Some Calculations on Multicomponent Transport with Cation Exchange in Aquifers

by C.A.J. Appelo[a]

Abstract

Multicomponent transport with cation exchange induces a separation of cations during displacement of waters in aquifers. The spatial separation is due to different retardations of the various cations which originate from differences in selectivity of the exchange complex. The composition patterns are complex, and calculated mostly with numerical models. However, a basic notion of features such as salinity fronts, chromatographic sequence, and front type is useful for general understanding of the processes. These aspects have not obtained the level of generality in hydrochemical studies that they deserve, and are introduced and applied in the paper. Demonstrated are: (1) the calculation of a multicomponent exchange complex from solution composition with the law of mass action; (2) the front type (broadening, indifferent, sharpening) that develops in relation to the slope of the sorption isotherm; (3) the calculation of a chromatographic pattern for the case of sharp fronts; (4) the effects of salinity changes on solution composition. All these features are illustrated with examples and then applied to calculate and compare water compositions in an observation well from two field studies, one of a salt-water injection which displays the salinity effects very clearly in accordance with theory, and one of a fresh-water injection for which the complete sequence of three ions Na^+, Mg^{2+}, and Ca^{2+} can be calculated simply with a quadratic equation.

Introduction

Time and again it turns out that cation exchange is an important regulator of water quality in aquifers. The reaction is evident when water is injected (Valocchi et al., 1981; Ceazan et al., 1989; Bjerg et al., 1993), and also prominent on a larger scale in aquifers that are salinizing or freshening (Back, 1966; Chapelle and Knobel, 1983; Plummer et al., 1990; Stuyfzand, 1993). A typical aspect is the multicomponent nature of cation exchange, as it involves the adaption of adsorbed and solute concentrations of various ions in response to a change in water quality. Natural cation exchangers exhibit different selectivity for different cations. This leads to varying sorbed over solute concentration ratios for the individual cations, and this in turn implies variable retardations. The result is that a spatial separation occurs of the solute cations while waters with different compositions are moving through the aquifer. The principles of this phenomenon are studied under the heading of ion chromatography (Sillén, 1951; Helfferich and Klein, 1970; Pope et al., 1978; Valocchi et al., 1981; Charbeneau, 1981, 1988; Bond and Phillips, 1990; Schweich et al., 1993).

A variety of numerical models has been developed to calculate the complex chromatographic patterns (e.g., Valocchi et al., 1981; Appelo et al., 1990; Friedly and Rubin, 1992), and it is clear that these are necessary to make a rapid progress. Still, basic theory can be useful to *comprehend* the effects of salinity changes, or to calculate the approximate retardation of a front. The methods to do these calculations are not yet part of the standard toolbox of hydrochemistry, at least not for multicomponent problems. It is the purpose of this paper to illustrate that the basic equations can find an important application in our discipline. It is shown how the exchange complex can be calculated, and how front type can be deduced by consideration of the slope of the isotherm. The case of sharpening fronts, which is normally valid for fresh-water injections, allows calculation of the chromatographic patterns if the effect of dispersion is neglected. The formulae are illustrated with the salt-water injection by Ceazan et al. (1989) and the fresh-water injection of Valocchi et al. (1981).

Exchange Calculations

The law of mass action and electroneutrality allow the calculation of exchangeable cations from given solution composition when exchange coefficients are known, and vice versa. It is easy to start with *homovalent* exchange, and then apply the same equations to *heterovalent* exchange. For the exchange reaction of Na^+ and K^+

$$Na^+ + K\text{-}X <\!\!-\!\!> Na\text{-}X + K^+ \qquad (1)$$

the mass action equation is:

$$K_{Na\backslash K} = \frac{[Na\text{-}X]\,[K^+]}{[K\text{-}X]\,[Na^+]} \qquad (2)$$

where $K_{Na\backslash K}$ is the exchange coefficient, with the ions in subscript written in the order of appearance as *solute* cations in the reaction (i.e., Na^+ is lost from solution, K^+ is gained by the solution). The bracketed species denote activities, which are concentration measures expressed as fractions with respect to a predefined standard state. These standard states may be different for different phases. For example, solute activities in water are calculated with respect to a standard state of 1 mol/kg H_2O, to provide a number that is con-

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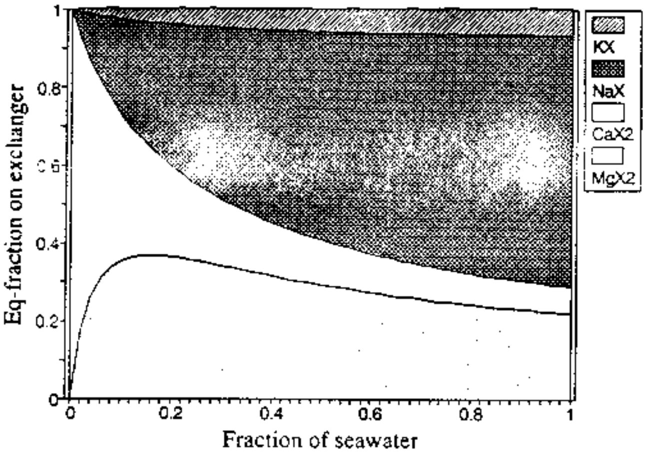

Fig. 1. Calculated composition of the exchange complex in equilibrium with pure $Ca(HCO_3)_2$ water admixed with sea water.

veniently comparable to the molal concentration. Activities of the exchangeable ions are often equaled to the equivalent fractions of total exchangeable cations (Gaines and Thomas, 1953). The equivalent fraction is obtained from $\beta_I = meq_{I\text{-}X} / CEC$, where $meq_{I\text{-}X}$ is milliequivalents of I^{i+} per 100 g sediment and CEC is the cation exchange capacity, also in meq/100 g. By putting $[I\text{-}X] = \beta_I$, it is assumed that the activity coefficient of the exchangeable cation is equal to 1. Since activities are dimensionless, the exchange coefficient is dimensionless as well.

Example 1

Consider a clay with CEC = 4 meq/100 g and $K_{Na\backslash K} = 0.2$, in equilibrium with a solution with 1 mol/kg H_2O of Na^+ and K^+ as the only cations; the activity coefficients for solute cations are also assumed to be equal to 1. The sum of the exchangeable cations (fractions) is $\beta_{Na} + \beta_K = 1$ and therefore, with equation (2):

$$\frac{\beta_{Na}}{(1 - \beta_{Na})} \frac{1}{1} = 0.2 \qquad (3)$$

Hence $\beta_{Na} = 0.167$ and $\beta_K = 0.833$. The amount of exchangeable Na^+ is β_{Na} CEC = 0.667 meq/100 g.

Example 2

For heterovalent exchange of cations with unlike charge, the same equations apply. For the exchange of Na^+ vs. Ca^{2+} the reaction is:

$$Na^+ + ½Ca\text{-}X_2 <\!\!-\!\!> Na\text{-}X + ½Ca^{2+} \qquad (4)$$

and the corresponding mass action equation:

$$K_{Na\backslash Ca} = \frac{[Na\text{-}X]\,[Ca^{2+}]^{1/2}}{[Ca\text{-}X_2]^{1/2}[Na^+]} \qquad (5)$$

Consider again a clay with CEC = 4 meq/100 g and $K_{Na\backslash Ca} = 0.4$ that is in equilibrium with a solution which contains 1 mol/kg H_2O of Na^+ and Ca^{2+} as the only cations. From the mass action equation we obtain

$$\beta_{Ca} = \frac{[Ca^{2+}]}{[Na^+]^2 \cdot K^2_{Na\backslash Ca}} \beta^2_{Na} \qquad (6)$$

Similar to the Na^+/K^+ example, this relation is introduced in the sum $\beta_{Ca} + \beta_{Na} = 1$, but in this case β_{Na} is solved from a quadratic equation. It provides $\beta_{Na} = 0.328$, and subsequently $\beta_{Ca} = 0.672$. The amount of exchangeable Na^+ in this case is β_{Na} CEC = 1.312 meq/100 g.

In multicomponent solutions the procedure is completely similar. The equivalent fraction β_I of any cation I^{i+} is expressed as a function of β_{Na} with the mass action equation, and introduced in the sum $\Sigma\beta = 1$. This gives an equation with β_{Na} as the only unknown, that allows for a solution. Subsequently the other fractions are obtained. For example, if sea water is mixed with pure $Ca(HCO_3)_2$ water, the theoretical fractions on the exchanger will change from pure $Ca\text{-}X_2$ to a mixture of K-X, Na-X, $Mg\text{-}X_2$ and $Ca\text{-}X_2$ as depicted in Figure 1. The figure illustrates that the exchanger in equilibrium with sea water will contain about 60% Na-X, while the remainder is made up of ca. 30% $Mg\text{-}X_2$, and smaller amounts of K-X and $Ca\text{-}X_2$. It is interesting to note that $Mg\text{-}X_2$ increases upon dilution of sea water down to a fraction of ca. 0.15, even though the diluting solution does not contain Mg^{2+}. The increase is at the expense of Na-X, and is due to charge effects that will be discussed more fully later on.

Table 1 gives the exchange coefficients that were used for Figure 1. These are commonly observed values for freshwater conditions (Bruggenwert and Kamphorst, 1982), but solute activity corrections have been neglected when the water composition changes from fresh water to sea water (or rather, it was assumed that the activity coefficient for the exchangeable and the solute cation is equal). The calculated percentage of Na-X in equilibrium with sea water is about 10-20% higher than normally observed in Dutch sediments (Van der Molen (1958) gives 40% Na-X), and the calculated fraction of $Ca\text{-}X_2$ is relatively low compared to observed values in Dutch sediments (about 15%). There are principally three reasons for these deviations. First, a sediment consists of a mixture of exchangers, each of which will exhibit a different selectivity for the different cations in solution. The exchanger with a high selectivity for Ca^{2+} will become relatively more important when Ca^{2+} is at relatively low concentrations as is the case in sea water. Second, for the plot of Figure 1, activity corrections have been assumed equal in solution and the exchanger, but these undoubtedly can be quite different. Interestingly, if only the solute activity correction was made in the standard way, the activities of Ca^{2+} and Mg^{2+} would reduce more than of Na^+, and the calculated fraction Na-X would become even greater. Third, there are often analytical problems with the determination of a sea-water exchange complex due to the relatively large contribution of solute ions (especially Na^+) to the total of solute and exchangeable ions which is displaced with an alien cation. Also, due to desorption of protons by a relatively concentrated displacing solution, calcite may dissolve

Table 1. Average Exchange Coefficients for the Reaction $Na^+ + 1/iI\text{-}X_i <\!\!-\!\!> Na\text{-}X + 1/iI^{i+}$

	Na^+	K^+	Mg^{2+}	Ca^{2+}
$K_{Na\backslash I}$	1.0	0.2	0.5	0.4

and contribute to the measured Ca-X_2. Still, the basic idea emerges that the above formulae can provide a reasonable first estimate of the exchangeable cations.

In the preceding examples, a CEC of 4 meq/100 g has been assumed. This can be related to pore-water concentrations by multiplying by $10\,\rho_b/\epsilon$, where ρ_b is the bulk density of the sediment, and ϵ is the water-filled porosity. This gives a total of exchangeable cations of about 240 meq/l for $\rho_b = 1.8$ kg/dm^3 and $\epsilon = 0.3$. These are substantial concentrations compared to fresh water with ca. 10 meq/l of solute ions, and will even be important for sea water with about 625 meq/l total cations in solution. Sandy aquifer sediments may have exchange capacities ranging from 0.5 to 1.5 meq/100 g (Reardon et al., 1983; Bjerg et al., 1993). The buffering action of the exchange reactions on water quality can be illustrated for a few simple cases, but first the different front types must be indicated.

Development of Front Type During Displacement

Three types of fronts can develop during the displacement of exchanging cations, viz. broadening, indifferent, or sharpening (DeVault, 1943; Sillén, 1951; Helfferich and Klein, 1970; Charbeneau, 1981). The condition for a front type can be obtained from the advection-dispersion-reaction equation:

$$\frac{\partial c_I}{\partial t} = D\frac{\partial^2 c_I}{\partial x^2} - v\frac{\partial c_I}{\partial x} - \frac{\partial q_I}{\partial t} \qquad (7)$$

where c_I is solute concentration (mol/l), t is time (s), D is the dispersion coefficient (m^2/s), x is distance (m), v is the pore-water flow velocity (m/s), and q_I is the sorbed concentration, expressed in mol/l of pore water. We assume that $D = 0$, and rewrite the equation as

$$\left[1 + \frac{dq_I}{dc_I}\right]\frac{\partial c_I}{\partial t} = -v\frac{\partial c_I}{\partial x} \qquad (8)$$

where dq/dc is the slope of the isotherm that relates sorbed and solute concentrations. Implicit differentiation of c(x, t) = constant gives

$$dc = 0 = \frac{\partial c}{\partial t}dt + \frac{\partial c}{\partial x}dx \qquad (9)$$

or

$$\left(\frac{\partial x}{\partial t}\right)_c = -\frac{\partial c}{\partial t}\frac{\partial x}{\partial c} \qquad (10)$$

where $(\partial x/\partial t)_c$ indicates the travel velocity v_c of a specific, constant concentration. On combining with equation (8), the travel velocity of a constant concentration of I can be expressed as a function of the water flow velocity:

$$v_{c_I} = \frac{v}{1 + \dfrac{dq_I}{dc_I}} \qquad (11)$$

A linear isotherm with constant dq/dc gives constant velocity for all concentrations. A convex isotherm (with a derivative that is greater than the curve at all points) shows an increasing dq/dc for smaller c. Hence, small concentrations have smaller velocity than large concentrations, and a broadening front results when the chemical is eluted. In a concave isotherm dq/dc decreases with c, and the velocity of a smaller concentration increases. In other words, smaller concentrations will tend to overtake higher concentrations, as they travel more rapidly. This effect counteracts spreading due to dispersion, and leads to sharp boundaries between the flushing and the flushed cation. Terms such as "sharpening front," "shock front," or "displacement chromatography" are logically connected to this behavior. The isotherms and the related fronts are illustrated in Figure 2.

Figure 2 shows elution curves that are related to pore volumes of a laboratory column, or the aquifer flowline. The velocities given by equation (11) can be related to pore volumes, noting that a conservative front will arrive at the outlet after one pore volume has entered the column. A retarded concentration needs proportionally more pore volumes before arrival, hence we have

$$\text{Pore volumes} = \frac{v}{v_{c_I}} = 1 + \frac{dq}{dc} \qquad (12)$$

A decreasing dq/dc is found in homovalent exchange when $K_{I\backslash J} < 1$, and a sharpening front occurs when I^{i+} is flushed by J^{j+}. In heterovalent exchange the concentration level in solution has an additional effect, higher charged cations being preferred more strongly when concentrations decrease. For most aquifers the usual preference series is $Al^{3+} > Ca^{2+} > Mg^{2+} > K^+ > NH_4^+ > Na^+$, and sharpening fronts result when a preferred cation increases in concentration, i.e., when salt water is displaced by fresh water with Ca^{2+} as dominant cation, or during acidification, when Al^{3+} concentrations increase.

Illustrative Cases from Column Elutions

Now let us consider, as a substitute for the aquifer flowline, a laboratory column in which different solutions are injected and from which the effluent is collected in small subsamples. The column has a pore volume V_0 (m^3). The exchangeable cations are expressed in terms of pore-water concentration, as noted above, i.e., there is for ion I^{i+} an adsorbed concentration of q_I in mmol/l pore water. Exchangeable I^{i+} in the column will then amount to $q_I \cdot V_0$ mmol. A solution is injected with J^{j+}, and $K_{I\backslash J} < 1$ so that a sharpening front develops. On both sides of the front there is a difference Δq_I in exchangeable I^{i+}. It must be flushed from the column by a difference in solute concentration between the resident and the incoming solution Δc_I. When this concentration difference is invariant for some time, a mass balance gives the volume V of incoming solution needed for flushing:

$$V = V_0\,\Delta q_I/\Delta c_I \qquad (13)$$

A *sharp front flushing factor* V^s can be defined which translates the volume V into column pore volumes:

$$V^s = \frac{V}{V_0} = \frac{\Delta q_I}{\Delta c_I} \qquad (14)$$

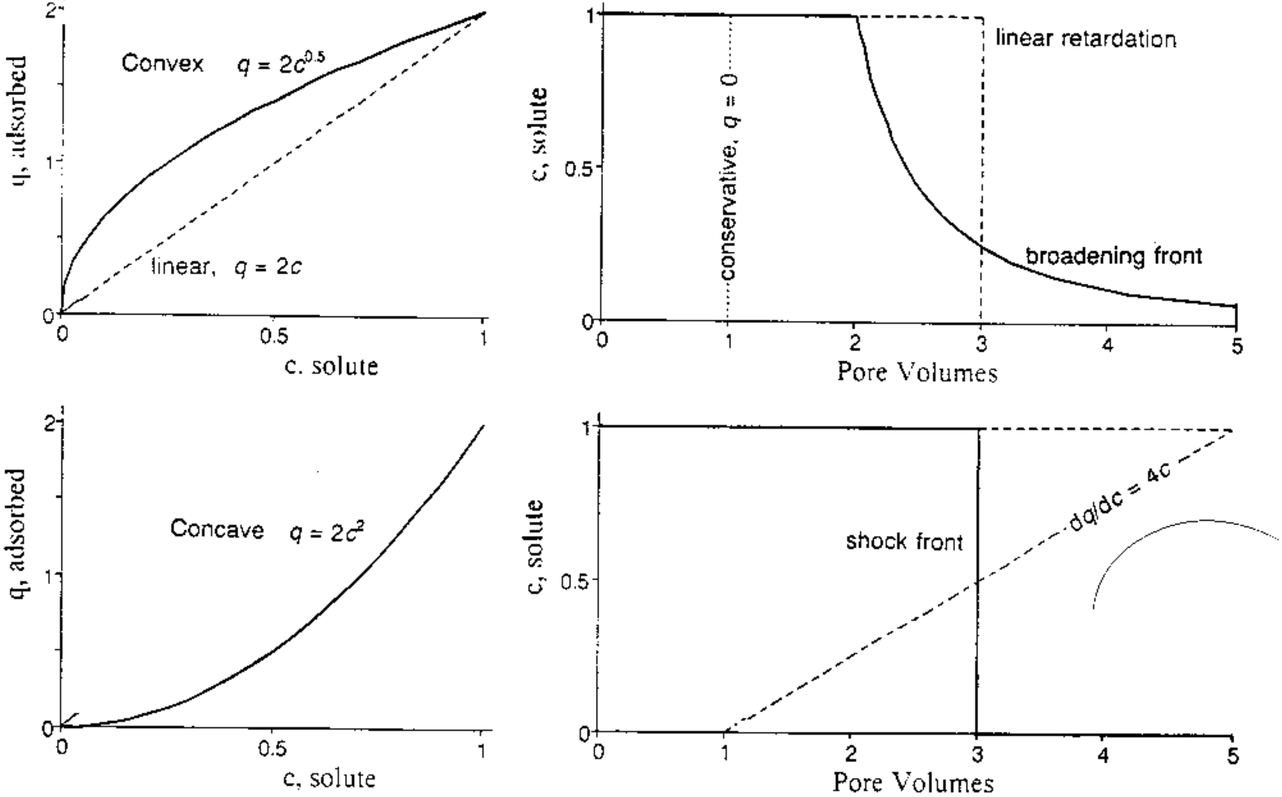

Fig. 2. The slope of the isotherm determines the type of front during displacement of an adsorbed ion. Upper: convex isotherm gives broadening front upon elution; linear isotherm shown for comparison. Lower: concave isotherm gives sharpening front with elution.

Note that this equation is similar to equation (12), the only difference being that the flushing factor starts after the conservative front V_0. A few examples may illustrate how easily the development of water quality can be calculated using the flushing factor.

Example 3a: Flushing Factor Calculated for a Single Ion

A column with 1 mmol/l NaCl in solution and 2 mmol/l Na-X on the exchanger is injected with 1 mmol/l KNO_3 (Figure 3). After injection of one pore volume, Cl^- is flushed and the concentration drops to zero in the effluent (we assume that dispersion is nil). NO_3^- from the injection solution has arrived at the column outlet and takes over. However, K^+ has not yet arrived there, because it is adsorbed by the exchanger where it displaces Na^+. The outlet solution therefore will be an $NaNO_3$ solution for a time period given by the flushing factor $V^s = \Delta q/\Delta c = 2/1 = 2$.

Example 3b: The Effect of Δc on the Flushing Factor

Now the same column is injected with 2 mmol/l KNO_3 solution. After one pore volume has been injected, the anion concentration in the effluent increases from 1 meq/l Cl^- to 2 meq/l NO_3^-. The anions must be balanced by cations, of course, which means that Na^+ should increase to 2 meq/l. The flushing factor $V^s = \Delta q/\Delta c = 2/2 = 1$, and K^+ arrives twice earlier at the outlet than in the former case (Figure 4).

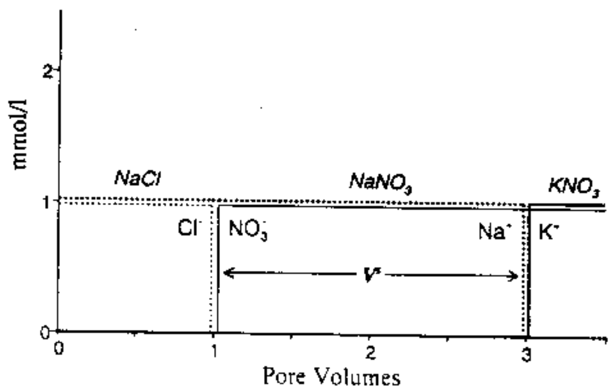

Fig. 3. A column with 1 mmol/l NaCl and 2 mmol/l Na-X is eluted with 1 mmol/l KNO_3. Concentrations at the outlet are plotted as functions of the column pore volumes.

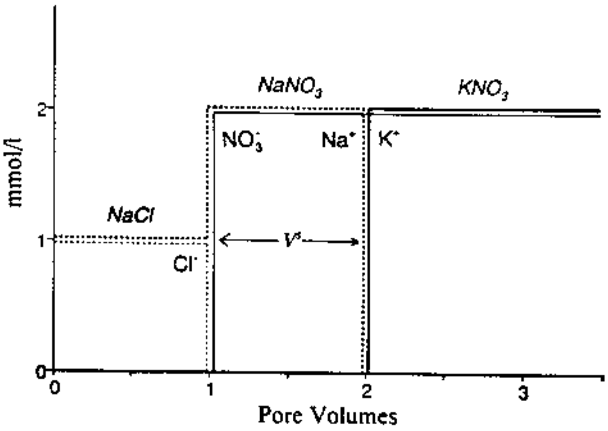

Fig. 4. An identical column as used for Figure 3, but the displacing solution is 2 mmol/l KNO_3.

We see that the flushing factor also gives the retardation $R = 1 + V^s$.

Example 4: Multicomponent Solutions

A similar reasoning can be applied to calculate the elution pattern of a column with a mixture of cations in solution and on the exchanger. For example, a column which has 1 mmol/l NaCl and 0.2 mmol/l KCl in solution and 2 mmol/l (Na + K)-X, is flushed with 0.6 mmol/l $Ca(NO_3)_2$ solution. The exchangeable fraction of Na^+ can be calculated as before, and yields $\beta_{Na} = 0.5$, and $\beta_K = 0.5$. The exchangeable cations therefore amount to Na-X = K-X = 1 mmol/l. After one pore volume has been eluted from the column, the Cl^- concentration falls to zero, and the NO_3^- concentration increases from 0 to 1.2 mmol/l. Again, the incoming cation Ca^{2+} is sorbed while it displaces Na-X and K-X, and has not yet arrived at the outlet. Only Na^+ and K^+ will be present in solution, in the ratio of $Na^+:K^+ = 1:0.2$ as initially, because equilibrium with the exchanger dictates that ratio. Since the initial ratio of *exchangeable* Na-X:K-X = 0.5:0.5, it is clear that Na-X is exhausted before K-X. When Na-X has been flushed the Na^+ concentration must become zero, and K^+ is the only cation that compensates the anion charge of 1.2 mmol/l NO_3^-. It is then also the only exchangeable cation, K-X = 2 mmol/l. After removal of K-X the $Ca(NO_3)_2$ solution will appear at last as injected.

Thus, following elution of the conservative Cl^- after one pore volume, a further two fronts mark the adaption of the cation concentrations. The first front is found from:

$$(V^s)_1 = \frac{(q_{Na})_1 - (q_{Na})_2}{(c_{Na})_1 - (c_{Na})_2} = \frac{1 - 0}{1 - 0} = 1 \qquad (15)$$

Or, alternatively from changes in the K^+ concentration over the front:

$$(V^s)_1 = \frac{(q_K)_1 - (q_K)_2}{(c_K)_1 - (c_K)_2} = \frac{1 - 2}{0.2 - 1.2} = 1 \qquad (15a)$$

The second front arrives when K-X is exhausted, i.e.,

$$(V^s)_2 = \frac{(q_K)_2 - (q_K)_3}{(c_K)_2 - (c_K)_3} = \frac{2 - 0}{1.2 - 0} = 1.667 \qquad (16)$$

The same V^s can be calculated using Ca^{2+}. Note that the fronts are accompanied by changes in concentrations of *all* the ions that are present and participate in the exchange reaction, both in solution and exchangeable. The chromatographic pattern of concentrations is depicted in Figure 5.

Example 5: The Effect of a Salinity Front in Heterovalent Exchange

Consider a column which has 1 mol/l NaCl and 1 mol/l $MgCl_2$ in solution, and 2 mmol/l (Na + Mg)-X on the exchanger which is eluted with 0.5 mmol/l $Ca(NO_3)_2$. The initial exchange equilibrium in the column is governed by

$$K_{Na\backslash Mg} = \frac{\beta_{Na}}{\beta_{Mg}^{1/2}} \frac{[Mg^{2+}]^{1/2}}{[Na^+]} = 0.5 \qquad (17)$$

which permits the fraction of exchangeable Na^+ to be calculated as illustrated before. The outcome is $\beta_{Na} = 0.39$ and $\beta_{Mg} = 0.61$, or Na-X = 0.78 mmol/l, and $Mg\text{-}X_2 = 0.61$ mmol/l. After one pore volume the anion concentration falls from 3 mol/l Cl^- to 1 mmol/l NO_3^-. The sum of the cations must likewise decline, while equilibrium with the initial exchanger is maintained. This induces a shift in the concentration ratio of cations with unlike charge, as can be seen as follows. From the mass action equation (17), the ratio $R_{Mg/Na} = [Mg^{2+}]/[Na^+]^2$ is constant:

$$\frac{[Mg^{2+}]}{[Na^+]^2} = \frac{\beta_{Mg}}{\beta_{Na}^2} \cdot K^2_{Na\backslash Mg} \qquad (18)$$

Neglecting the difference between activity and molal concentration allows to write:

$$[Na^+] + 2[Mg^{2+}] = [NO_3^-] = 0.001 \qquad (19)$$

Inserting equation (18) gives a quadratic equation:

$$2R_{Mg/Na}[Na^+]^2 + [Na^+] - 0.001 = 0 \qquad (20)$$

Solving for $[Na^+]$ yields $[Na^+] = 0.998 \cdot 10^{-3}$ and $[Mg^{2+}] = 1.0 \cdot 10^{-6}$ mol/l. The exchangeable Na^+ will be flushed $(V^s)_1$ pore volumes after the conservative front of Cl^-, where

$$(V^s)_1 = \frac{(q_{Na})_1 - (q_{Na})_2}{(c_{Na})_1 - (c_{Na})_2} = \frac{0.78 - 0}{0.998 - 0} = 0.782 \qquad (21)$$

Again, $(V^s)_1$ could also have been calculated from changes of the other cation Mg^{2+}:

$$(V^s)_1 = \frac{(q_{Mg})_1 - (q_{Mg})_2}{(c_{Mg})_1 - (c_{Mg})_2} = \frac{0.61 - 1.0}{0.001 - 0.5} = 0.782 \qquad (21a)$$

The second front arrives when $Mg\text{-}X_2$ has been flushed, i.e.,

$$(V^s)_2 = \frac{(q_{Mg})_2 - (q_{Mg})_3}{(c_{Mg})_2 - (c_{Mg})_3} = \frac{1 - 0}{0.5 - 0} = 2.0 \qquad (22)$$

The calculated pattern is shown in Figure 6.

Salinity Effects in Well Injections

It is important to note that the dilution of the solution has induced the ratio of $Mg^{2+}:Na^+$ to decrease nearly a thousand times. It follows from equations (18) and (19) that a fixed exchanger composition dictates that the ratio of the sum of the divalent ions over the Na^+ concentration should vary as

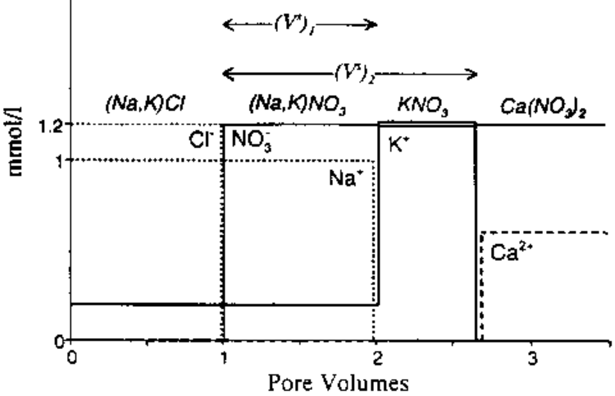

Fig. 5. A column with 1 mmol/l NaCl and 0.2 mmol/l KCl, and 2 mmol/l (Na + K)-X is eluted with 0.6 mmol/l $Ca(NO_3)_2$.

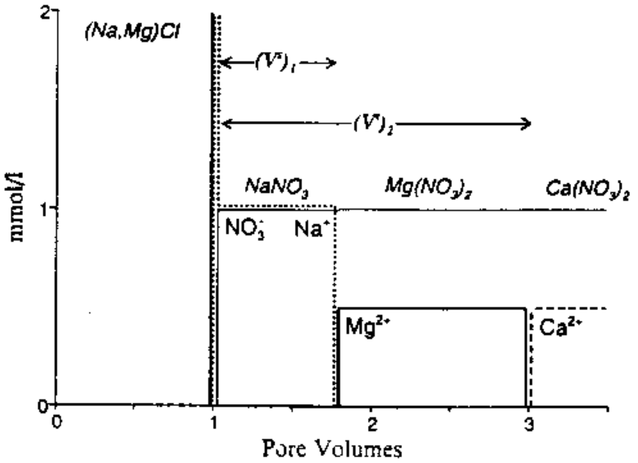

Fig. 6. A column with 1 mol/l NaCl and 1 mol/l $MgCl_2$ in solution, and 2 mmol/l (Na + Mg)-X on the exchanger is eluted with 0.5 mmol/l $Ca(NO_3)_2$.

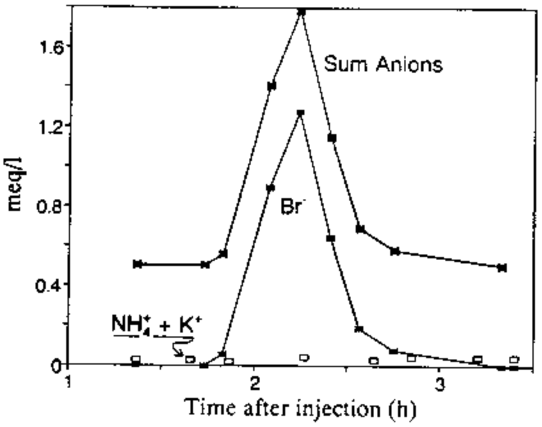

Fig. 7. Concentrations of ions in the NH_4Br injection experiment of Ceazan et al. (1989).

$$\frac{c_{2+}}{c_{Na}} = \frac{-1 + (1 + 8R_{2+/Na}N)^{1/2}}{4} \qquad (23)$$

where c_{2+} indicates the sum of the divalent cations in mol/l, $R_{2+/Na}$ is the sum of the ratios of the divalent cations as defined in equation (18), and N is the normality (i.e., the total anion concentration, eq/l). The salinity effect will be particularly clear when saline water is diluted by fresh water since the concentration difference Δc in solution is small in that case, providing a large flushing factor which will show up in extended plateaus of a water quality. This effect has been recognized and described by Valocchi et al. (1981) who injected fresh water in a brackish aquifer.

It can also be observed when salt solutions are injected if the exchangeable cations continue to dominate over solute cations, and the case described by Ceazan et al. (1989) may serve as an illustration. Ceazan et al. injected NH_4Br solution in an aquifer with water having low background anion concentrations of ca. 0.5 meq/l. In an observation well located 1.5 m downstream from the injection well, the passage of the injected fluid was monitored. The arrival of Br^- after two hours was accompanied by an increase of total anion concentrations to 1.8 meq/l, as illustrated in Figure 7. The NH_4^+ concentration remained unaffected at that time because of adsorption (Figure 7), but the divalent cations Ca^{2+} and Mg^{2+} also showed a marked increase (Figure 8). The ratio c_{2+}/c_{Na} increased from 0.33 in native water to a maximum of 0.78 at the peak of the Br^- concentration. This increase follows from equation (23) with $R_{2+/Na} = 1111$ in the native water, and the resultant c_{2+} is shown in Figure 8. Note that in the calculation only the sum of anions enters as a variable, which means that the explanation of the phenomenon should be coupled to that parameter, rather than to cation exchange in the strict sense of one cation displacing another one from the exchanger.

Chromatographic Pattern in a Well Injection

Field situations are more complicated because the displacing solution will not be made up of a single cation (and also because of dispersion and side reactions such as carbonate reactions). However, the dominant cations in many natural settings are Na^+, Mg^{2+}, and Ca^{2+}, and a freshening pattern can still be calculated without much difficulty. An illustrative case is the fresh-water injection in a brackish-water aquifer described by Valocchi et al. (1981). Brackish water with ca. 150 meq/l cations was displaced by fresh water with 14.66 meq/l cations. The resulting dilution front and subsequent chromatographic pattern has been fully recognized and was modeled numerically by Valocchi et al. (1981, 1981a). The features of example 5 discussed above were matched almost perfectly in a number of observation wells, and the changing pattern of cation concentrations has exerted a fascinating attraction to modelers of ground-water quality. Charbeneau (1988) has disclosed perhaps the most illustrative modeling of this case, using a fast algorithm to reproduce the observations. An approximation in which dispersion is neglected can be obtained by solving the two sharp front flushing factors in combination with the exchange equilibria, but the necessary algebra is rather awkward (Appelo et al., 1993). However, example 5 as discussed, can be extended relatively easily and applied to this experiment, and requires now only the solution of a quadratic equation. The basic conditions are noted in Table 2, i.e., the native and injected water compositions, and calculated exchange composition according to the exchange constants given by Valocchi et al. (1981).

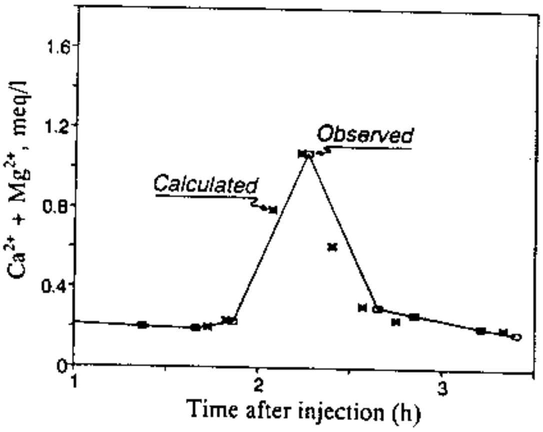

Fig. 8. Observed and calculated concentrations of Ca^{2+} and Mg^{2+} during passage of the Br^- peak in the injection experiment of Ceazan et al. (1989).

Table 2. Concentrations of Na^+, Mg^{2+}, and Ca^{2+} in Native Water and Exchanger, After Arrival of the Dilution Front, and Final Injected Water During the Fresh-Water Injection in a Brackish-Water Aquifer (Valocchi et al., 1981); 2nd Plateau Concentrations from Appelo et al. (1993)

	— — *Solute* — —			— *Exchangeable* —		
Stage	*Na*	*Mg*	*Ca*	*Na*	*Mg*	*Ca*
Native	86.5	18.2	11.1	160.60	141.59	153.11
Dilution	13.28	.43	.26	160.60	141.59	153.11
2nd plateau	9.47	1.67	0.92	64.18	173.0	169.91
Injected	9.4	.5	2.13	56.35	40.55	306.27

(Observation well S23. Concentrations in mmol/l in pore water.)

First there is a dilution front, marked by the decrease in Cl^- concentration in the observation well. The decrease of anions will induce a relative increase of Na^+ in solution as reflected by the calculated water composition noted in Table 2. This water composition ends with

$$(V^s)_1 = \frac{(q_{Na})_1 - (q_{Na})_2}{(c_{Na})_1 - (c_{Na})_2} \tag{24}$$

where, to a good approximation, the Na^+ concentrations of the second plateau are identical to those of the injected water, i.e. $(q_{Na})_2 = (q_{Na})_3$, and $(c_{Na})_2 = (c_{Na})_3$. Over the front, there is also an adjustment of Mg^{2+} concentrations in the exchanger and in solution:

$$(V^s)_1 = \frac{(q_{Mg})_1 - (q_{Mg})_2}{(c_{Mg})_1 - (c_{Mg})_2} \tag{24a}$$

and similar for Ca^{2+}.

The problem is that all three ions are present in the second plateau, and the solution is not as simple as before. However, solute and exchangeable ions are governed by equilibrium, and with this relation the unknowns can still be found relatively simply. Together with the electroneutrality equation a quadratic equation can be derived as follows. The sharp flushing factor formulae [equation (24)] for Mg^{2+} and Ca^{2+} give:

$$\begin{aligned}(q_{Mg})_2 &= (V^s)_1(c_{Mg})_2 + (q_{Mg})_1 - (V^s)_1(c_{Mg})_1 = \\ &\quad (V^s)_1(c_{Mg})_2 + Q_1 \\ (q_{Ca})_2 &= (V^s)_1(c_{Ca})_2 + (q_{Ca})_1 - (V^s)_1(c_{Ca})_1 = \\ &\quad (V^s)_1(c_{Ca})_2 + Q_2\end{aligned} \tag{25}$$

These equations are entered into:

$$\frac{(q_{Mg})_2}{(c_{Mg})_2} = K_{Mg\backslash Ca}\frac{(q_{Ca})_2}{(c_{Ca})_2} \tag{26}$$

to give:

$$Q_4 + \frac{Q_1}{(c_{Mg})_2} = \frac{Q_3}{(c_{Ca})_2} \tag{27}$$

We also have the electroneutrality equation:

$$(c_{Ca})_2 = \{N - (c_{Na})_2 - 2(c_{Mg})_2\}/2 = N_2 - (c_{Mg})_2 \tag{28}$$

and obtain finally:

$$-Q_4(c_{Mg})_2^2 + \{Q_4N_2 - Q_1 - Q_3\}(c_{Mg})_2 + Q_1N_2 = 0 \qquad \ldots (29)$$

where:

$$Q_1 = (q_{Mg})_1 - (V^s)_1(c_{Mg})_1$$
$$Q_3 = K_{Mg\backslash Ca}Q_2 = K_{Mg\backslash Ca}\{(q_{Ca})_1 - (V^s)_1(c_{Ca})_1\}$$
$$Q_4 = (V^s)_1(1 - K_{Mg\backslash Ca})$$
$$N_2 = \{N - (c_{Na})_2\}/2;\ (c_{Na})_2 = (c_{Na})_3$$
$$K_{Mg\backslash Ca} = 0.564$$
$$N = 14.66 \cdot 10^{-3}\ \mathrm{eq/l}$$

With $(V^s)_1 = 26.9$ (from Na^+ flushing), the equation solves to one positive root $(c_{Mg})_2 = 1.7$ mmol/l, and subsequently $(q_{Mg})_2 = 176$ mmol/l, and $(V^s)_2 = 112.8$. When V^s is multiplied with the volume of water that is injected for a conservative front to arrive at the observation well, the volume of injection water for a sharp front is obtained. This allows for a direct comparison with the data presented by Valocchi et al. (1981) as shown in Figure 9 for observation well S23. The c_{Mg} has been multiplied here with 24.3 g/mole to obtain c in mg/l. The positions of the fronts is similar to the computer simulation by Valocchi et al., albeit much sharper here since the effect of dispersion was neglected. The solution obtained here is also very close to the full sharp front solution given by Appelo et al. (1993), who obtained $(V^s)_1 = 25.3$, $(c_{Mg})_2 = 1.67$ mmol/l, and $(V^s)_2 = 113.2$. According to this formal solution, the Na^+ concentration decreases first to 9.47 mmol/l in the second plateau, and thereafter to the final 9.4 mmol/l in the injected water.

The present solution is illustrative in the sense that it provides the basic insight in the chromatography of cation exchange during transport. Other solutions for multicomponent chromatography exist, but only for homovalent exchange (Helfferich and Klein, 1970). Helfferich and Klein (1970) have called it the theory of coherence, and a basic feature of the multicomponent theory is present in the heterovalent case discussed here: there is only one Mg concentration in the second plateau possible when the concentrations of all cations that participate in the exchange pro-

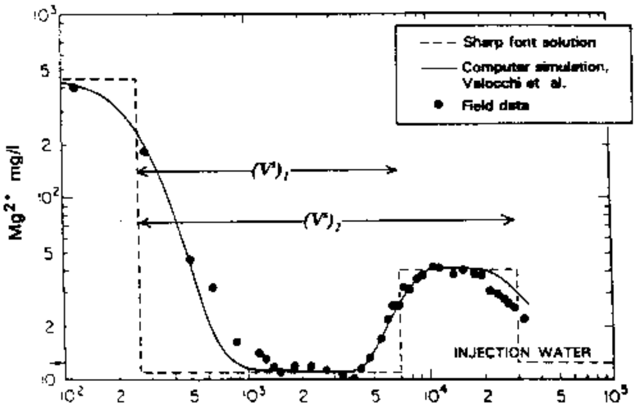

Fig. 9. Concentration of Mg^{2+} in water from observation well S23 during injection of fresh water (Valocchi et al., 1981). Also shown are the results of the simple approximation method derived in the text.

cess adapt concomitantly over a front, and while equilibrium is maintained.

Conclusions

Cation exchange in aquifers is always a multicomponent phenomenon with various cations competing for the exchanger sites. The compositions of a multicomponent exchanger can be calculated without difficulty from solution composition, using average exchange coefficients. Displacements with differing water qualities lead to separation of the cations due to different retardations of the ions. Compositions are divided by fronts which can be broadening, indifferent or sharpening, a dependence that can be found from the exchange (sorption) isotherm. In the case of sharpening fronts, easy displacement formulae can be derived, based on mass balance. They allow calculation of the chromatographic pattern, as was illustrated with a few simple column examples. When salt water is displaced by fresh water, we expect spatially separated, relative increases of Na^+, Mg^{2+}, and Ca^{2+} along a flowpath in the upstream direction from the salinity front. Even the simple formulae allow for an accurate description of the complicated pattern that was produced during the fresh-water injection into a brackish-water aquifer presented by Valocchi et al. (1981). Thus, we have obtained a basic insight into how chromatographic separations will take place during injections in aquifers or larger scale ground-water displacements.

Notation

β	equivalent fraction on exchanger (-);
c	solute concentration (mol/l);
CEC	cation exchange capacity (meq/100 g);
D	dispersion coefficient (m^2/s);
$K_{I\backslash J}$	exchange coefficient (-);
q	sorbed concentration (mol/l);
$R_{I/Na}$	ratio $[I^{i+}]/[Na^+]^i$, in equilibrium with (fixed) exchanger composition (-);
v	pore-water flow velocity (m/s);
v_{c_I}	flow velocity of a given concentration of solute I (m/s);
V	volume (m^3);
V_0	pore volume of column or flow line (m^3);
V^s	sharp front flushing factor (-);
[I]	activity of I (-);
$(V^s, c, q)_i$	front number i with flushing factor $(V^s)_i$, preceded by concentrations $(c, q)_i$, followed by concentrations $(c, q)_{i+1}$.

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