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GEOCHEMICAL CALCULATIONS AND OBSERVATIONS ON SALT WATER INTRUSIONS, I. A COMBINED GEOCHEMICAL/MIXING CELL MODEL

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ABSTRACT

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A combined geochemical/mixing cell flow model has been developed. The geochemical model is based on the computer program EQ3/6 (Wolery, 1982), has been modified to include cation exchange reactions and is incorporated in a one-dimensional mixing cell model for stationary one-dimensional transport. Dispersion or diffusion is calculated by mixing the cell contents with neighbouring cells. Relationships between mixing factors and dispersivity and diffusion coefficients are derived.

The model is used to simulate concentration changes during salt water intrusions. Fundamental differences are shown to exist between diffusion of salt water from a stagnant water body and dispersive intrusions during marine transgressions or flooding events. With dispersive flow, characteristic water compositions develop in space and time as a result of cation exchange. With diffusion, these steep concentration gradients are smoothed out and "mixed" compositions occur.

The concept that characteristic concentrations occur during dispersive flow is used to obtain paleohydrological information in a Dutch polder. The depth of the fresh/salt water interface before polder development is deduced from a simulation of observed exchange reactions in the polder groundwater.

INTRODUCTION

The interpretation of the composition of salt groundwater in terms of origin, flowlines and chemical reactions along flowlines is difficult. However, cation exchange reactions alter the groundwater composition and can indicate whether refreshening or salt water intrusion takes place (Appelo and Geirnaert, 1983). In addition to cation exchange other reactions commonly occur; viz., $CO_2/CaCO_3$ reactions, oxidation of organic material or methane production, reactions with sulfurous compounds, iron oxidation/reduction, and others (Matthess, 1982; Stuyfzand, 1985). These reactions can be accurately simulated with geochemical computer models and when combined with a flow model, allow a complete description of water qualities in space and time. Garven and Freeze (1984) have shown the possibilities of such a model for gaining insight into ore-forming processes by groundwater flow.

An alternative combined model is presented here, based on the EQ3/6 geochemical model (Wolery, 1982) and a mixing cell flow model. The model is used to calculate changes in composition which occur when salt water intrudes fresh water aquifers and considers both dispersive flow and diffusion. It is then applied to calculate fluxes in the polder Groot Mijdrecht (The Netherlands) from data on water composition and exchangeable cations in the sediment.

GEOCHEMICAL MODELS

A number of computer models have been developed which allow the calculation of water compositions when minerals dissolve, water types mix, temperature changes, or redox reactions occur. The programs can be envisaged as models of batch experiments: geochemical reactions are calculated for an isolated part of the aquifer, assuming stagnant water. Basic to the calculations is an aqueous model in which solute ions associate in complexes. Equilibrium constants are used to calculate the distribution of complexes and species in water, and activity coefficients are calculated with a Debije–Hueckel type equation. The resulting set of linear (mass balances) and logarithmic equations (chemical equilibria) are solved using the Newton–Raphson technique (Smith and Missen, 1982). Well-known are REDEQL2 (McDuff and Morel, 1973, see also Stumm and Morgan, 1980), GEOCHEM (Sposito and Mattigod, 1979), PHREEQE (Parkhurst et al., 1980), EQ3/6 (Wolery, 1982), MINTEQ (Felmy et al., 1983, in Kincaid et al., 1984) and CHARON (De Rooy, pers. commun., 1985). A number of these models have been recently evaluated by Kincaid et al. (1984).

Cation exchange

Variable water compositions resulting from flow generally require the inclusion of adsorption and ion exchange reactions (Van Beek and Raj Pal, 1978; Valocchi et al., 1981; Schulz and Reardon, 1983). Parkhurst et al. (1980) suggest an exchanger with fixed composition. In their model this becomes a buffer which fixes the ratios of the "exchangeable" ions in solution. In GEOCHEM (Sposito and Mattigod, 1979) ion exchange can be calculated as a kind of precipitation–dissolution reaction, which is not related to measured compositions of ion exchange complexes.

It is possible to include cation exchange as an ion association reaction in the geochemical model. This possibility becomes evident when cation exchange is written as two "half reactions". The exchange of Na for Ca:

$$Na^+ + Ca_{0.5}X \rightleftharpoons NaX + 1/2\,Ca^{2+} \tag{1}$$

can be considered the sum of:

$$Ca_{0.5}X \rightleftharpoons 1/2\,Ca^{2+} + X^- \tag{2}$$

and:

$$Na^+ + X^- \rightleftharpoons NaX \tag{3}$$

The term "half reaction" is used by analogy with oxidation–reduction reactions, with the exchanger X^- being similar to a "free electron"; it disappears from the exchange reaction when two "half reactions" are properly balanced.

Concentrations are replaced by activities when the law of mass action is applied to eqns. (2) and (3). The calculation of activity in solution is straightforward in the geochemical models. However, the calculation of activity of the adsorbed cations is a subject of continuing debate (Van der Molen, 1958a; Bolt, 1967; Sposito, 1977; Harmsen, 1980). Equation (1) agrees with the Gapon convention, since it uses the equivalent fraction of the exchanger X^- as basis for the activity of the adsorbed ions. If, on the other hand, the activities of the adsorbed ions are assumed proportional to their own equivalent fractions, eqn. (1) should be written as:

$$2\,Na^+ + CaX_2 \rightleftharpoons 2\,NaX + Ca^{2+} \tag{1a}$$

with half reactions:

$$CaX_2 \rightleftharpoons Ca^{2+} + 2\,X^- \tag{2a}$$

and:

$$2\,Na^+ + 2\,X^- \rightleftharpoons 2\,NaX \tag{3a}$$

Equation (1a) agrees with the Kerr or Vanselow convention.

Either the Gapon or the Kerr equation can be used in the ion association model, differences becoming manifest only at $Na/\sqrt{Ca}$ activity ratios greater than 0.3 in solution; use of the Kerr equation gives higher proportions of adsorbed Na ions. Sposito (1977) argues that the Gapon equation has no direct molecular interpretation since an atom of Ca cannot be split to occupy a single exchange site. However, it should be realised that $Ca_{0.5}X$ expresses a chance to find a calcium ion at an exchange site. The Gapon equation can thus indeed be obtained from the theory of regular mixtures (Harmsen, 1980).

From an empirical point of view, one might prefer the Gapon equation (Bolt, 1967; Bolt and Bruggenwert, 1978). It forms the basis for calculating *SAR* (Ayers and Westcot, 1985) and describes the relation between the Sodium Adsorption Ratio (*SAR*, the ratio of Na over Ca + Mg in water) and the exchangeable sodium percentage (*ESP*, the ratio of adsorbed ions in the soil) quite well (Shainberg and Oster, 1978). Van der Molen (1958a), on the other hand, found that the Gapon equation did not fit the log–log plots of Na/Ca equilibria on two Dutch soils, though the Gapon equation actually gives a slightly better fit than the Kerr equation when all Van der Molen's data are combined in a linear plot.

From the empirical evidence, the present authors thus resolved to use the Gapon equation, i.e. equations of type (2) and (3). A concentration of "free" X^- is written in eqns. (2) and (3), which does not exist in reality. This concentration will become very small if the association constant is very large, and the concentration of cations is larger than that of X^-. Hence for reaction (3):

$$\frac{[NaX]}{[Na^+][X^-]} = K$$

TABLE 1

Association constants used to model cation exchange

Association reaction	Log (association constant)
$Na^+ + X^- \rightleftharpoons NaX$	14
$K^+ + X^- \rightleftharpoons KX$	14.7
$0.5\ Ca^{2+} + X^- \rightleftharpoons Ca_{0.5}X$	14.3
$0.5\ Mg^{2+} + X^- \rightleftharpoons Mg_{0.5}X$	14.2

where K is the association constant. For example, when K is 10^{14} (mol/kg solution)$^{-1}$, "free" X will be less than 10^{-12} in most cases. The competition of cations for the exchange complex can be expressed in the relative value of the association constant of the cations with X^-. Relative values can be obtained from published selectivity coefficients: for example, the selectivity coefficient for reaction (1) is 0.5; when the association constant for reaction (3) is 10^{14}, the value for reaction (2) is $10^{14}/0.5 = 10^{14.3}$. Table 1 shows the association constants used in the presented model. The selectivity coefficients were selected from Bolt (1980), and multiplied by the chosen association constant for Na exchange of 10^{14}.

It should be noted here that it is difficult to obtain literature values for the selectivity coefficients. There are on the one hand experimental difficulties which lead to conflicting results, and on the other hand one can expect different selectivity coefficients for different types of exchanger (organic matter, different clay minerals, oxides and hydroxides). Moreover, there are interionic effects in a multi-ion solution which are not accounted when selectivity coefficients are used which were obtained from binary exchange experiments (Van der Molen, 1958a; Sposito and LeVesque, 1985).

Incorporation of reactions with very high association constants led to convergency problems in PHREEQE and GEOCHEM, the problem being to find a good starting value for the Newton–Raphson iteration. The program EQ3/6 solved the set of equations without problems, and was therefore used. (A newer version of PHREEQE, released in 1985, could handle the problems equally well.)

THE MIXING CELL MODEL

A good description of natural water quality requires a complete geochemical model with minerals dissolving, gas reactions, etc. The number of interacting elements may increase to 20 or more, so that tracking of individual solutes is no longer feasible. A mixing cell approach is thus indicated.

Mixing cells have been used by several authors, e.g. Dance and Reardon (1983), Schulz and Reardon (1983), and Van Ommen (1985). There are two types in use. The first describes flow that is independent of the cells, and which mixes within each cell. This model shows numerical dispersion (Van Ommen, 1985 gives a recent account of this type of mixing cell model). The other type simulates flow by transporting single-cell volumes in batches. Dispersion is

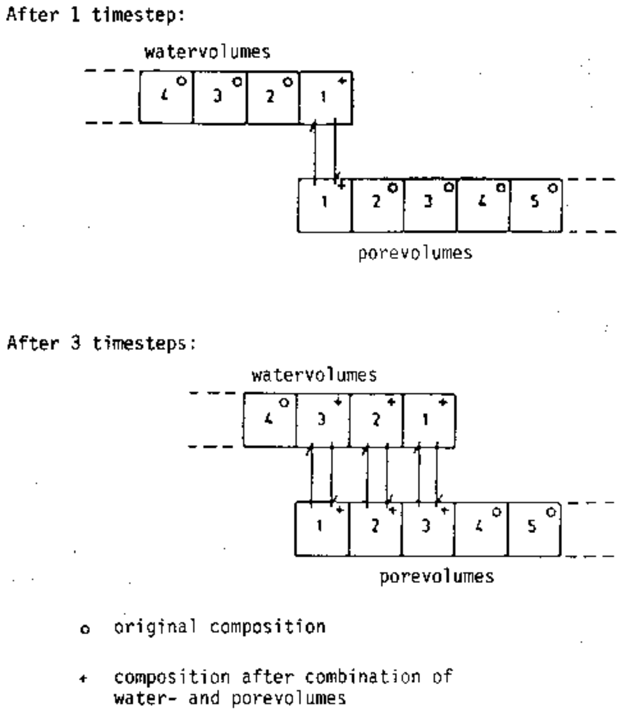

Fig. 1. Operation of the mixing cell model.

then simulated by partial exchange with neighbouring cells. The latter approach is used here, and it will be shown how the mixing factors, regulating the exchange, are related to dispersivity and diffusion coefficients.

The model

The basic concept of the model is shown in Fig. 1. With each time step, water volumes are batchwise transported to the next cell and equilibrated with the aquifer matrix. The aquifer matrix is described as a pore volume: the pore volumes have specific chemical properties, like a cation exchange capacity, minerals with which water equilibrates, gas pressures, etc. These are included in the geochemical model. Dispersion can be simulated by mixing cell contents at each time step (Dance and Reardon, 1983) and a mixing factor is used to mix part of each cell with the two neighbouring cells. Table 2 gives a summary of how concentrations are calculated. The relation between mixing factor f and dispersivity α or diffusion coefficient D_d is formally derived as follows.

The equation describing concentration as a function of space and time is:

$$\partial c/\partial t = D\partial^2 c/\partial x^2 - u\partial c/\partial x \qquad (4)$$

TABLE 2

Formulas used in the mixing cell model

Mixing cell formulae
Dispersive flow
$c_{i+1} = f*c_i + (1 - f)*0.5*(c_{i+1} + c_{i-1})$
$f = 1 - \dfrac{2\alpha}{\Delta x}$
Diffusion
$c_i = f*c_i + (1 - f)*0.5*(c_{i+1} + c_{i-1})$
$f = 1 - 2D_d\dfrac{\Delta t}{(\Delta x)^2}$

α = dispersivity (m); D_d = diffusion coeff. ($m^2 s^{-1}$); f = mixing factor; Δx = cell size (m); and c_i = concentration in cell i.

where: c = concentration ($mol\,m^{-3}$); D = dispersion coefficient ($m^2 s^{-1}$); u = water flow velocity ($m\,s^{-1}$); $D = \alpha u + D_d$, where α = dispersivity (m); D_d = diffusion coefficient ($m^2 s^{-1}$).

For the boundary conditions of a sudden input of 1 at $x = 0$, $t = 0$:

$$c(x, t) \;=\; 0 \text{ for } t < 0, \text{ all } x;$$

and:

$$c(0, 0) \;=\; \delta(0)$$

where $\delta(t)$ is the Dirac delta function. The analytical solution is, for $t > 0$:

$$c(x, t) \;=\; \frac{1}{\sqrt{4\pi Dt}} \exp^{-(x-ut)^2/4Dt} \tag{5}$$

This is a normal (Gaussian) distribution with variance $\sigma^2 = 2Dt$. The variance increases linearly with t:

$$\Delta\sigma^2 \;=\; 2D\Delta t \tag{6}$$

When diffusion can be neglected, $D = \alpha u$, which gives in eqn. (6):

$$\Delta\sigma^2 \;=\; 2\alpha\Delta x \tag{6a}$$

The variance for a mixing cell model can be calculated from:

$$\sigma^2 \;=\; \frac{\Sigma c_i x_i^2}{\Sigma c_i} - \left(\frac{\Sigma c_i x_i}{\Sigma c_i}\right)^2 \tag{7}$$

The spread of a slug in a mixing cell can be calculated from the scheme given in Table 3. If initially $\sigma_{i-1}^2 = 0$ and $c_{i-1} = 0$, eqn. (7) yields:

TABLE 3

The calculation of variance in a mixing cell model

Cell:	$i-1$	i	$i+1$	Sum
x_i	$(i-1)\Delta x$	$i\Delta x$	$(i+1)\Delta x$	$3i\Delta x$
c_i	$(1-f)/2$	f	$(1-f)/2$	1
$c_i x_i$	$(i-1)(1-f)\Delta x/2$	$i\Delta x f$	$(i+1)(1-f)\Delta x/2$	$i\Delta x$
$c_i x_i^2$	$(i-1)^2\Delta x^2(1-f)/2$	$i^2\Delta x^2 f$	$(i+1)^2\Delta x^2(1-f)/2$	$\Delta x^2(i^2+1-f)$

$$\Delta\sigma^2 = \Delta x^2 i^2 + \Delta x^2 - f\Delta x^2 - i^2\Delta x^2$$

$$\Delta\sigma^2 = \Delta x^2(1-f) \tag{8}$$

Comparison of the analytical and mixing cell solution, eqns. (6a) and (8), shows that:

$$f = 1 - 2\alpha/\Delta x \tag{9}$$

Similarly, for diffusion without translation, $u = 0$ and $D = D_d$. Combination of eqns. (6) and (8) gives:

$$f = 1 - 2D_d\Delta t/\Delta x^2 \tag{10}$$

Dimensions of the mixing cells

The dimensions of the cells shown in Fig. 1 are not specified. A cell length of 1 m and water flow of 1 m yr^{-1} gives the same results as a cell length of 10 m which is flushed every year. However, it is not difficult to relate dimensions to the specific situation to be modelled.

The introduction of a mixing factor sets the relation between cell size Δx and flush time (or time step) Δt according to the formulae given in Table 2. These relations leave only one degree of freedom in the choice of Δx, Δt, or f when throughflow u and dispersion coefficient D are given quantities, as for example obtained from a field situation. However, with nonconservative ions there is still a scale dependency. This can be easily deduced from an example with cation exchange: ten cells need more flushes for equilibrating the exchange complex of all ten cells than a single cell (with an appropriately adapted mixing factor so that dispersivity remains the same). Scale problems are even more difficult when water equilibrates with minerals. The time step and cell length should then be related to the scale at which differences in water quality become of interest.

The problem of defining the dimensions of mixing cells is similar in the concept of theoretical (or effective) plates as used in ion chromatography (Helfferich, 1962). In this, the concept is used to describe binary exchange in a chromatographic column; each theoretical plate corresponds to a region in which equilibrium between solution and exchanger is complete. The column is

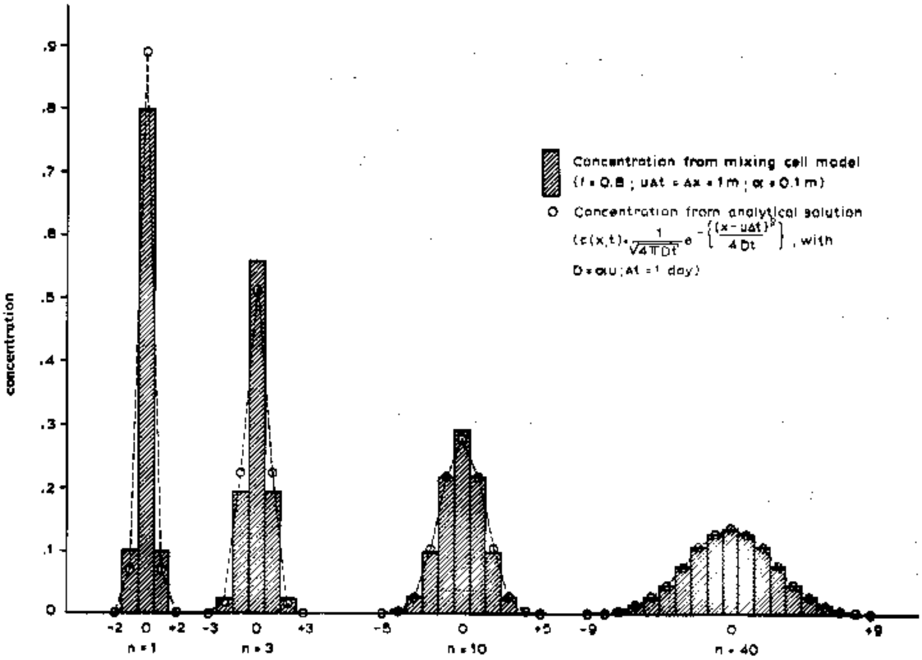

Fig. 2. Comparison of mixing cell model and analytical solution for dispersion of a slug.

considered to be made up of a series of plates, but the plate height (or number of theoretical plates in the column) has to be determined experimentally in an elution experiment.

Comparison with analytical solutions

Figure 2 shows a comparison between the analytical solution of slug transport and the concentrations calculated with the mixing cell model. After 40 time steps the differences between the analytical and numerical results are negligible. After three time steps the differences are about 10% and after ten time steps the differences are less than 5%, sufficiently accurate for almost all applications.

Figure 3 shows the comparison for diffusion profiles after a step function input at $x = 0, t = 0$. The analytical solution is the error function complement (Carslaw and Jaeger, 1959) and the figure clearly shows the similarity between this and the mixing cell model calculation.

Dance and Reardon (1983) fitted a mixing cell model to field data using $f = 0.85$ and $\Delta x = 0.25$ m. Schulz and Reardon (1983) modelled the same field data with $\alpha_L = 0.026$ m and $\alpha_T = 0.011$ m, which means that $\alpha = \sqrt{\alpha_L \alpha_T} = 0.017$ m. From the mixing cell parameters it is calculated, using eqn. (9), that:

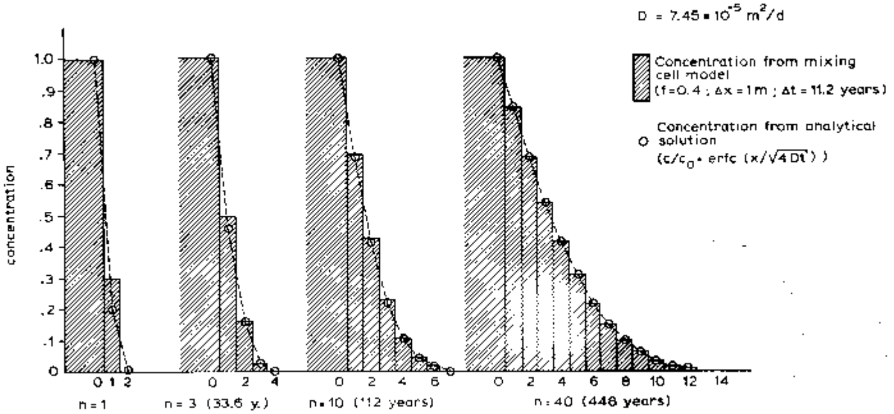

Fig. 3. Comparison of mixing cell model and analytical solution for diffusion from a reservoir with constant concentration.

$$\alpha = \frac{(1 - f)\Delta x}{2} = 0.019\,\mathrm{m}$$

The agreement is excellent.

SIMULATION OF SEA WATER INTRUSION

Two different views have been expressed to explain the occurrence of salt water in continental Pleistocene aquifers in the western part of The Netherlands. One is based on the observation of Cl diffusion profiles in the Zuiderzee area (Volker, 1961). It relates the salt water to diffusion from sea water during marine transgressions in Pleistocene and Holocene times, or from diffusion of salt from Tertiary marine layers (Volker, 1961). However, diffusion is too slow to explain salt water at intermediate depths in fluviatile Pleistocene aquifers. Meinardi (1974) therefore suggested that the salt could have diffused from below into flowlines which follow the regional pattern. This view contrasts with the idea that during marine transgressions salt water has intruded the aquifers as density flows (De Vries, 1981; Engelen, 1981). This may occur where surface water is in direct contact with the aquifer (Van der Molen, 1958b).

In the former case diffusion is the main mechanism and in the latter it is active flow with dispersion. In both cases fresh water aquifers will become brackish or salty, and hence cation exchange should be manifest in the groundwater composition. It is therefore of interest to investigate the effect of the flow mechanism on cation compositions of this water.

Modelling results

Figure 4 shows how salt water composition changes when it intrudes a fresh water aquifer. Initial fresh- and salt-water compositions are given in Table 4.

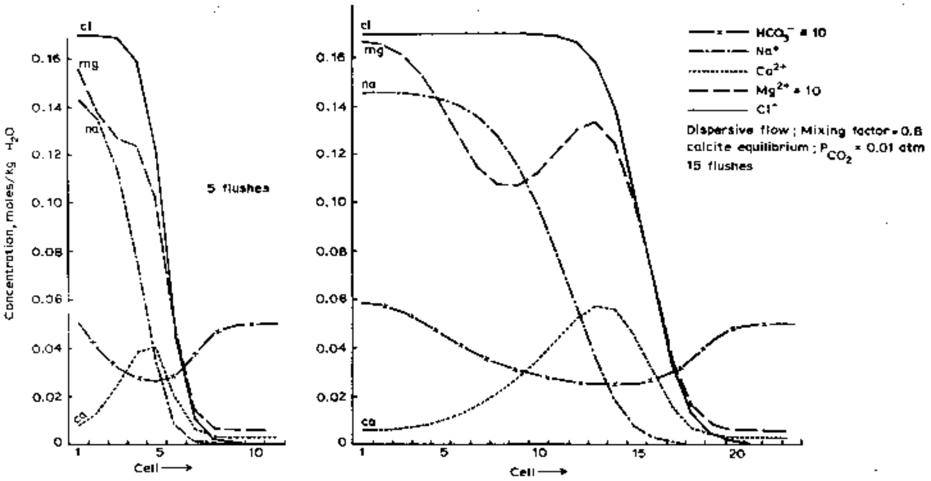

Fig. 4. Simulation of salt water intrusion: dispersive flow.

Concentration of the salt water is three times diluted sea water, which approximates former Zuiderzee water. The water is equilibrated with calcite at a CO_2 pressure of 0.01 atm and the cation exchange capacity is set to 200 meq l^{-1}, which is equal to about 2.5 meq 100 g $^{-1}$ sediment. Figure 4 shows the results after 5 and 15 flushes in successive cells.

With respect to the conservative Cl-ion Na^+ is retarded, being exchanged for Ca^{2+} from the fresh water sediment. The resulting increase of Ca^{2+} is conspicuous in Fig. 4, just behind the Cl front. Part of the exchanged Ca^{2+} will precipitate as calcite, as can be seen from the decrease of HCO_3 . Still, the increase of Ca^{2+} is so high that Mg^{2+} is also driven from the exchange complex. This is in contrast to the commonly held opinion that Mg^{2+} is depleted from seawater in exchange for Ca^{2+} when seawater intrudes a fresh water aquifer. Actually, it may be driven out by the initially high Ca concentrations. An

TABLE 4

Compositions of fresh and salt water used as model input (mmol l^{-1})

	Fresh water	Salt water
Na^+	0.1	145
K^+	0.1	3.23
Ca^{2+}	Calcite	Calcite
Mg^{2+}	0.5	16.3
H^+	el. neutr.	el. neutr.
HCO_3^-	P_{CO_2} = 0.01	= 0.01 atm
Cl^-	0.1	169
SO_4^{2-}	0.4	0.90

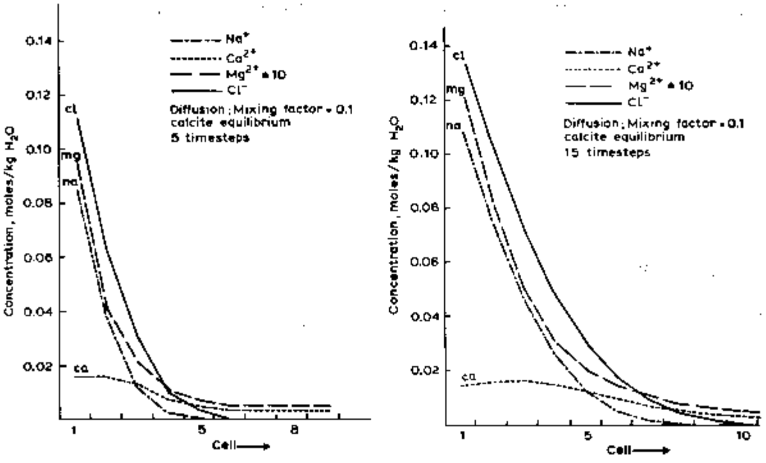

Fig. 5. Simulation of salt water intrusion by diffusion.

interesting pattern of concentrations will develop, which leads to characteristic combinations and ratios of Na/Cl, Ca/Cl and Mg/Cl in both time and space.

Figure 5 shows the influence of diffusion of the same salt water into the fresh water aquifer. The process is much slower; with the parameters given in Fig. 5 and a cell size of 1 m, the time step is equal to 17.6 yr. The fifteen time steps shown in Fig. 5 are thus equal to 264 yr.

Figure 5 indicates that with salt water diffusion there is no concentration build-up of exchanged Ca^{2+} as expected with dispersive flow. Rather, a gradual mixing of salt and fresh water seems to take place, on which cation exchange has little influence. In hindsight, it seems indeed reasonable that diffusion

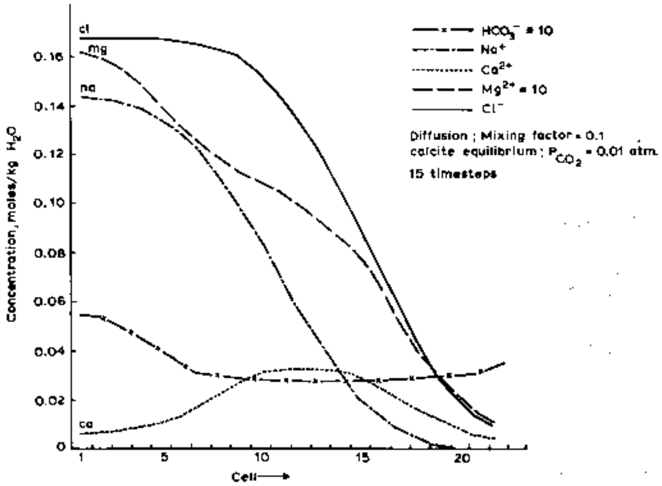

Fig. 6. Effect of diffusion on concentrations obtained after dispersive intrusion shown in Fig. 4.

smoothes out concentration gradients as fast as they develop. If in fact dispersive flow stops, diffusion tends to level out the concentration gradients. This is illustrated in Fig. 6 where diffusion has acted on the concentrations from the dispersive model (Fig. 4) during fifteen time steps.

The conclusion from these modelling exercises is that diffusion of salt water in a fresh water aquifer (or the reverse, refreshening) gives "mixed" concentrations. Furthermore, if groundwater flow either stops or is slow enough for diffusion to become important (i.e. less than 1 m yr^{-1}), "mixed" water types will develop. In a former publication (Appelo and Geirnaert, 1983) such "mixed" water types in which no signs of cation exchange are visible were attributed to repeated flushing by and equilibration with a saline surface water source (an estuary for example). It will be clear that diffusion in stagnant flow situations should also be considered as an explanation for "mixed" watertypes.

APPLICATION OF THE DISPERSIVE FLOW MODEL TO A FIELD SITUATION

In dispersive flow characteristic concentrations or concentration ratios may be found, and it is of interest to apply this concept to a field situation. The polder Groot Mijdrecht in The Netherlands (Fig. 7) was drained around 1870. Upward water seepage is 2 m yr^{-1} on the average over the polder area. In the eastern part this water comes from the Vinkeveense Plassen (fresh water lakes) to the east of the polder. Upconing of salt water occurs in the centre, this pattern being reflected in the electrical conductivity of ditch water shown in Fig. 8. In bore hole 176 (Fig. 7), water sampled at 23 and 80 m below surface has a lake water origin. This follows from $\delta^{18}O$ values of − 3‰ (Boekelman, 1983), similar to the lake water, and indicating surface water of which part has evaporated. Except for Ca and Mg the ion concentrations are also similar to lake water concentrations (Table 5). The ratio of Ca/Mg changes from 2 in lake water to 0.6 in groundwater from bore hole 176, but the sum of both ions (in mmol l^{-1}) remains the same. This indicates that cation exchange is still active in altering the composition of groundwater, and that salt water has been replaced by more dilute water.

The situation is modelled in the following way. At bore hole 176 the upward seepage is estimated to be 5 m yr^{-1} (Darcy velocity, or 20 m yr^{-1} pore velocity). During the hundred years of polder existence water now found at 23 and 80 m depth has thus covered a distance of at most 2000 m. From the mixing zone between fresh and salt water in the ditches (Fig. 8) it is estimated that the subsoil transversal dispersivity is about 1 m (after 2000 m flow). The longitudinal dispersivity is assumed to be 10 times higher, or 10 m. With this value and cell lengths of 100 m, the mixing factor becomes 0.8. However, the chosen cell length is a first estimate and its real dimensions should be obtained from the comparison of model results and field water qualities. This is similar to the experimental determination of the number of theoretical plates (Helfferich, 1962). The exchange capacity of the soil is 2 meq 100 g^{-1} (from laboratory determinations, Appelo and Geirnaert, 1983), which is equal to 160 meq l^{-1}. The

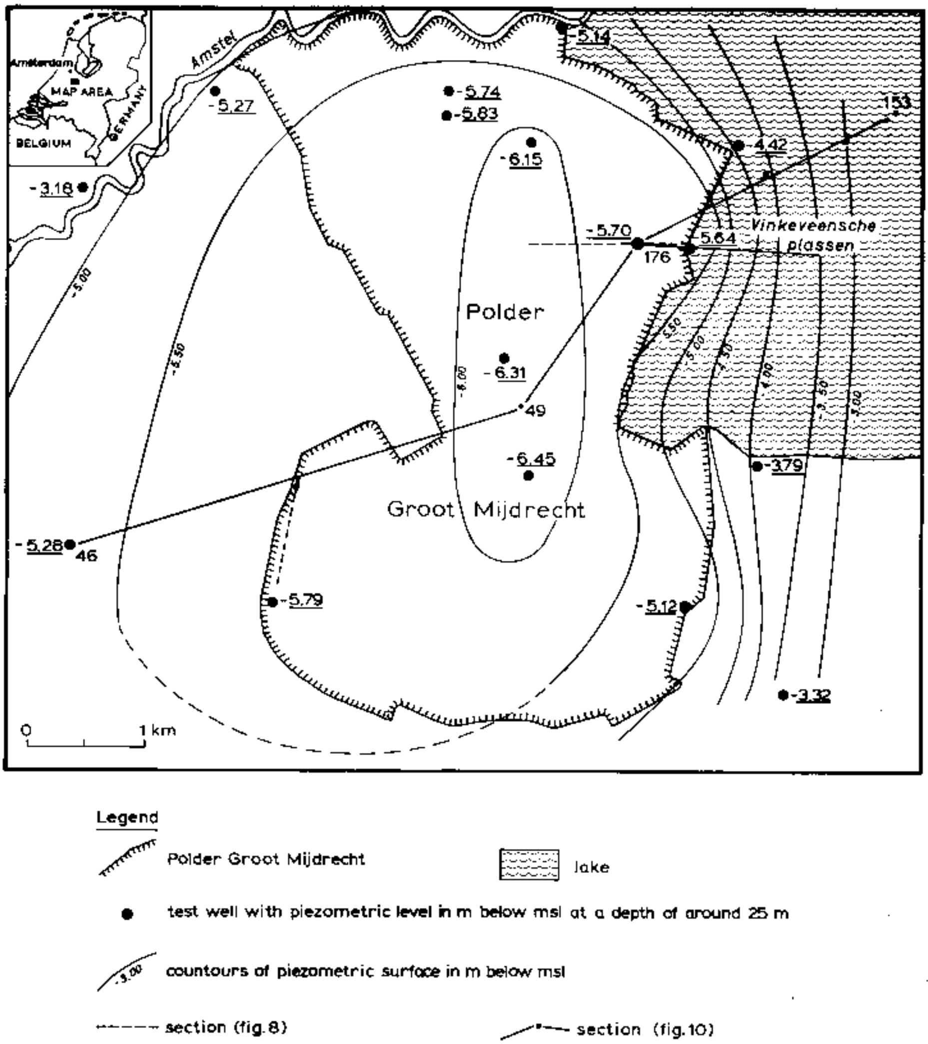

Fig. 7. Situation sketch of the polder "Groot Mijdrecht", The Netherlands.

exchange complex in the model is initially brought to equilibrium with salt water found at 120 m below surface in bore hole 176, and then flushed with lake water having the same Cl concentrations as the shallow groundwater. Results are shown in Fig. 9 and the water analyses are presented in Table 5.

From the model output it was found that concentrations in cell 5 best approached the observed groundwater composition. In earlier cells the difference between Ca and Mg concentrations remained too low when the Na exchange was finished, whereas in later cells it became too high. This reflects

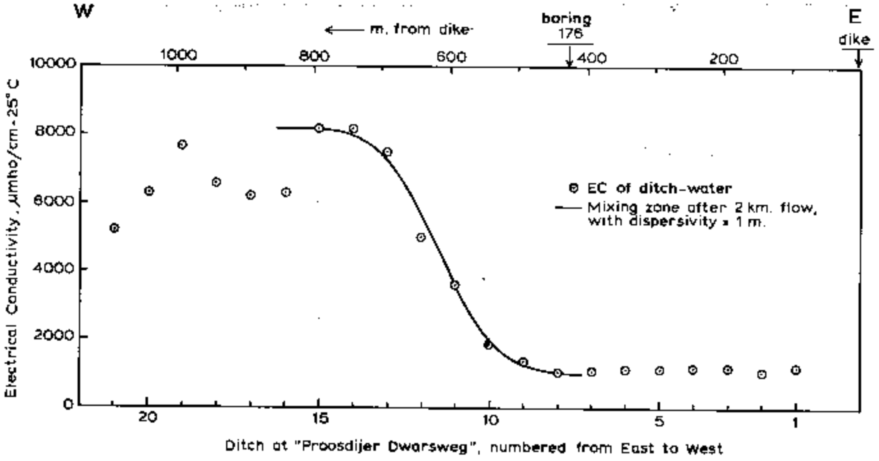

Fig. 8. Electrical conductivity of water in ditches in the polder "Groot Mijdrecht".

TABLE 5

Composition of surface water and groundwater in the polder "Groot Mijdrecht", The Netherlands (mmol l^{-1})

	Surface water		Groundwater in bore hole 176		
	Vinkeveen	model input	23 m	80 m	120 m
Na^+	7.9	5.5	5.4	5.9	125
Mg^{2+}	1.0	1.0	1.8	2.2	13.2
Ca^{2+}	2.2	2.08	1.1	1.4	10.0
Cl^-	9.3	6.5	6.2	7.8	143

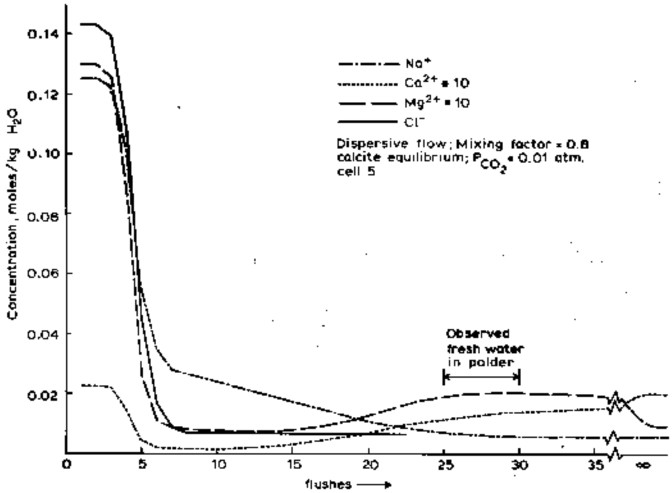

Fig. 9. Simulation of lake water quality as it flows through the subsoil into the polder "Groot Mijdrecht". Quality changes with time (or flushes in the mixing cell model) are shown for a fixed point (cell 5).

the uniqueness of concentrations in space and time when cation exchange alters the water composition. Figure 9 shows that cell 5 needs to be flushed 25–30 times before the observed concentrations are obtained. In other words, cell contents were replaced every 4–3.3 years in the 100 yr of polder existence. Flow velocity is 20 m yr $^{-1}$, so that one cell has a length of 80–66 m. (Note that the mixing factor of 0.8 gives a longitudinal dispersivity of 8 m when cell length decreases to 80 m.)

The modelled flow line is shown schematically in Fig. 10 with hatching to indicate cell lengths of 80 m. Cell 5 coincides with the upper 80 m of bore hole 176, and cell 1 lies 320 m to the east of the boring. The first cell also marks the boundary between salt and fresh water before "poldering": when water started to flow after polder development, fresh water must have been near the location of cell 1 as indicated in Fig. 10. The location is also near the limits of the Calais transgressions at the surface, which is reasonable. The interesting point here is that reasonably precise information is obtained about a former hydrological situation from buffering reactions between sediment and water.

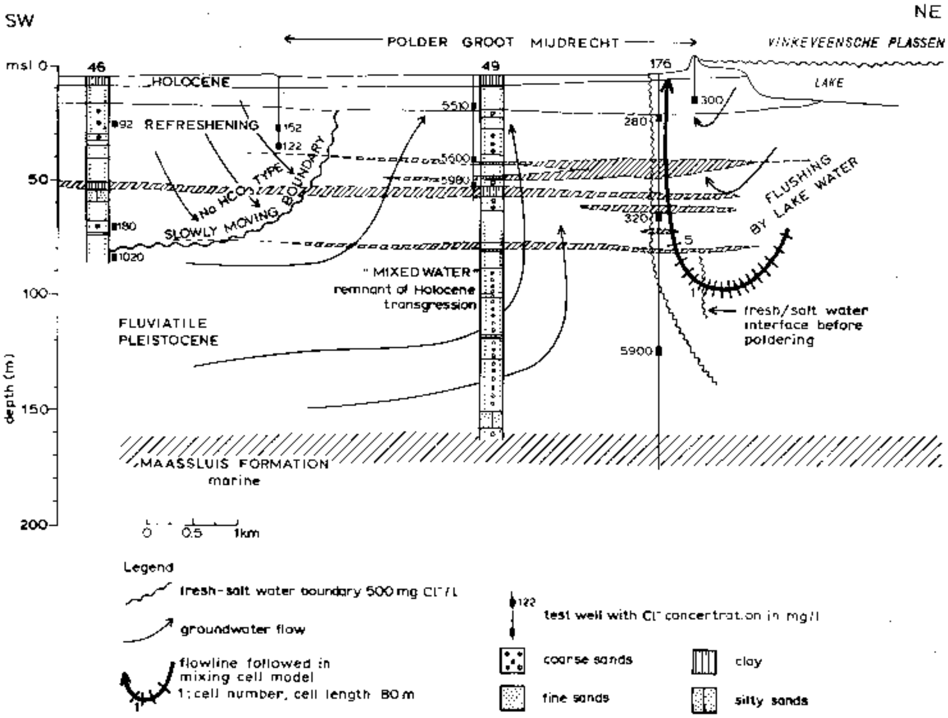

Fig. 10. Cross section over the polder "Groot Mijdrecht", with implied former salt/fresh water interface before "poldering".

CONCLUSIONS

A combined geochemical/mixing cell flow model has been developed. The geochemical model allows the calculation of reactions; for example, equilibration with minerals, temperature changes, addition of gases or acids or bases, etc., as well as exchange reactions. Although it originally calculates the composition of a single volume of water (Wolery, 1982), it is incorporated here with a mixing cell model in which dispersion and diffusion is simulated by mixing contents of each cell with neighbouring cells. The model is verified against analytical solutions.

The model is subsequently used to simulate composition changes in salt water when it enters a fresh water aquifer. Two models are given, dispersive flow when the salt water intrudes into the fresh aquifer through e.g. density flow, and diffusion from a more stagnant salt water body. The model calculations show that during dispersive flow characteristic concentrations of Na, Ca and Mg develop in both time and space as a result of the cation exchange. With diffusion, concentration gradients are smoothed out and "mixed" compositions occur. In this "mixed" water signs of cation exchange are only slightly visible. Diffusion is therefore another cause of "mixed" water compositions in addition to situations where the sediment has been repeatedly flushed by water of a "mixed" composition.

The dispersive model is hence applied to a specific flow situation in a Dutch polder, allowing estimation of the fresh/salt water interface location before polder development from the simulation of observed exchange reactions in the polder groundwater. The technique thus shows how a paleohydrological situation can be deduced from buffering reactions between groundwater and sediment. Buffering by cation exchange is evident in the water composition for at least a hundred years in this case, and will be visible for many decades more, because amounts of exchangeable cations are relatively high compared to concentrations in water.

Cation exchange between water and solid aquifer material is also important when water with other ion concentrations is either infiltrated or injected into an aquifer (Valocchi, 1981), particularly in the case of heavy metal pollution. Modelling of the accompanying quality changes requires a complete geochemical model, with more attention to cation exchange reactions than is available with a single adsorption isotherm (Reardon, 1981). The geochemical models now available offer the possiblity of more detailed equilibrium calculations, such as illustrated in this paper. A major drawback, however, is that knowledge of the cation exchange thermodynamics in aquifers is limited. The difficulty resides not only in the complexity of the natural materials which act as exchangers (clay minerals, organic matter, oxides and hydroxides), but also in the fact that natural water is a multicomponent solution in which more than two ions compete for the exchanger sites.

The study and modelling of salt/fresh water interactions can produce information about the type of exchange equation which gives best results, depending on aquifer characteristics. Such basic information is also important for other fields of hydrochemical modelling as well. A following contribution will describe experimental data obtained from a laboratory column percolated in succession with fresh- and seawater.

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