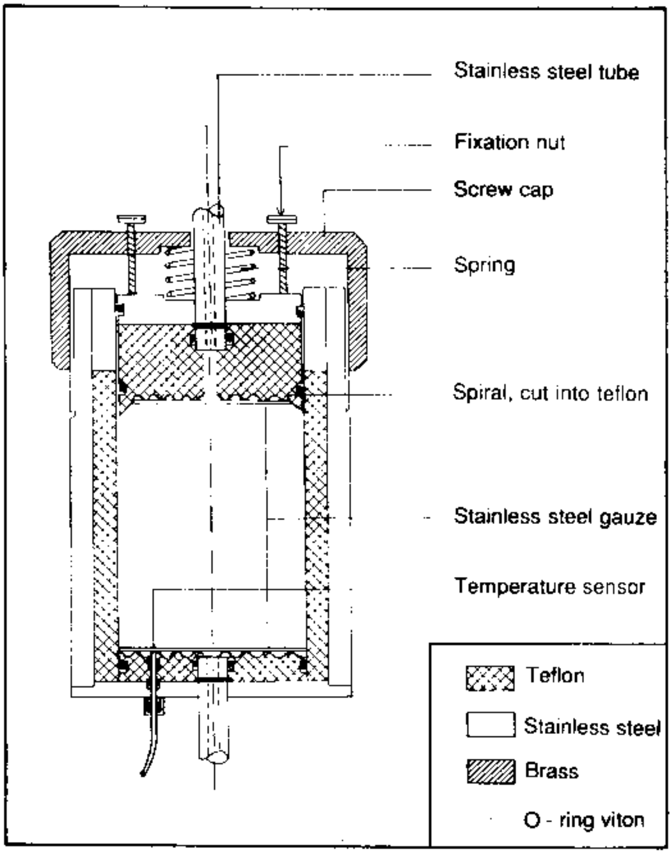

Fig. 2. Construction details of the laboratory column.

sediment cores, and with the movable piston, sample length is ~ 7.5 cm. The column is installed in a thermostated waterbath in which four columns can be connected in series. The water inlet and outlet are connected with 1-mm stainless tubing to the column with Swagelock fittings.

Introducing samples into the column

Samples from the PVC liner are cut to the desired length with a diamond saw after immersion in a liquid N_2 bath. The saw-edges are cleaned, and the liner is cut along its length, but not completely through the PVC. In the meantime, the displacing solution is pumped into the column to the stainless steel filter. Liquid nitrogen is poured into the column to remove air; the plastic liner is broken, and the sediment sample introduced into the column. Finally, the piston is inserted and fixed with a screw cap. Thereafter the sample is allowed to thaw, while pressure is maintained on the piston with two screws. This pressure is necessary to settle the sample against the teflon wall, thus minimising the possibility of short circuit flow. The whole assembly and outlet tubes are maintained under an N_2 atmosphere during installation. When the sample is thawed, as registered by a thermocouple in the base of the column, the displacing solution is pumped into the column.

Maintaining anaerobic conditions for the displacing solutions

Displacing solutions are pumped into the column with a HPLC pump with double pump-head to ensure a smooth, continuous flow. Artificial solutions are bubbled with N_2 gas which has been hydrated by flow through seven washing bottles, of which the first five are filled with an $FeCl_2$ solution and the last two with distilled water. The N_2 gas is led off via one empty bottle to minimise back diffusion of air. When reduced native groundwater is used, it is sampled in the field with a submersible pump, and kept in a 1-m long stainless steel tube of 10 cm diameter. A polypropylene piston caps the water. Since the stainless steel tube has an irregular inner surface, it was found necessary to use a thick piece of polypropylene with 3 viton rings to close off the water from the atmosphere. In the laboratory, the tube is placed upright, and about 7 atm pressure is applied to the piston to drive the water out. This setup could keep ferrous iron in solution at the concentrations measured in groundwater for periods of more than two months.

Controls of the experimental setup

Short circuit flow along the container wall was tested by displacements with $SrCl_2$, where a short-cut is indicated by an early breakthrough of Sr. Oxidation of sediment and pore water was controlled by analysing for Fe^{2+} and NH_4 in the first displaced samples of pore water, and for SO_4^{2-} on a more regular basis during displacement.

Flow velocities during displacements

Most theories of column behaviour in chromatographic analysis rely on Glueckauf's theory of dispersion in a chromatographic column (Glueckauf, 1955; Helfferich, 1962; Giddings, 1965; Vermeulen et al., 1984). Peak broadening is seen as a combined effect of:
(a) transverse and longitudinal dispersion;
(b) film diffusion across boundaries between mobile and immobile (stagnant) regions;
(c) diffusion in stagnant regions;
(d) kinetics of the chemical reaction or the adsorption process which affects reactive solutes.

As a result of the physical processes (a), (b) and (c), activities may not be equal in a cross-section of the column, which is thus attributed to physical nonequilibrium. It affects both conservative and reactive molecules. As a result of slow kinetics (process (d)), there may not be equilibrium between solute and adsorbed molecules, a condition which is called chemical nonequilibrium; it affects reactive molecules only. Several authors have shown that the different processes lead to identical mathematical formulations which can describe column behaviour (Giddings, 1965; Van Genuchten and Wierenga, 1976; Nkedi-Kizza et al., 1984). The processes are thus indiscernible in column elution curves for reactive molecules.

Physical and chemical non-equilibrium is related to pore water flow velocity. A high velocity sweeps away solutes too rapidly, before homogenisation with respect to diffusion and reactions has been attained (James and Rubin, 1979; Valocchi, 1985; Jennings, 1987; Bahr and Rubin, 1987). A low velocity can be used to gain local equilibrium, but diffusion at too low velocity blurs the chromatographic separation (Glueckauf, 1955; Van Deemter et al., 1956). Since our geochemical transport model is based on the local equilibrium assumption at least for exchange reactions, it is important to find the optimal velocity for a column experiment. An approximate idea of maximal flow velocity at which physical equilibrium is still maintained can be obtained from Valocchi's (1985) analysis based on time moments of the concentration breakthrough curves. The second time moment yields the degree of spreading (variance) of a pulse input; hydrodynamic dispersion (process (a)) in combination with diffusion into spherical aggregates (process (c)) gives a variance according to Valocchi (1985, table 2):

$$\mu_2 = \frac{2\,(x/L)\,R^2 D}{v\,L} + \frac{2\,(x/L)\,(1-\beta)^2 R^2 a^2 v\,\theta_m}{15\,D_a L\,\theta_{im}} \tag{1}$$

with R, R_m and β defined as:

$$R = 1 + \rho K_d/\theta$$

$$R_m = 1 + \rho\,p\,K_d/\theta_m$$

$$\beta = \theta_m R_m/\theta\,R$$

where: x is distance travelled in a column of length L; v is pore water flow velocity; a is aggregate radius; D is hydrodynamic dispersion coefficient; D_a is diffusion coefficient inside the aggregate; θ_m and θ_{im} are mobile and immobile porosities, respectively, where total porosity, $\theta = \theta_m + \theta_{im}$; ρ is bulk density of the porous medium; p is the ratio of adsorbed mass in the mobile pores over total adsorbed mass; K_d is the distribution coefficient. R_m is the retardation factor for the mobile fraction, and R the total retardation factor.

If we assume that surface characteristics of the porous medium are the same throughout, p is identical to the mobile pores over total pores, $p = \theta_m/\theta$. This assumption is reasonable for sandy sediments with the (inert) quartz grains uniformly coated with oxides, clay minerals and organic matter which act as ion exchangers. A 'stagnant' zone could occur where the grains are locally cemented, with a central pore area accessible for cations via diffusion. In this case $R_m = R$, and eqn. (1) becomes:

$$\mu_2 = \frac{2\,(x/L)\,R^2 D}{vL} + \frac{2\,(x/L)\,\theta_{\mathrm{im}}\theta_{\mathrm{m}} R^2 a^2 v}{15\,D_{\mathrm{a}} L\,\theta^2}$$

or, for simplicity, $\mu_2 = A + C$.

Part A describes the variance as a result of hydrodynamic dispersion, and the second part, C, the variance as a result of diffusion in a stagnant region. We may now calculate the flow velocity where part C contributes less than 1% to the total variance, i.e. $C < 0.01\ A$. This gives after rearrangement of terms:

$$v^2 < \frac{0.15\ D\ D_{\mathrm{a}}\theta^2}{\theta_{\mathrm{im}}\theta_{\mathrm{m}} a^2} \tag{2}$$

Equation (2) can be further simplified, when the hydrodynamic dispersion coefficient is $D = \alpha v$, $\theta^2/(\theta_{\mathrm{im}}\theta_{\mathrm{m}})$ is minimal $= 4$, and the approximation is made that dispersivity $\alpha = 2a$ (i.e. dispersivity is equal to size of (stagnant) inhomogeneity):

$$v < 2.4\ D_{\mathrm{a}}/\alpha \tag{3}$$

or

$$D < 2.4\ D_{\mathrm{a}}$$

which is similar to the criterion noted by James and Rubin (1979), that the local equilibrium assumption applies when the hydrodynamic dispersion coefficient is similar to the effective molecular diffusion coefficient.

Figure 3 shows a plot of velocity vs. the dispersivity according to eqn. (3) for two values of the diffusion coefficient. The higher value of 1E-5 $\mathrm{cm^2\,s^{-1}}$ would

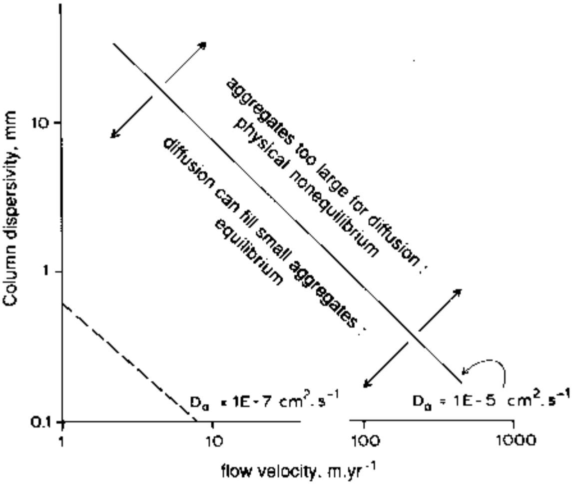

Fig. 3. Physical equilibrium as a function of pore water flow velocity and column dispersivity for two values of the diffusion coefficient.

be valid for open pores, the lower value of 1E-7 $cm^2 s^{-1}$ for partially collapsed interlayer spaces of clay illites or vermiculites (Keay and Wild, 1961; Freer, 1981). Note that we assumed that the dispersivity equals the diameter of the spherical stagnant zone, so that it can be linked to some extent with size of the heterogeneity. A flow velocity < 75 m $year^{-1}$ is necessary for columns with 1 mm dispersivity. This flow velocity is also sufficiently low for clay interlayers of about 10 μm diameter to gain physical equilibrium with the displacing solution.

Chemical nonequilibrium has been related to the nondimensional Damkohler number D_k (Valocchi, 1985; Jennings, 1987; Bahr and Rubin, 1987):

$$D_k = K_{fb} L/v$$

where K_{fb} is the reaction rate (s^{-1}) for first order adsorption. Valocchi (1985) and Jennings (1987) have found that Damkohler numbers > 100 are necessary for the local equilibrium assumption to be valid. Bahr and Rubin (1987) used a more elaborate method in which all terms influenced by chemical kinetics are accounted for, so that other kinetic rate mechanisms can be included. It is not easy to obtain kinetic data on more complex ion exchange reactions, but the single case with valid local equilibrium analysed by Bahr and Rubin (1987) had a flow velocity of 51 m $year^{-1}$. This case, a column experiment by Hornsby and Davidson (1973) had a dispersion coefficient of 1.7 E-5 $cm^2 s^{-1}$, and is thus within the expected range for physical equilibrium as well. This corroborates the conclusion by Helfferich (1962) and Ogwada and Sparks (1986), that exchange reactions are generally limited by diffusion, and not by kinetics of the reaction.

The pore flow velocity in the experiments described later varied between 20 and 80 m $year^{-1}$, which is supposed to be low enough for local equilibrium with respect to exchange reactions. Still, a somewhat retarded elution was observed of K^+ from a clay sample, which is related to solid state diffusion from the (partially collapsed) interlayer space of illite. Diffusion of interlayer cations in a contracted interlayer space has been described as a very slow process (Keay and Wild, 1961; Freer, 1981), and such diffusion leads to the nonequilibrium tailing discussed above.

RESULTS

Three sediments obtained from various aquifers in The Netherlands have been subjected to column elutions to test the geochemical model. The sediment types and experimental conditions are summarised in Table 1. One sediment ('Alphen'), from a former tidal sand bar, is calcite-free, and has organic matter (from dispersed peat) as a major exchanging compound. This sediment has been flushed alternately with native groundwater and once-diluted seawater (Beekman and Appelo, 1990). Another sediment ('Delft') is a very coarse-grained quartz sand with calcite shell fragments and a low exchange capacity. The native water has been flushed from the sediment with a $SrCl_2$ solution, and the sediment has subsequently been used for experiments on ATES (Griffioen

TABLE 1

Characteristics of the sediments used in column elutions

	Alphen	Delft	Ketelmeer
	(fine sand)	(coarse sand)	(clay)
Av. grain size (mm)	0.24	0.41	n.d.
$CaCO_3$ (%)	< 0.3	1.5	n.d.
C (%)	n.d.	0.05	n.d.
CEC (meq per 100 g)	1.3	0.51	10.1
Pore volume (%)	36.8	39.7	49.0
Native groundwater	Fresh, anaerobic	Brackish, anaerobic, CH_4	**Fresh**
Dispersivity (mm)	1.5–4.5[1]	20	9.8
Pore flow v (m year^{-1})	80	40	22

[1] Salt and fresh water displacements showed different dispersivities (cf. Beekman and Appelo, 1988).
n.d. = not determined.

and Appelo, 1990). The third sediment is a clay with relatively high cation exchange capacity from 'Ketelmeer', deposited in the brackish to salty former inland sea the 'Zuiderzee'. At present a lake exists, which receives heavily polluted mud from the River Rhine. This sediment has also been eluted with $SrCl_2$ to obtain information about the mobility of adsorbed heavy metals.

Modelling the experimental data

The displacement experiments have been modelled as described in the literature (Appelo and Willemsen, 1987), except that now PHREEQE (Parkhurst et al., 1980) has been used as the basic geochemical model instead of EQ3NR (Wolery, 1983). Results for simple equilibrium calculations with one mineral are essentially identical for the two models (depending only on values for equilibrium constants used in the database). However, the transport part could be included more easily in the PHREEQE-code, which was advantageous with regard to execution time (Willemsen et al., 1988). The exchange constants are calculated from ion activity ratios in pore water and exchangeable meqs using the Gapon formulation (cf. Bolt, 1982). For example, for Na/Ca exchange:

$$1/2\ Ca^{2+} + Na\text{–}X \leftrightarrow Ca_{0.5}\text{–}X + Na^{+} \qquad (4)$$

with exchange constant:

$$K_{Ca\cdot Na} = \frac{[Ca_{0.5}\text{–}X]\,[Na^{+}]}{[Na\text{–}X]\,[Ca^{2+}]^{0.5}}$$

where [$Ca_{0.5}$–X] and [Na–X] are exchangeable cations (meq dm^{-3}, or meq per 100 g), as obtained by experiment; [Na^{+}] and [Ca^{2+}] are solute activities (mol.

per kg H_2O); K_{Ca-Na} is the experimentally observed exchange constant, which can vary for different sediments.

The exchangeable cations are introduced in the geochemical model as a complex with a new "master species" X^-, and the exchange reaction is split into two separate association reactions; e.g. for eqn. (4):

$$1/2\ Ca^{2+} + X \leftrightarrow Ca_{0.5}\text{–}X \tag{4a}$$

$$Na^+ + X^- \leftrightarrow Na\text{–}X \tag{4b}$$

It can be seen that eqn. (4) can be obtained by subtracting eqn. (4b) from eqn. (4a). The association constant for (4b) is set to an arbitrary value (but high enough to keep 'free' X^- at negligible concentrations). The other association constants are then fixed via the calculated exchange equilibrium. As an example for Ca in association reaction eqn. (4a):

$$K(4a) = K(4b) \cdot K_{Ca-Na}$$

Dispersion and/or diffusion is simulated by mixing of adjacent cells; the value of the dispersion coefficient was calculated using CXTFIT (Parker and Van Genuchten, 1984) from the experimental Cl-breakthrough curves.

$SrCl_2$ elution of Ketelmeer sediment: effects of exchange formulation

This clay sample proved difficult to elute because of a tendency for short circuit flow along the container wall in short samples. After exhaustive tests it was decided to use a full 7.5 cm core. The high CEC then made a long elution necessary with a total of 2.5 l of 0.05 N $SrCl_2$ solution. Pore water in this sediment is principally River Rhine water. The composition of pore water and exchangeable cations of the sediment are given in Table 2.

Figure 4 shows the elution curves and modelled concentrations. Exchange constants for the model were computed from the experiment (as shown for

TABLE 2

Pore water composition in Ketelmeer sediment, and sediment exchange complex

	Groundwater concentration (m mol. l^{-1})	Exchangeable amount (meq per 100 g)
pH	6.30	
Na	3.3	0.207
K	0.4	0.212
Mg	1.2	2.44
Ca	1.1	6.20
NH_4	1.0	0.280
Fe + Mn		0.66
		10.00
Cl	4.5	
Alk.	4.7	
SO_4^{2-}	0.07	

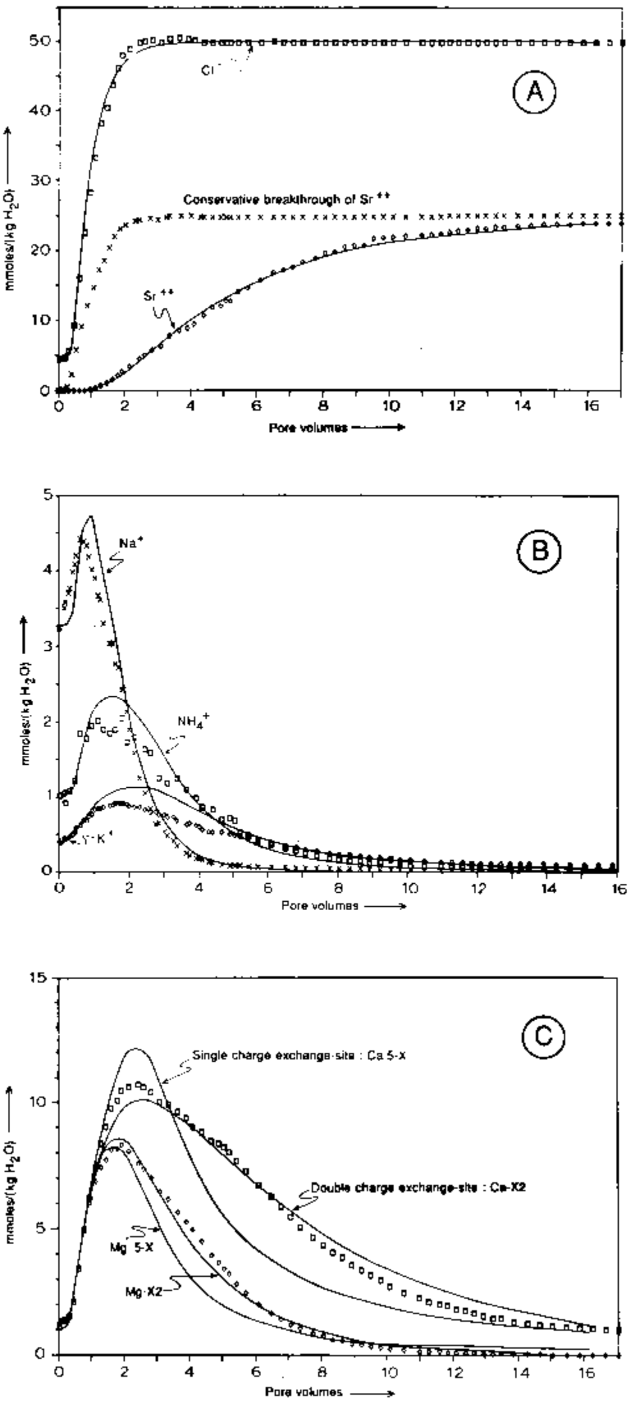

Fig. 4. Displacement of pore solution and exchangeable cations from Ketelmeer sediment.

Na–Ca exchange in eqn. (4)). This leads automatically to identical total mass for each element in the model and experiment, both in solution and as exchangeable ions. However, the form of the modelled elution curves can still be different from those derived experimentally, thus providing a test of model assumptions.

Comparing elution curves of monovalent cations shows close agreement for Na (Fig. 4B). Modelled concentrations of NH_4^- and K^+ are too high for the initial elution peak and (necessary for a mass balance) too low in the tail; the long tailing is attributed to slow release of NH_4^+ and K^+ from closed interlayers of illite. Changes in the selectivity constant, with K^+ and $NH_4^{\cdot}$ more tightly held by the exchanging surface when concentrations in solution are low, cannot be excluded, but seem less likely since even a divalent ion like Mg^{2+} is eluted to lower concentrations at the end of the experiment.

Two model curves are shown for each of the divalent ions Ca^{2+} and Mg^{2+} (Fig. 4C). One is for a single charge site as used in the Gapon exchange equation, the other for a double charge exchange site. The two formulations give remarkably different results, which can be explained as being a result of the Gapon formulation with multicomponent exchange.

The Gapon formulation for Ca and Mg with respect to a single exchange site is:

$$1/2\,Mg^{2+} + Ca_{0.5}\text{–}X \leftrightarrow Mg_{0.5}\text{–}X + 1/2\,Ca^{2+} \qquad (5)$$

with an equilibrium constant:

$$K_{Mg\ Ca} = \frac{[Mg_{0.5}\text{–}X]\,[Ca^{2+}]^{0.5}}{[Ca_{0.5}\text{–}X]\,[Mg^{2+}]^{0.5}}$$

which relates a linear ratio on the exchanger with an (unwanted) square root of the ratio in solution! The result is that minor concentrations in solution are strongly favoured by the exchanger. The reader can see in Fig. 4 that this exchange model is not adequate for the divalent cations.

The same experiment has been modelled on the basis of $2X^-$, or:

$$Mg^{2+} + Ca\text{–}X_2 \leftrightarrow Mg\text{–}X_2 + Ca^{2+} \qquad (6)$$

with an equilibrium constant:

$$K_{Mg\text{–}Ca} = \frac{[Mg\text{–}X_2]\,[Ca^{2+}]}{[Ca\text{–}X_2]\,[Mg^{2+}]}$$

which relates a linear ratio on the exchanger to a linear ratio in solution, as is usual in other exchange equations (Gaines and Thomas or Vanselow convention, cf. Bolt, 1982). Incorporation of the exchange on this basis in the geochemical transport model results in a more adequate description of the experimental points, as shown in Fig. 4. There is still a slight deviation for Ca^{2+} when about 10 pore volumes have left the sediment. It may be that this deviation is related to changes in selectivity for the Ca–Sr pair and could be modelled as such. However, it is difficult to evaluate such a curve fitting procedure without further experiments on similar sediments. It should be noted here that the high CEC of this clay sediment gives long elution curves, which show the crucial shortcoming of the Gapon formulation in a multicomponent exchange model. The high CEC also maintains high Ca^{2+} concentrations in the eluate, so that calcite dissolution is not important during this experiment.

$SrCl_2$ elution of Delft sediment, showing proton buffering and calcite dissolution

In this experiment native groundwater was displaced by 0.022 N $SrCl_2$ to determine native groundwater composition, CEC of the sediment and absorbed amounts of individual cations. The sediment is an unconsolidated, coarse, quartz-rich sand (Table 1). X-ray diffraction analysis of the clay fraction collected on a 0.45 μm filter at the end of an experiment indicated illite/mica and chlorite as main clay minerals with some smectite and kaolinite. Groundwater in the aquifer can be characterised as anaerobic, hard and brackish. The presence of Fe, NH_4 and Mn and absence of NO_3 and NO_2 in the initial effluent indicates that the anaerobic environment is maintained (Table 3). The Fe concentration is identical to the concentration in groundwater sampled near the coring site.

When a neutral $SrCl_2$ solution is used to flush a sediment containing calcite, the alkalinity approaches zero and pH increases to 10. This pH is attained when water with a very low CO_2 pressure equilibrates with calcite. However, in this experiment the alkalinity remained significantly non-zero: at the end of the experiment, after 500 ml $SrCl_2$ solution had percolated the column, the solution had 0.37 meq l^{-1} alkalinity and a pH of 7.15. The alkalinity is attributed to

TABLE 3

Pore water composition in Delft sediment, and sediment exchange complex

	Groundwater concentration (m mol. l^{-1})	Exchangeable amount (meq per 100 g)
pH	6.83	
Na	21.40	0.0205
K	0.693	0.0186
Mg	1.93	0.0977
Ca	2.95	0.324
NH_4	2.05	0.0382
Fe	0.320	0.0111
Mn	0.0092	0.00049
		0.511
Cl	21.05	
Alk.	14.37	
SO_4	0.142	
NO_3	< 0.005	
NO_2	< 0.0005	
Si	0.470	

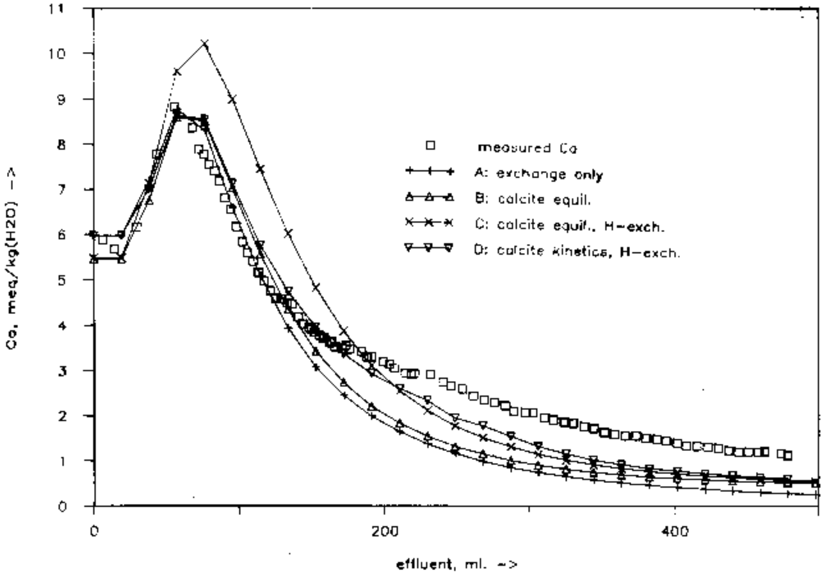

Fig. 5. Modelling Ca elution from Delft sediment with different options.

dissolution of $CaCO_3$ as a result of proton-buffering of the sediment in reaction to the pH increase during displacement:

$$CaCO_3 + H_2O \leftrightarrow Ca^{2+} + HCO_3^- + OH^- \tag{7a}$$

$$\text{Mineral–O–H} + OH^- \leftrightarrow \text{Mineral–O}^- + H_2O \tag{7b}$$

The total amount of proton buffering for an increase in pH from 6.83 to 7.15 was calculated from the measured alkalinity to be 0.07 meq per 100 g (as compared with CEC = 0.51 meq per 100 g at pH = 6.83). Calcite saturation indices, calculated with WATEQP (Appelo, 1988) show undersaturation in the tailing part of the elution curve.

The exchangeable quantity of an individual cation is calculated from the total eluted amount minus the amount in native groundwater (Table 3). The amount of Ca is also corrected for calcite dissolution by subtracting the measured alkalinity increase. Summation of all cations gives the CEC at native pH (6.83). The exchange constants used in the model are derived from the experimental results as shown earlier (cf. eqn. (4)). Calcite dissolution in combination with proton buffering is manifest in this sample and the following text emphasises this aspect of the modelling exercise.

Measured and modelled Ca concentrations are shown in Fig. 5. Modelling of the Ca elution as an exchange process gives the lowermost curve (curve A) in Fig. 5. The curve adequately follows the experimental Ca peak, but gives too low concentrations in the tail. Inclusion of calcite equilibrium in the model hardly improves the results (curve B), since only limited amounts of calcite can dissolve in the CO_2-free $SrCl_2$ solution. Moreover, the pH of the modelled eluate increases to 9.6, which is far higher than the observed pH of 7.1. Clearly, proton buffering has to be included as an additional reaction. It was assumed that proton buffering by the sediment could be modelled as a cation exchange reaction:

$$H^+ + X^- \leftrightarrow HX; \quad K = \frac{[HX]}{[H^+][X^-]} \tag{8}$$

The model value of the association constant was calculated from the pH of native groundwater (gives $[H^+]$), and the observed amount of proton buffering (gives [HX]). Inclusion of this reaction together with calcite equilibrium gives curve C in Fig. 5. The amounts of Ca which are eluted from the column are now identical in experiment and model, since the assumptions underlying the model calculation are wholly obtained from experiment. However, the calculated initial Ca peak is too high and Ca concentrations in the tail are too low; this suggests that calcite dissolution is slower in practice and does not reach equilibrium (undersaturation was calculated with respect to calcite in the eluate). Dissolution kinetics were then introduced to the model as a last reasonable step to try and fit the experimental data. The geochemical model calculates Saturation Ratios (*SR*), which are defined as:

$$SR = IAP/K$$

where *IAP* = Ion Activity Product $[Ca^{2+}]$ $[CO_3^{2-}]$, and *K* = equilibrium constant for calcite dissolution (= *IAP* when solution is in equilibrium with calcite).

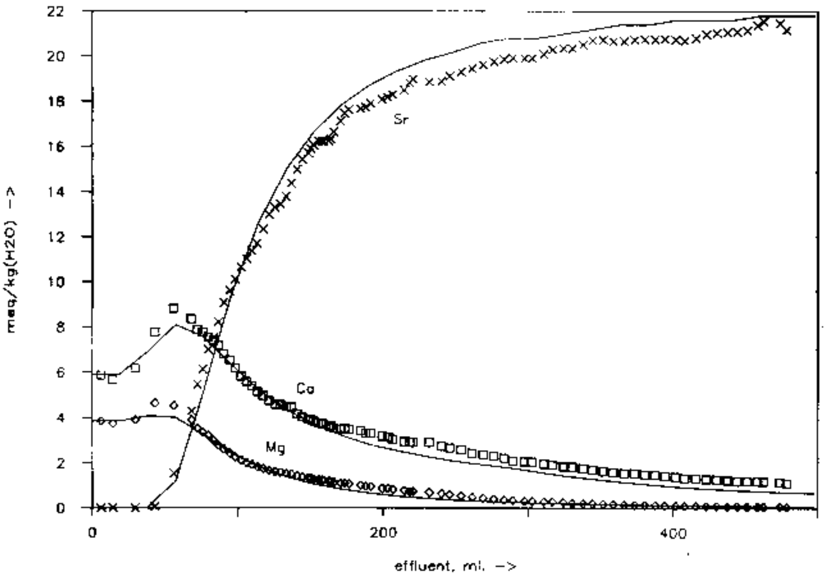

Fig. 6. Experimental points and modelled curves for Ca and Mg elution by $SrCl_2$, with proton buffering and calcite dissolution.

The *SR* can be used in rate equations describing calcite dissolution which are of the form (Berner and Morse, 1974; Massard and Desplan, 1980; Sjöberg and Rickard, 1984):

$$\frac{d(Ca)}{dt} = kA\ (1 - SR) \qquad (9)$$

where $d(Ca)/dt$ = rate of calcite dissolution or precipitation, and kA = rate of the reaction, which incorporates a rate constant k, and a surface area A.

With a trial and error value for the term kA of 5 E-8 mol $l^{-1} s^{-1}$, the fourth modelled line D in Fig. 5 results. This gives a reasonable description of the measured data. Curves for Mg and Sr are given together with the data for Ca in Fig. 6.

It is appropriate to recall here that the use of more variables makes model applicability more haphazard. Even though the step-by-step modelling sequence shown here has a logical, and intuitively reasonable background, the assumed values for the constants are derived by experiment and are therefore not of universal value. It appears that the kinetics of mineral dissolution and precipitation might indeed be the most formidable task to resolve before general geochemical models can be applied to environmental problems.

Fresh/salt water displacements through Alphen sediment

The last experiment considers multicomponent exchange, which occurs with fresh and salt water displacements. It can be considered the ultimate experiment, since our original aim was to obtain experimental data on cation

TABLE 4

Composition of fresh and salt water and exchange complex of Alphen sediment

	Solution (m mol. l^{-1})		Exchange complex[1,2] (meq per 100 g)	
	Salt	Fresh	Salt	Fresh
pH	7.40	6.85		
Na	180.9	5.6	0.40	0.05
K	3.9	0.7	0.19	0.13
Mg	20.6	1.9	0.57	0.47
Ca	4.2	2.0	0.04	0.50
NH_4	0.0	0.8–0.5	0.00	0.04
			1.20	1.19
Cl	212.0	4.5		
Alk.	1.1	10.0		
SO_4	11.1	0.1		

[1] Exchange Complex composition after equilibration.

[2] CEC is calculated after duplication of the experiments and flushing with $BaCl_2/NaClO_4$ solutions.

exchange which accompanies salt water intrusion in aquifers. Calcite dissolution as a complicating factor was circumvented by selecting a calcite-free sediment for these experiments.

The sediment used in the experiments consisted of fine-grained unconsolidated sand (Table 1). X-ray diffraction analysis of a gel on a 0.45 μm membrane filter, collected during one of the experiments, indicated the presence of the clay minerals illite, smectite and kaolinite. Porosity, calculated from conservative breakthrough of chloride and determined by gravimetric analysis, amounted to 36.8%.

Fresh and salt water displacements were carried out by flushing the sediment with once-diluted seawater and fresh groundwater sampled near the coring location. Repeating the experiments showed a good reproducibility. Cation composition of the exchange complex in equilibrium with both fresh and seawater (as given in Table 4) was obtained from additional experiments with synthetic solutions.

Seawater intrusion

Results of a 'seawater intrusion' experiment are shown in Fig. 7. The sediment sample had a relatively low dispersivity so that the initial water composition could be sampled over a longer interval than in earlier described experiments. Calcium and NH_4 show up in peaks when exchangeable ions are replaced by Na, Mg and K from salt water. It is interesting that Mg is also eluted in a peak together with Ca, even though the exchange complex shows a final net increase of Mg (Table 4).

The initial increase of Mg concentration is caused by the rise in salinity (salinity front, or salinity plateau). The ionic ratios in salt water are adjusted to equilibrium with the fresh water exchange complex, i.e. the ratio of the homovalent ions Mg/Ca becomes 1 which is the ratio in fresh water. When Ca is exhausted, Mg is taken up again from sea water as shown by the drop in Mg concentrations.

The lines in Fig. 7 show modelled concentrations. Values for the exchange constants were calculated in the first instance from water and exchanger composition as noted above (eqn. (4)). However, the Ca/Mg selectivity is higher for fresh water than for salt water (cf. Table 5), and indeed, the Ca and Mg peaks could not be modelled with exchange constants calculated for fresh water equilibrium. It was expected that the Gapon exchange equation influences the elution of these ions as noted for the Ketelmeer sediment. It was observed, moreover, that the cation exchange capacity of Alphen sediment could be ~15% higher in salt water than in fresh water, caused by proton buffering and salinity effects; Beekman and Appelo (1988) offer a more detailed discussion of some enigmatic aspects of this sediment.

The idea hence emerges that exchange constants and cation exchange capacity, which are assumed constant within a single simulation run, can be expected to vary in reality. It is difficult to quantify the factors which govern the variation of these parameters, so that incorporation of variability in the

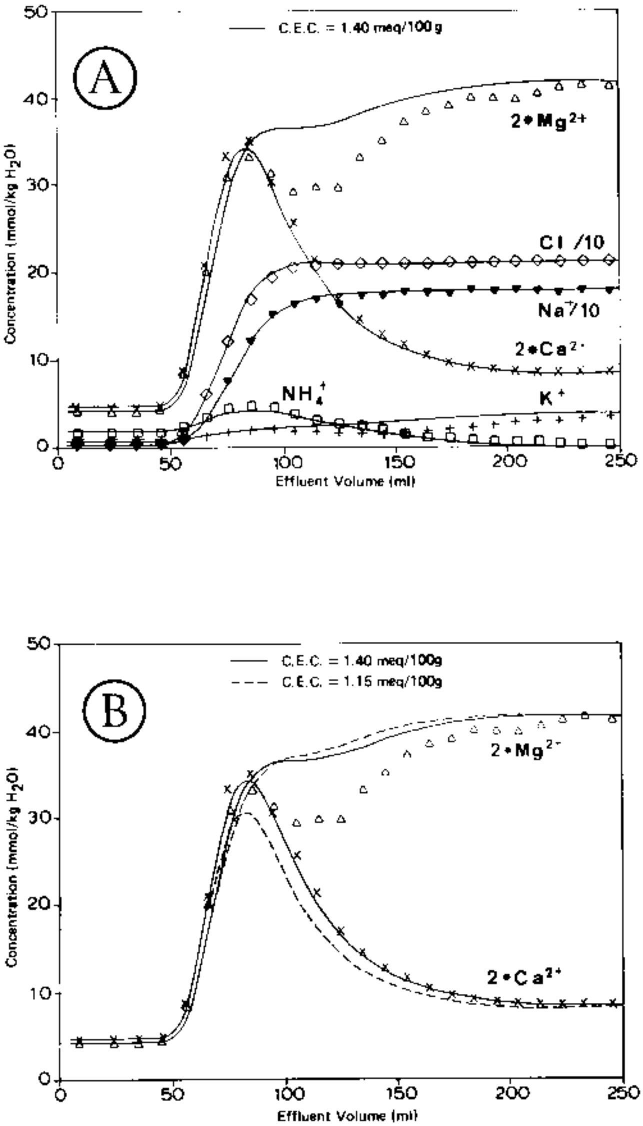

Fig. 7. Salt water in fresh sediment.

model was considered a futile operation at present. Rather, test runs have been performed with different, but fixed values for the parameters. The results were specially screened for effects on the Ca and Mg peaks, since this is the most conspicuous feature of salt water displacement. It was found that a Ca/Na selectivity of 0.4 (as observed in salt water) or 1.47 (in fresh water, cf. Table 5) yielded a higher Mg than Ca peak. The Ca/Na selectivity had to be increased to 3.16 for results which approach the observations (value used for the results presented in Fig. 7). A low selectivity of Mg with respect to Na gives a

TABLE 5

Observed and (for Alphen sediment) optimal exchange coefficients for three sediments

Exchange equation: $\frac{1}{z}M^{z+} + Na\text{–}X \leftrightarrow M_{(1/z)}\text{–}X + Na^{+}$

Ion "M"	Ketelmeer	Delft	Alphen		
			Fresh	Salt	Optimal
Na	1	1	1	1	1
K	8.4	28	20.7	22.1	–
NH_4	4.3	19	5.6	–	–
Mg	1.2	2.8	1.42	2.5	1.75
Ca	3.3	7.6	1.47	0.4	3.16

continuous increase of Mg after the peak to saltwater concentrations. The observed marked adsorption of Mg could not be modelled however; it is attributed to changes in Mg/Ca selectivity which perhaps follows the Sposito and Levesque (1985) observation that this selectivity may increase when Na makes up a larger proportion of exchangeable cations. Similar variation in exchange selectivities which depend on salinity have been noted by Van der Molen (1958) and Neal and Cooper (1983). The latter authors have tried to explain the variations with extensive calculations using electrostatic double layer models which included activity coefficient corrections. However, the apparent lack of success of these model calculations indicates that more theoretical and experimental research is needed, before an incorporation in general transport models is attempted.

Adjustment of the relative exchange constants disturbs the mass balance which exists when exchange constants are derived only by experiment. When the curve fitting procedure has given a satisfactory reproduction of trends in concentration, CEC can be varied to fit model and experiment. Results for Ca and Mg with CEC values of 1.15 and 1.40 meq per 100 g are shown in Fig. 7B. It should be noted that modelling of the monovalent cations did not impose particular problems, except that the adsorption of K seems to be relatively retarded.

Fresh water intrusion

Results of a freshwater displacement are shown in Fig. 8. All cations decrease in concentration initially. This is primarily a result of dilution of the solution by fresh water (cf. Valocchi et al., 1981), opposite to the salinity front observed with saltwater intrusion. It is remarkable that the Mg concentration becomes even lower than in fresh water at this stage. Mg is adsorbed since a low concentration suffices to maintain exchange equilibrium with respect to Na in the saltwater exchange complex. When Na has been eluted, K and Mg are

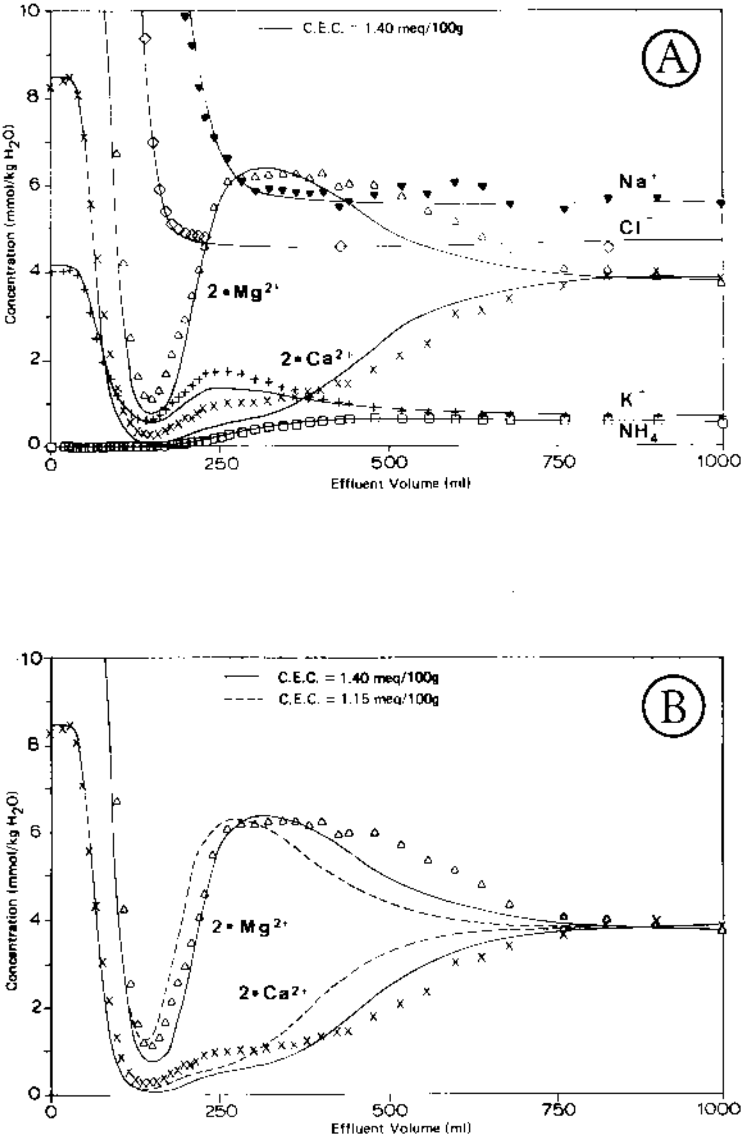

Fig. 8. Fresh water in salt sediment.

displaced by Ca from fresh water. This is the expected chromatographic sequence.

Figure 8 also shows model curves. The same exchange constants have been used as noted before when discussing Fig. 7, and also the same two exchange capacities. Use of other exchange constants had an effect on concentrations in the elution curve where Na is dominant, but less so in later parts where Mg has become the dominant cation. The reason seems to be that changes in selectivity mainly bear on cations which are present in lower concentrations. Magnesium must be eluted and is the major cation which balances the electro-neutrality of the eluate. A two-fold change in selectivity can easily be matched by a two-fold change in the (low) Ca concentration; this only slightly alters the Mg concentration, as needed to maintain electro-neutrality. With this concept in mind, it is no surprise that a decrease of Ca/Na selectivity from 3.16 (the 'optimal' value in salt water displacement) to 1.47 (the observed value in fresh water) was found to give a higher Ca concentration in the Mg-dominated part of the eluate, and a better match for observed Ca concentrations. Modelling of the monovalent cations presented no special problems.

It should be noted, however, that another problem arises when modelling the fresh water displacement. Ca is clearly the favourable cation for the exchange complex, so that a chromatographic sequence develops in which the cations are displaced according to exchange strength (displacement analysis in chromatography). The ions are separated by self-sharpening fronts while travelling along the column. Modelling these sharpening fronts showed numerical dispersion in the mixing cell model, similar to the effect noted by Van Ommen (1985). This numerical dispersion is less prominent in the other experiments, where fronts are broadening (in saltwater intrusion), or where column dispersion is relatively high. The numerical dispersion can be counteracted by increasing the number of cells (Vermeulen et al., 1984), though it will not disappear without adaptation of the transport algorithm used at present. This is something which needs further attention, since a multicomponent transport model in which retardations are influenced by different reactions has different cell Peclet numbers for each individual component.

CONCLUSIONS

The purpose of this contribution was to present a validation scheme for an earlier described multicomponent transport model, based on column experiments with aquifer sediments. The most important and time-consuming work was connected with design and proper operation of the experimental procedures. Most aquifers studied in The Netherlands are anaerobic, and sediment sampling requires strict conservation and prevention of oxidation by atmospheric oxygen. A technique where cores are immediately frozen offers the best conservation strategy. The cored samples are introduced into columns which have been tested for gas-tightness up to 10 atm, and careful introduction can maintain the anaerobic status of the sediment cores. This was verified by comparison of Fe^{2+} and NH_4 concentrations, as well as alkalinity and pH, in displaced pore solutions and samples from field-wells.

Two examples are given in which pore solutions and exchangeable cations are displaced with $SrCl_2$ solution. Another sediment has been subjected to alternative displacements with fresh and salt water. In all instances it was possible to model the experimental results with satisfactory precision. However, this required the following adaptations to the original model.

(1) The Gapon exchange equation was found inappropriate for a multicomponent solution when large elution volumes are required for removal of exchangeable divalent cations; the Gaines and Thomas equation offered a better description.

(2) Dissolution of calcite in a sediment was triggered by proton buffering; substantial increase in exchange capacity is associated with proton buffering even over a small pH increase from 6.8 to 7.1. A sediment with 1.5% calcite could not saturate the displacing solution with respect to calcite in ~8 h residence time; this necessitated a kinetic extension for mineral equilibrium in the geochemical model.

(3) With fresh and salt water displacements it was observed that exchange coefficients were not identical in fresh and salt water, and that the exchange capacity could vary; modelling with due consideration of such variations has not been attempted. Recently, Mansell et al. (1988) have assumed a binary variability of exchange of Na, Mg and Ca in modelling the column experiments of Lai et al. (1978).

(4) With self-sharpening fronts a numerical dispersion becomes manifest when multicomponent transport is modelled.

This last point concerning numerical dispersion is perhaps the easiest to solve; the other points are directly related to nature's variability. The elution curves could be satisfactorily modelled when experimental data were used explicitly, i.e. the 'local data' gathered experimentally for a specific sediment. It is interesting to note the large range in selectivities which were observed for the three sediments for the various cations (Table 5). This range prohibits the immediate application of a multicomponent transport model to any field situation; it requires a better insight into factors which govern the differences in selectivities among different sediments. For calcite dissolution kinetics and proton buffering by sediments, a similar improvement is required.

At the same time, it is clear that the processes which affect major cation transport in aquifers can now be calculated by computer simulation. An amazingly good fit can be obtained between experiment and model when 'local data' are available. It is undoubtedly the accuracy of our own analytical data, obtained in the laboratory, which led to further detailing of the earlier model. Perhaps the global possibilities are sufficient for field simulations. The next step, therefore, must be to look for field situations where data have been gathered which are adequate for what the transport model can offer. We believe that the fresh/saltwater distribution pattern in Dutch aquifers can offer further valuable information on the general applicability of multicomponent transport models. A further contribution is currently being prepared on this field applicability.

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