

Chromatographic Interpretation of Cation Exchange Processes in Soil Columns Treated with Na-Salt Solutions

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It is well-known that SIGMOND — independently of GEDROIZ, but at the same time — recognized the importance of sodium ions in the sodification of soils.

SIGMOND studied the occurrences and interdependences in detail and he demonstrated the necessity of dynamic investigations for the identification of the rules of different processes. We endeavoured to follow his initiative and to explain the exchange of sodium and calcium ions within a dynamic system.

If solutions of different compositions pass through the soil column the cation composition in the liquid and the solid phases of the soil changes as a function of depth.

The application of ion exchanging chromatography seems to be suitable for the evaluation of the process, for the prediction of the distribution of the cations according to depth. It should be noted, however, that the rules of cation exchange which takes place in the column, refer to homogeneous, synthetic resins of well defined composition. Therefore in case of ion exchangers of more complicated composition, such as soils, the validity and applicability of theoretical relationships must be examined.

GAPON and GAPON [2] were the first researchers to give a chromatographic description of the distribution of exchangeable cations according to depth. It was demonstrated by RIBLE and DAVIS [4] that the equilibrium distribution of the various cation-pairs (in the case of cations of different valence) depended on whether the cations of higher valence or those of lower valence were in exchangeable or dissolved state at the beginning of the process.

THOMAS and COLEMAN [6] found WALTER's equation to be suitable for the description of K-adsorption.

BOWER et al. [1] determined the cation concentration of the effluent by using the models of HIESTER and VERMEULEN [3, 7].

Since the chromatography theory allows

- a) the prediction of the constituents in question in the effluent;
- b) the calculation of the amount of the material fixed along the column

and

c) the estimation of the concentration of the same constituent in the liquid phase of the soil,

we decided to examine the above process in detail, and to prove it by applying the chromatographic approach.

Experimental

In order to complete and to extend the investigations made so far we conducted experiments to compare the breakthrough curves of:

NaCl solutions of different concentrations (0.05 N and 0.1 N) and those of Na-salt solutions of identical concentration (0.05 N) containing different anions (Cl^- , SO_4^{2-} and HCO_3^-),

then we tried to determine experimentally the compositions of the exchangeable cations and the concentrations of soil solutions corresponding to the different sectors of the breakthrough curve.

Afterwards it was examined whether the reaction kinetic theory [3] was suitable to characterize, depending on depth, the breakthrough curves, the distribution of exchangeable cations, and the change of cation concentration in the liquid phase of Ca-soil columns treated with Na-salt solutions.

The 0.25–2.00 mm grain fractions of the upper stratum of a leached chernozem soil were used in our model experiments. 16 cm high soil columns were prepared by packing the calcareous soil into plastic tubes (4.63 cm in diameter) closed by a sieve. Then different amounts of Na-salt solutions were allowed to percolate through the columns until they were saturated to water capacity. The fluid above the soil columns was kept at a constant level. The breakthrough curves were plotted by measuring the concentration of the Ca- and Na-ions in given volumes of the solutions passed through the soil columns. The flow of the exchanging solution was stopped when the Na-concentration of the effluent more or less corresponded to that of the solution added to the column ($C/C_{0\sim 1}$).

In one series of the soil columns we endeavoured to follow up, on the one hand, the distribution of the exchangeable cations according to depth, on the other hand — given the knowledge of the breakthrough curves — the different phases of the exchange. For this purpose we treated 3–3 columns, each with a different amount (75, 150, 700 mm) of 0.05 N NaCl, Na_2SO_4 and NaHCO_3 solutions. The above volumes of the solutions corresponded to the following sectors of the breakthrough curve: 1. initial; 2. steeply rising; 3. approaching dynamic equilibrium.

The solutions were allowed to percolate through the columns, then the columns were divided into 5 layers each (0–2, 2–5, 5–8, 8–12, 12–16 cm) and the exchangeable and soluble Na-content in each layer was determined [5].

Discussion

From among the well-known chromatographic theories describing the changes going on in the cation content of the soil, the model evolved by HIESTER and VERMEULEN [3, 7] appears to be the most suitable. This model applies the kinetic theory of secondary reversible reactions for the interaction between the ions of the moving solution and the exchanging surface. This theory assumes a laminar flow in a material with homogeneous pores. Another condition is that during the experiment the exchange constant (K) and the cation exchange capacity of the material should not change. The channel effect as well as ion diffusion are negligible.

The cation exchange between the moving fluid and the solid phase is described by two partial differential equations. On the one hand, it is true that

the change of the cation concentration of the solution passed through the column is identical with the excess quantity of ions fixed on the exchanger, on the other hand, the ratio between the ions in the solutions and those fixed on the exchanger depends on the value of the kinetic constant (k_{kin} ml/me/min). Based on these functions some dimensionless parameters can be defined which allow concrete calculations.

In the case of the Na-Ca exchange in question $K < 1$, and the ion exchange column originally contained only Ca-ions while the exchanging solution contained only Na-ions. Hence the breakthrough curves may be studied by the following reduced equations:

$$\lambda = C/C_0 = \frac{r \sqrt{t/s} - \sqrt{r}}{(r-1)t/s} \quad (1)$$

where

$$t/s = \frac{C_0(V - X \cdot f)}{Q \cdot t_{fs} \cdot X} \quad (2)$$

The amount of cations adsorbed from the solution can be calculated from the equation

$$\omega = \frac{q}{Q} = \frac{1}{r-1} \cdot \sqrt{\frac{rt}{s}} - 1 \quad (3)$$

In this case the equations describing the process are independent of the value of the k_{kin} constant.

Symbols used

- λ = dimensionless parameter of the phase concentration of the solution;
- C_0 = cation concentration in the influent, me/ml;
- C = concentration of the studied cation in the effluent, me/ml;
- r = equilibrium parameter, dimensionless; in the case of ion exchange $r = 1/K$; (K = exchange constant);
- t = capacity parameter of the solution, dimensionless;
- s = capacity parameter of the column, dimensionless;
- V = volume of the solution (influent) added to the column, ml/cm²;
- X = depth of the investigated soil stratum, cm;
- t_{fs} = bulk density of the dry soil, g/cm³;
- f = part of the volume of the column filled up with water, dimensionless;
- ω = concentration parameter of the adsorbed cation, dimensionless;
- Q = cation exchange capacity of the ion exchanging material, me/g;
- q = concentration of the cation in the adsorbed phase, me/g.

The value of r can be determined from the breakthrough curves, if the C/C_0 values are plotted as a function of t/s calculated on the basis of equation (2). On this basis of $\lambda = C/C_0$ corresponding to the $t/s = 1$ experimental data, r can be calculated from equation (1).

The amount of the Na-ions fixed at different depths from the Na-salt solution passed through the column can be calculated from equation

$$q_{Na} = \frac{1}{1-K} \cdot \left[\sqrt{C_0 \cdot K \cdot Q \cdot t_{fs} \frac{V - X \cdot f}{X}} - K \cdot Q \right] \quad (4)$$

and the Na-concentration of the solution from the equation

$$C_{Na} = \frac{1}{1 - K} \cdot \left[C_0 - \sqrt{C_0 \cdot K \cdot Q \cdot t_{fs} \frac{X}{V - X \cdot f}} \right] \quad (5)$$

where q_{Na} is the exchangeable Na (me/g), C_{Na} is the Na-content of the soil solution (me/ml) and K is the GAPON equilibrium constant. When the concentration of the exchangeable Ca- and Na-ions in the Ca-soil equilibrated with Na-salt solutions at 25 °C, as well as the concentration of the same cations measured in the solutions are known, the exchange constant can be calculated from the equation

$$K = \frac{Na_x \cdot \sqrt{(Ca)}}{Ca_x \cdot (Na)} \quad (6)$$

In equation (6) the quantities in parentheses mean the concentration of the cations measured in the solution phase in mol/l, and the members with index mean the equilibrium concentration of the exchangeable cations in me/100 g.

Conclusions

From Fig. 1 it is evident that the shape of the breakthrough curves is similar to that of chromatographic curves. The concentration of the Na-ions in the effluent rapidly increases at a certain solution volume (breakthrough volume), then it gradually approaches the concentration level of the influent. The product of the breakthrough volume and the Na-concentration of the influent gives the breakthrough capacity of the column, which is characteristic of the given ion, and of the same column only at a given flow velocity, at a given concentration of the solution and at constant temperature.

In the case of 0.1 N NaCl — under identical experimental conditions — the breakthrough volume is about half of the value measured in case of 0.05 N NaCl-solution, and the slope of the breakthrough curve is steeper.

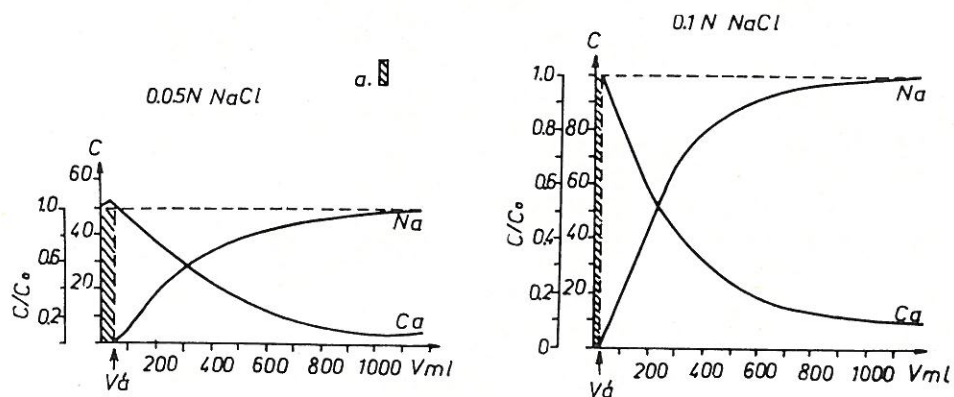


Fig. 1

Breakthrough curves of NaCl solutions of different concentration in a chernozem soil column. V_b — breakthrough volume. a. breakthrough capacity of the column

The Ca-concentration of the eluate initially decreases rapidly, then slowly approaches equilibrium. The two sectors of different slope of the curve may correspond to the exchange of cations fixed at different parts of the adsorbent, and to their dilution from the liquid phase.

In the following the validity of the applied equations will be studied by comparing the calculated and measured data. The main characteristics of the soil and salt solutions used in the experiments are given in Table 1. The

Table 1
 Characteristics of the soil column and the salt solutions

Denomination	Value
Influent concentration, C_0	0.05 g/l
Bulk density of soil, t_{fs}	1.05 g/cm ³
Amount of solution added to the column (in cm), V	{ 7.5 cm { 15.0 cm { 70.0 cm, i.e. { 50.0 cm (NaHCO ₃)
Solution factor of the column, f	0.46 —
Cation exchange capacity of the soil, Q	0.193 me/g

breakthrough curves of the different Na-salts are shown in Fig. 2. The theoretical curves follow with lesser or greater deviations those plotted on the basis of the experimental data. This proves that the clarification of fundamental relationships can be promoted by the application of the chromatographic theory. It can be observed that the shapes of the experimental curves slightly deviate in the case of the different Na-salt solutions.

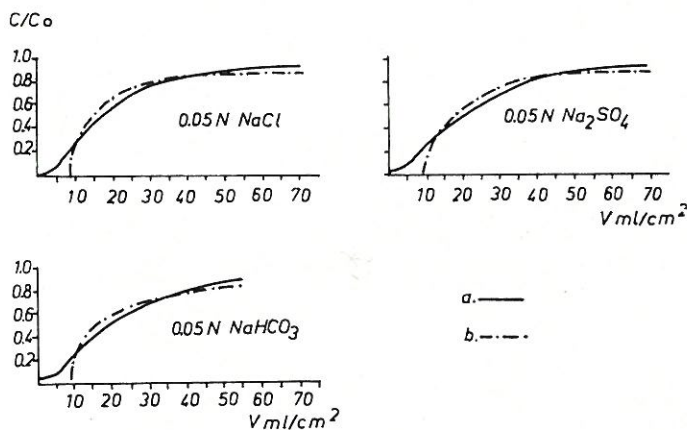


Fig. 2

Breakthrough curves of Na-salt solutions containing different anions. a. measured data; b. values calculated from equation (1)

The distribution according to depth of the exchangeable Na-content of the Ca-soil treated with different amounts of different Na-solutions is shown in Fig. 3. For the easy survey of the Figure, the data measured after the smallest amount of solution passed through the column were represented only at the treatment with NaCl.

By comparing the obtained curves, the following conclusions may be drawn:

1. NaHCO_3 caused the highest Na-adsorption (in this case the max. amount of solution passing through the soil was not more than 50 cm). 0.05 N

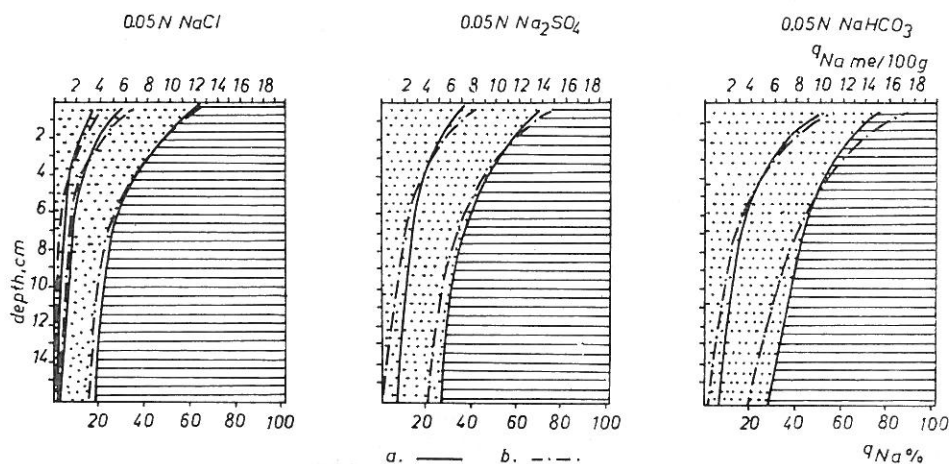


Fig. 3

Distribution — according to depth — of the exchangeable Na-content of a Ca-soil treated with various amounts of different Na-salt solutions. a. measured data; b. values calculated from equation (4)

Na_2SO_4 caused higher alkalization than the NaCl solution. The effect of NaHCO_3 and Na_2SO_4 differing from that of NaCl may be due, on the one hand, to the restricted solubility of the compounds formed in the soil solution. On the other hand, the cation exchange capacity of the exchanging material (thus, the total amount of the fixed cations) as well as the activity of the ions are subject to change depending on the anion environment.

2. The amount as well as the proportion of exchangeable Na increases with the volume of the solution passed through the soil. In the upper strata higher Na-adsorption takes place than in the lower third of the column, and the sodium ions, under the given conditions, cannot entirely replace the adsorbed Ca-ions, even when reaching dynamic equilibrium.

3. The data indicates that equation (4) combined with the GAPON-exchange constant is suitable to give an approximate description of the cation exchange process taking place under the above experimental conditions. On the other hand, it appears that in the case of NaCl the theoretical values follow the curves based on the measured data more closely than in the case of the two other Na-salt solutions.

The results relating to exchangeable Na are in good agreement with the values of the Na-concentration of the soil solution (Fig. 4).

The differences between the theoretical and the experimental data can be accounted for by the simplified conditions of the theoretical model (passing by ion diffusion, channel effect, etc.) apart from experimental errors. Another modifying factor can be that the pore distribution of the column is far from being even: changes in the values of the cation exchange constant and cation exchange capacity, as well as their deviation from the constant value assumed by the theory, are probably also responsible for the differences. It is also

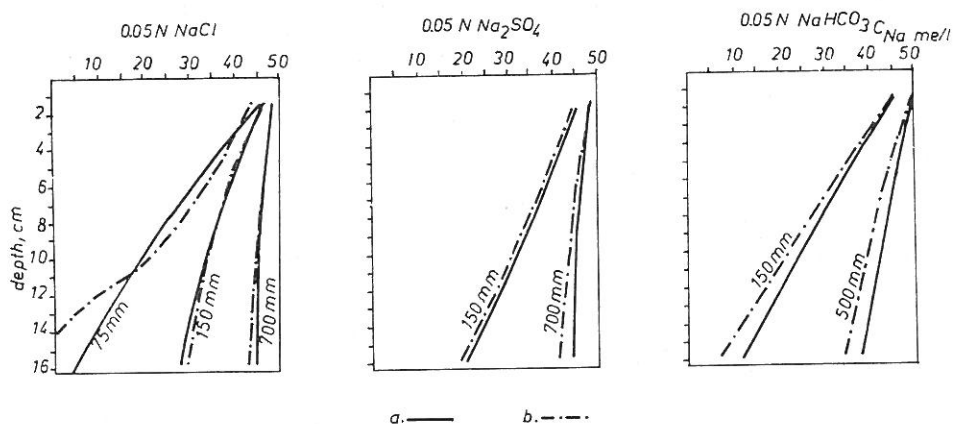


Fig. 4

Na-concentration of the soil solution changing with depth. a. measured data; b. calculated data

possible that under the given conditions equilibrium could not be reached in the required degree since due to dynamic reciprocity the exchange does not take place uniformly in the whole mass of the soil which is in contact with the solution, but some grains are in different phases of exchange (saturation).

Nevertheless, the theoretical relationships seem to be suitable for studying certain regularities, and revealing certain part processes. By widening the application sphere of the theory (extending it to different soils, heteroin systems) we may contribute to the solution of a number of practical problems.

Summary

The influence of Na-salt solutions of different anion compositions passed through monoion Ca-chernozem soils was studied on the basis of the chromatographic theory, relying on the reaction kinetic principles. The theoretical relationships were applied to calculate the breakthrough curves, and to describe the concentration of the exchangeable Na-ions and the cation concentration of the liquid phase (as a function of depth). The curves — representing the distribution according to depth of the exchangeable Na-content of the Ca-soil treated with various amounts of different Na-salt solutions — indicate that:

1. The NaHCO_3 solution caused the highest Na-adsorption. The Na_2SO_4 solution caused a higher extent of alkalization than the NaCl solution.

2. Both the amount and proportion of exchangeable Na increase with the volume of the solution passed through the soil, and Na-fixation is higher in the upper strata than in the lower third of the column.

3. The chromatographic equation combined with the GAPON exchange constant is suitable to give an approximate description of the cation exchange process taking place under the above conditions.

The differences between the theoretical and experimental data can be explained by the simplified conditions of the chromatographic model, and by experimental errors. It is possible, furthermore, that the equilibrium could not be established to the required extent under the given conditions, since the exchange did not take place uniformly in the total mass of the soil but the different soil grains constituting the soil aggregates were in different phases of exchange.

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