5. Chemical and Physico-Chemical Aspects of Soil Salinization and Alkalization Processes

5.1. The salinity aspect in the modelling of soil salinization

The formation and accumulation of salts are due to a large number of geochemical processes taking part in the upper strata of the earth's crust.

Salts soluble in water can originate in two ways, namely, they may be of magmatic origin, or they can form by the weathering of crystalline rocks.

During the geological periods, the magma forming processes and the volcanic and post-volcanic phenomena occurring in the earth's crust facilitated the accumulation of large quantities of chlorides, sulphates and borates in the solutions circulating on the earth and in the ocean, in continental and marine deposits.

Every stage of volcanic activity has resulted in a rise to the surface of new masses of easily soluble salts of magmatic origin. It is probable that the chlorides and sulphates in rocks, soils and oceans trace back at least in part to volcanic action. In the early period of the formation of the earth's surface the salt reserves in the oceans and earth crust were dominated by salts of magmatic origin, particularly by ammonium salts.

The chemical composition of the salts in oceans and continents has changed in the course of the geological and geochemical history of the earth, due to the effects of weathering, biogenesis and soil formation on the continents and of geochemical and biochemical transformation in the oceans. In the geological history of the earth's crust a process of exchange has occurred between land and oceans with a kind of rotation of easily soluble salts. The balance of this circulation is, on the whole, in favour of the oceans, where the total salt reserve consequently grows.

The present composition of ocean salts is the result of the constant inflow from the continents of sulphates and carbonates, and that of sodium, potassium, calcium and magnesium and the formation of the chlorides of these cations. On the other hand the oceans constitute both direct and indirect sources of the salts accumulated on the continents.

In the recent period the weathering of rocks can be considered as one of the main sources of easily soluble salts entering into natural waters, sediments and soils. HILGARD [1910], discussing the origin of salt affected soils, wrote: "They are the natural result of low rainfall, insufficient to leach out of land the salts, that always form in it by progressive weathering of the rock powder of which all soils largely consist". GLINKA [1914] pointed out that salt accumulation is connected with the weathering of rocks, with the transport of weathering products and with the accumulation of transported weathering products in areas with a dry climate and poor drainage.

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According to FERSMAN [In: International Source Book 1967], the geochemistry of salts on land is determined by the sequence of extraction in the course of weathering, by the mobility of the compounds formed and by the sequence of precipitation of the weathering products. POLYNOV and KOVDA [In: International Source Book 1967] applied the FERSMAN [In: International Source Book 1967] theory to the accumulation of salts in soils.

It was recognized very early that salt affected soils can differ in the total quantities of soluble salts accumulated, in the chemistry of soil salinization, in the distribution of water soluble compounds along the soil profile and in the area covered by the complex population of these soils [KOVDA 1946, 1965; KOVDA et al. 1954].

The distribution of soluble salts, and the processes of salt accumulation are influenced by the type of relief under certain geomorphological and hydrogeological conditions.

Geomorphologically, salt accumulation is connected with lowlands, or parts of lowlands, such as: flood plains, deltas, low river terraces, lakes or coastal terraces.

From the point of view of hydrology, the accumulation processes are usually related to regions with temporarily or permanently high water tables. Salt accumulation may often prevail where runoff is slight or virtually absent.

Climatic conditions where evaporation exceeds the runoff either permanently or at least for some time can be characterized as regions of salt accumulation.

The geological, geomorphological and hydrogeological conditions and the climate are determining factors in the type and degree of soil salinization. In non-salt affected soils the salt sources may not be present or the leaching processes may prevail over the processes of accumulation.

For the prediction and description of soil salinization and/or alkalization the following factors have to be analysed [DARAB 1962; DARAB and SZABOLCS 1960].

1. The main actual and potential sources of salts soluble in water have to be identified and quantitatively determined. Such types of salt sources may be salty ground waters, deep sub-surface waters, artesian waters, irrigation waters; seepage waters from high lands, irrigated areas, irrigation canals, reservoirs; inundation of runoff waters; salt water intrusion; salty parent material and geological layers; products of local weathering; air-borne salts; etc.

2. The main features of the salt regime must be known. This involves the knowledge of the variation in the total salt content in the soil with time, solute transport in saturated and unsaturated soil layers; the factors influencing salt movement, such as diffusion, solubility changes, interactions between the solid and liquid phases of the soil, etc.

3. The natural conditions (environmental factors), such as geological, hydrological, geochemical, hydrogeochemical, geomorphological factors and the effect of relief, climate, etc. on the soil salt regime must be analysed and taken into account in modelling soil salinization and desalinization.

4. The impact of human activity can also be an important factor of salt accumulation and leaching.

The most simple model summarizing the effects of different environmental factors and human activity on soil salinization and desalinization is the salt balance. In its simple form, the salt balance expresses the change in the salt

content of soils at a given depth and for a given period [Szabolcs, Darab and Várallyay 1969].

$$\Delta S = S_2 - S_1$$

S_2 = quantity of salts at the end of the observation period (t/ha)
S_1 = quantity of salts at the beginning of the observation period (t/ha)
ΔS = change in salt content in the period of the control; salt balance.

The factors in the general form of the salt balance can be given in more detail.

$$\Delta S = (P + Y + R + G + W + F) - (l_p + l_i + r + g + u)$$

ΔS = salt balance
P = quantity of salts derived from the atmosphere (air-borne salts, rainfall, wind action, etc.)
Y = quantity of salts added with irrigation water
R = horizontal inflow of salts transported by surface waters (runoff, flood, water-logging)
G = horizontal inflow of salt transported by sub-surface water (ground water, layer water, etc.)
W = quantity of salts derived from local weathering products
F = quantity of salts added as chemical amendments (fertilizer, gypsum, etc.)
l_p = quantity of salts leached out by atmospheric precipitation
l_i = quantity of salts leached out by irrigation
r = horizontal outflow of salts transported by surface waters
g = horizontal outflow of salts transported by sub-surface waters
u = quantity of salts assimilated by plants and transported with yield from the area.

The type of balance and the length of the observation period may differ according to the kind of problems to be solved. The balance can be calculated
a) for the total salt content, or for various ions if information is required on salt movement or on specific ion effects,
b) for the whole soil profile from the surface to the water table (general information), for various layers or horizons (if salt profile redistribution, risk of resalinization, leaching efficiency are being studied, etc.),
c) for soil profiles, mapping units or territories,
d) for vegetation periods, irrigation seasons, seasons, years or longer periods of time.

The accuracy and probability of salt or ion balance depends on the homogeneity of the territories to be characterized and the reference period studied, on the accuracy, probability and applicability of the data and information available concerning soil properties and the environmental conditions mentioned above. Consequently, soil investigations should be carried out in sufficient detail to provide adequate data and information on the factors influencing salt movement for the scale of the survey and the aim of the study.

The applicability of salt and ion balances is quite general and it can be useful in solving several theoretical and practical problems.

The results of the salt balances are always the summarized effects of different factors and elements in the balances. To establish limit values for the

Table 5.1

The dissolution of CaCO₃ in solutions containing different concentrations of Na₂SO

The concentration and the composition of equilibrium solutions in $10^3 \cdot$ mole/l					
I	Na^+	Ca^{2+}	SO_4^{2-}	HCO_3^-	CO_3^{2-}
1.41	—	0.51	—	0.77	—
10.07	5.91	0.66	2.67	0.89	—
17.37	10.44	0.83	4.98	1.05	—
82.82	58.29	0.95	25.58	1.23	—
162.92	107.01	1.07	53.22	1.68	—
805.10	539.40	1.23	265.30	1.86	0.09

classification, amelioration and prevention of soil salinization, the origin and properties of mean salt compounds accumulating in salt affected soils and the interpretation of the effect of different soil and environmental factors are necessary.

From the point of view of chemistry, the solubility of salts is one of the most important properties characterizing the mobility of salts in soils and it is the property which influences the degree of salinization and the distribution of salts with different chemical compositions.

The solubility of salts is characterized by the activity product of the ions formed from the salt under investigation. The activity product of the ions, the "thermodynamic solubility product" of the salt is constant and does not depend either on the composition or the total ionic concentration of the solution, if it is saturated with the salt to be described by its solubility product:

$$(C)^{\nu A} \cdot (A)^{\nu B} = K_{CA} \tag{5.1}$$

(C) = the activity of the cation in saturated solution, mole/l
(A) = the activity of the anion in saturated solution, mole/l
ν_A = the number of cations in the salt
ν_B = the number of anions in the salt
K_{CA} = the thermodynamic solubility product of the salt $C_{\nu_A} \cdot A_{\nu_B}$

The activities of the ions can be expressed as the product of the concentrations and activity coefficients of the same ions:

$$K_{CA} = \left(\gamma_C^{\nu A} \cdot [C]^{\nu A} \right) \cdot \left(\gamma_A^{\nu B} [A]^{\nu B} \right) \tag{5.2}$$

γ_C = the activity coefficient of the cation
γ_A = the activity coefficient of the anion
$[C]$ = the concentration of the cation, mole/l
$[A]$ = the concentration of the anion, mole/l

The activity coefficients of the ions are measures of the electrostatic interactions between ions with opposite charges. The electrostatic interaction between the ions increases with an increase in the total ionic concentration of the solution [ADAMS 1971; BABCOCK and MARION 1972]. This means that an increase in the ionic concentration of the solution decreases the activity of the ions and increases the solubility of the salts saturating the solution and

the ion concentration product of the saturating salt (Table 5.1). In a mixed salt solution the solubility of the salts containing common ions decreases with an increasing concentration of the common ions (Table 5.2).

In many cases of the dissolution of salts the water acts not only as the solvent, but chemical processes take place by which the dissolving salt combines with water to form an acidic and a basic part.

In the case of calcium carbonate dissolution the following reactions take place:

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$$

$$CO_3^{2-} + HOH \rightleftharpoons HCO_3^- + OH^-$$

$$HCO_3^- + HOH \rightleftharpoons H_2CO_3 + OH^-$$
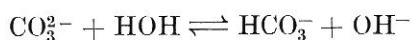
If the system is in equilibrium, the dissolution of calcium carbonate can be described by the following equations:

$$K_{CaCO_3} = (Ca^{2+}) \cdot (CO_3^{2-})$$

$$K' = \frac{(HCO_3^-) \cdot (OH^-)}{(CO_3^{2-})}$$

$$\frac{K'}{K_w} = \frac{(HCO_3^-)}{(CO_3^{2-}) \cdot (H^+)} = \frac{1}{K_2} \tag{5.3}$$

$$K'' = \frac{(H_2CO_3) \cdot (OH^-)}{(HCO_3^-)}$$

$$\frac{K''}{K_w} = \frac{(H_2CO_3)}{(HCO_3^-) \cdot (H^+)} = \frac{1}{K_1} \tag{5.4}$$

$$\frac{1}{K_{d_1} K_{d_2}} = \frac{(H_2CO_3)}{(CO_3^{2-}) \cdot (H^+)^2} \tag{5.5}$$

K' and K'' = the first and second constants of carbonate ion hydrolysis
K_{d_1} and K_{d_2} = the first and second dissociation constants of carbonic acid
K_w = the ion activity product of water
( ) = ion activity, mole/l

Expressing the carbonate ion activity using equation (5.5) and substituting this value in the solubility product of calcium carbonate, it is found that the solubility of calcium carbonate depends on the pH value and the carbonic acid concentration of the solution

$$(Ca^{2+}) = \frac{K_{CaCO_3}}{K_1 K_2} \cdot \frac{(H_2CO_3)}{(H^+)^2} \tag{5.6}$$

<p style="text-align:center">Table 5.2</p>

The dissolution of $CaSO_4 \cdot \frac{1}{2} H_2O$ in saturation extracts of salt affected soils with different ionic concentrations

Treatment	I $10^3 \cdot$ mole/l	(SO_4) percentage	Ca^{2+}	SO_4^{2-}	K_{CaSO_4} $10^4 \cdot$ (mole/l)^2
			$10^3 \cdot$ mole/l		
a	12.67	9.52	0.59	0.53	
b	75.13		15.56	17.08	2.66
a	14.80	16.34	0.49	1.01	
b	81.06		15.84	19.41	3.09
a	15.27	12.70	0.65	0.66	
b	76.53		15.54	18.56	2.88
a	15.27	28.80	0.55	2.78	
b	76.81		15.40	18.30	2.82
a	16.20	22.24	0.47	1.52	
b	80.70		14.19	19.83	2.81
a	18.19	34.10	0.38	2.28	
b	87.21		15.96	20.88	3.33
a	27.39	43.46	0.76	4.40	
b	92.37		15.55	21.10	3.28
a	27.32	55.03	0.57	5.88	
b	96.76		15.45	25.67	3.97
a	36.37	32.83	2.98	3.92	
b	121.10		18.83	25.52	4.81
a	36.79	53.76	1.73	6.65	
b	105.39		14.53	25.88	3.76
a	60.21	52.54	0.78	11.16	
b	127.42		15.40	32.81	5.05
a	61.42	63.48	0.26	15.02	
b	103.42		13.31	24.91	3.32
a	130.34	75.50	0.90	35.32	
b	185.08		14.90	50.76	7.56
a	204.60	79.70	0.98	50.47	
b	240.70		12.94	65.27	8.45
a	207.60	80.60	0.78	58.60	
b	252.90		14.12	67.56	9.53
a	209.80	74.70	7.26	55.16	
b	272.80		21.14	64.90	13.70
a	223.80	84.40	0.90	66.68	
b	256.10		12.48	68.56	8.56

a = before saturation with calcium sulphate
b = after saturation with calcium sulphate

Sulphate percentage $= \dfrac{SO_4^{2-}}{\Sigma \text{anion}} \cdot 100$

K_{CaSO_4} = ion concentration product of $CaSO_4$

As the carbonic acid concentration increases, the hydrogen ion concentration also increases, resulting in an increase in calcium carbonate solubility [SUAREZ 1977]. The solubility of calcium carbonate decreases in the case of increasing carbonate concentration and pH value and decreasing carbonic acid concentration in the solution.

The solubility of salts accumulated in soils under different conditions plays an important role in the formation and amelioration of saline and alkali soils.

The soluble salt content of soils is usually low and the total ionic concentration of the soil solution does not exceed 0.01 mole/l. In the case of salt affected soils, the ionic concentration of the soil solution increases and it can be as high as 0.1 — 5 mole/l or even more [International Source Book 1967; DARAB, CSILLAG and PINTÉR 1977].

The salts accumulate in reverse sequence of their solubility. This is why the sparingly soluble salts, such as Ca- and Mg-bicarbonate, are dominant in the liquid phase of non-salt affected soils.

Salt accumulation develops if the leaching of salts becomes restricted and/or the soil layer is connected with salt sources, such as mineralized ground water, irrigation water, etc.

As the salt accumulation prevails over the leaching the absolute and relative quantities of salts with better solubility increase. If the leaching processes become the dominating processes in a salt affected soil, the readily soluble salts occur in the drainage water with the highest concentration of all the salts leached out and in the soils the concentration ratio shifts in favour of salts with poorer solubility. This results in the vertical distribution of the salts, and the changes in the ionic composition of the salts along the soil profile reflects the dominating process (leaching or accumulation) in the soil. The horizontal distribution of soluble salts gives information about the factors regulating the salt regime and salt balance in the soil cover of the investigated area or territory and about the efficiency of these factors.

The accumulation of salts affects the water and nutrient uptake of the plants and the water regime, the physico-chemical and chemical properties of the soil. The physical, chemical and physiological effects of the salts accumulated depend on the composition and on the properties of the main compounds leading to the formation of different types of salt affected soils.

The main kinds of salts which lead to the formation of salt affected soils, together with their origin and properties, are summarized in Table 5.3.

From the point of view of modelling the salt movement in the soil, the salts can be distinguished by their solubilities and adsorbabilities.

Among the salts taking part in the accumulation, the chlorides are the most mobile compounds. The sodium, calcium and magnesium chlorides have high solubility. They are partly of magmatic origin and are partly the product of the weathering of crystalline rocks. They occur in saline ground water, lakes and soils in desert and semi-desert regions. They are the main compounds in sea water, in the salts accumulated on sea shores and in marine deposits. Due to this high solubility of chloride compounds their quantities increase with increasing soil salinity. The chloride part of the salts moves freely with the water. The exchange between the cations of the solid and liquid phases of the soil in chloride containing systems leads to an equilibrium at a low degree of sodium saturation due to the easy solubility of the exchange products.

Table 5.3

**Origin and properties of main salt compounds which may accumulate
in salt affected soils**

Origin and properties of salts	General feature	Ca-salts	Mg-salts	Na-salts
Carbonates		$CaCO_3$	$MgCO_3$	Na_2CO_3
Occurrence	Every region, in soil, subsoil, ground water, surface water	In fresh river water, fresh ground water, soils (5 – 80%), mostly in steppe and desert regions	As for $CaCO_3$	In surface and ground water when mineralization reaches 0.5 – 3 g/l, in soils (mainly in the absence of gypsum), in deposits of every region
Origin	Predominantly weathering products	Predominantly weathering products in sedimentary rocks, and from ground water	Predominantly weathering products	Weathering products, Hilgard reaction, Gedroiz reaction, sulphate reduction, and from plants
Solubility	Varying	Low, depending on CO_3^{2-} and CO_2 concentration, pH value in solution $K = 9.3 \cdot 10^{-9}$ $[CaCO_3] = 9.8 \cdot 10^{-3}$ g/l	Low, but higher than that of $CaCO_3$ $K = 2 \cdot 10^{-4}$ $[MgCO_3] = 1.2$ g/l dolomite: dissolution is poor	Highly soluble
pH in solution	Alkaline	Alkaline	Alkaline	Up to pH 12
Toxicity to plant	Different depending on solubility	No toxicity	Toxic due to alkaline hydrolysis	Very toxic due to the high solubility and alkaline reaction
Effect on soil	Different, depending on mobility and solubility	Different in forms: medium concretions, hardpan, etc.	Rare in free form mainly dolomite or dolomitized $CaCO_3$ concretions	Peptization of soil colloids, low water permeability, poor water-physical properties, non leachable
Sulphates		$CaSO_4$	$MgSO_4$	Na_2SO_4
Occurrence	In deposits, soils and ground water of desert and steppe regions	In ground water and soils of desert and semi-desert regions	In saline soils and saline ground water, in desert and semi-desert regions	In saline ground water, saline lakes, and saline soils of desert and semi-desert regions

Table 5.3 continued

Origin and properties of salts	General feature	Ca-salts	Mg-salts	Na-salts
Sulphates		$CaSO_4$	$MgSO_4$	Na_2SO_4
Origin	Partly weathering products, partly of magmatic origin	Partly weathering products, and partly formed secondarily from SO_4^{2-} of magmatic origin in sediments due to the reaction of Na_2SO_4 and $CaCl_2$	The same as for $CaSO_4$	Partly weathering products, partly of magmatic origin
Solubility	Variable, but better than carbonates	$K_{\text{gyps.}} = 1.3 \cdot 10^{-4}$ $C = 2$ g/l $K_{CaSO_4} = 6.1 \cdot 10^{-5}$ $C = 1$ g/l	High solubility $C = 262$ g/l	High solubility 280 g/l (25 °C), depends very much on the temperature
pH in solution	Nearly neutral, or slightly acidic	Slightly acidic	Slightly acidic	Nearly neutral
Toxicity to plant	Different, depending on solubility and concentration	No toxicity	Very toxic	Two or three times less toxic than that of $MgSO_4$
Effect on soil	Different, depending, on compounds	Forms transparents, nodules, compact layer used for soil amelioration	Always accumulates in combination with other soluble salts, reclamation by leaching	Accumulates together with other easily soluble salts, in warm period dehydration, Reclamation by leaching in the dry season
Chlorides		$CaCl_2$	$MgCl_2$	NaCl
Occurrence	In saline ground water, saline lakes and saline soils of desert and semi-desert regions	In waters of saline lakes (at salinity 400 — 500 g/l), deeply-lying ground water	Common in saline ground waters, saline lakes, saline soils, only at very high salinity	In sea water and marine sediments of coastal area, saline surface water, saline ground water, saline soil of desert and semi-desert regions
Origin	Partly of magmatic origin, partly weathering products	Partly of magmatic origin, partly weathering products	Partly magmatic, partly weathering products	Magmatic and only partly weathering products

Table 5.3 continued

Origin and properties of salts	General feature	Ca-salts	Mg-salts	Na-salts
Chlorides		CaCl$_2$	MgCl$_2$	NaCl
Solubility	High solubility	High solubility	High solubility 353 g/l	High solubility 264 g/l
pH in solution	Nearly neutral or slightly acidic	Slightly acidic	Nearly neutral	Nearly neutral
Toxicity to plant	High toxicity	Toxic at high concentration	Very toxic	Very toxic
Effect on soil	Saline soil physiological effect	Seldom present in soil (forms CaCO$_3$ or CaSO$_4$), only at very high salinity	Together with CaCl$_2$ very hygroscopic, saline soils containing CaCl$_2$ and MgCl$_2$ remain humid for a long time after rain, reclamation by intensive leaching	In saline soil together with Na$_2$SO$_4$ and MgSO$_4$, amelioration by leaching in absence of gypsum, alkalization

The mobility of sulphates and their role in the formation of salt affected soils are more diverse. They are partly weathering products, and may be partly of magmatic origin. They occur mainly in the ground water, deposits and soils of deserts and semi-desert regions. Their mobility, their role in soil formation and their effect on the plant growth depend on the kind of cation to which the sulphate is bound. Calcium sulphate has moderate solubility and mobility. It can occur in soils in different quantities and different forms, ranging from transparents and nodules, to a compact porous layer. Calcium sulphate occurs in two forms in nature, differing from each other in crystal structure and in solubility. The solubility of gypsum is 2 g/l, while in the case of anhydrite, the saturated solution has a calcium sulphate concentration of 0.7 – 1 g/l. Their thermodynamic solubility products also differ from each other by an order of magnitude [BENNETT and ADAMS 1972, 1976]. The presence of gypsum in soils indicates that there is a relatively stable concentration of calcium ions in the soil solution. The value of the sodium adsorption ratio depends on the total ionic concentration of the liquid phase of the soil, if the soil solution is saturated with calcium sulphate. When modelling the soil forming processes, the solubility product of calcium sulphate and the way it changes with the total ionic concentration have to be taken into account [BENNETT and ADAMS 1972, 1976].

Magnesium sulphate has high solubility. The concentration of a saturated magnesium sulphate solution is as high as 262 g/l. Due to its easy dissolution it is one of the most toxic salts for plants.

Magnesium sulphate is a typical compound of saline soils in desert and semi-desert regions. In soils it always accumulates in combination with other soluble salts. It can be removed from saline soils by leaching.

From the point of view of cation exchange it is taken for granted that the magnesium ions behave identically with the calcium ions [USDA Handbook No. 60. 1954].

In approximate models of the soil processes this assumption can be accepted. The fact that magnesium can occur in the crystal network of layer silicate has to be taken into account even in the case of a very simple model.

Sodium sulphate dissolves easily in water. The saturation concentration of sodium sulphate is 280 g/l at 25 °C, and it depends very much on the temperature. It is a typical compound of saline soils, saline ground waters and lakes in desert and semi-desert regions. As a result of the temperature dependence of the solubility, sodium sulphate accumulates in the summer period together with other easily soluble salts. In the winter its solubility decreases and most of the sodium sulphate remains in the top layer of the soil. When modelling the leaching of sulphate saline soils in winter the temperature dependence of sodium sulphate dissolution has to be taken into account.

The carbonates are predominantly weathering products and they can occur in every region in the soil, subsoil, ground water, surface water and marine deposits. The role of carbonate in soil forming processes, its effect on colloid properties and the water regime of soils and the toxic effect on plants depend very much on the type and character of the carbonate-containing compounds, on the quantities of carbonate accumulated and on the solubility of the carbonate compounds. A common feature of all the carbonates occurring in soils is that, being salts of a weak acid and a strong base, they are subject to alkaline hydrolysis and therefore have alkaline reactions in solution.

Calcium carbonate can occur in every region in fresh river water and ground water and in soils. Its quantity in the soil varies in a wide range (between $5-80\%$). Calcium carbonate is found in sediments and soils in the form of pseudomycelia, concretions with different diameters, hardpan, etc. Calcium carbonate is a salt with very low solubility. Its solubility product amounts to $0.93 \cdot 10^{-8}$. Assuming that the activities and concentrations of calcium and carbonate ions are equal in a very diluted solution, or in pure water, a solution saturated with calcium carbonate has a concentration of about 10 mg/l. As the partial pressure of the carbon dioxide in the soil solution increases, the dissolution of calcium carbonate increases rapidly as a result of the formation of calcium bicarbonate.

When modelling soils processes, the solubility product of calcium carbonate and the factors influencing dissolution, such as carbon dioxide concentration, the pH value of the soil solutions, and the variation of the first and second dissociation constants of carbonic acid with the ionic concentration of the soil solution, have to be taken into consideration.

Large amounts of calcium carbonate can pass into the soil horizons from sediments and from the ground water, if it lies close to the surface. Horizons containing a high amount of calcium carbonate may be strongly cemented and practically impenetrable both for plant roots and for water.

Magnesium carbonate has higher solubility than calcium carbonate. The concentration product of magnesium and carbonate ions is $2 \cdot 10^{-4}$ at 20 °C.

The concentration of water saturated with magnesium carbonate amounts to about 1.2 g/l. During the dissolution, alkaline hydrolysis takes place and the saturated solution of magnesium carbonate may be highly alkaline. The strong alkaline reaction may cause stress in plants. The accumulation of mag-

nesium carbonate in a free form is very rare in soils. This is due to the adsorption of magnesium by clay and also to the formation of dolomitized calcite and dolomite during the accumulation of carbonates in sediments and soils. The solubility of minerals dolomitized to different degrees is a complex function. In some cases it has been shown that Mg^{2+} ion favoured the precipitation of aragonite over calcite.

According to DONER and PRATT [1969] calcium carbonate precipitated in $MgCl_2$ solution is more soluble than calcite. HASSETT and JURINAK [1971] suggest that the effect of Mg^{2+} ion concentration in water on the precipitation and dissolution of carbonates is a complex function. The dissolution of the carbonate minerals depends on the specific surface, the magnesium content of the minerals and the chemistry of the solution in equilibrium with the solid phases. In relation to the cation exchange phenomena the behaviour of calcium and magnesium ions is taken as being the same.

Sodium carbonate is a highly soluble compound. As a result of hydrolysis, a solution containing sodium carbonate is always alkaline up to pH 12. Because of its high solubility and strong alkalinity, sodium carbonate solution is always very toxic to plants and causes the peptization of soil colloids, low water permeability and poor water physical properties in soils [SZABOLCS 1965, 1969].

Sodium carbonate can occur in surface and ground water in deposits and soils in every region [KOVDA and SAMOYLOVA 1969]. The main source of the accumulation of sodium carbonate is the weathering of crystalline rocks in water containing carbon dioxide, but it can form in smaller quantities due to chemical reaction [HILGARD 1910], ion exchange [GEDROITZ 1922] and biological processes as well. In solutions with a medium degree of mineralization $(0.5-3 \text{ g/l})$ sodium carbonate is usually the dominant compound of the salts to be dissolved.

The reactions of a solution containing sodium carbonate are determined by the partial pressure of carbon dioxide and the total ionic concentration of the solution. When modelling the behaviour of sodium carbonate solution, the dependence of the first and second dissociation constants of carbonic acid on the total ionic concentration has to be taken into account.

Due to the highly alkaline reaction of sodium carbonate solution and the poor solubility of the compounds formed in the cation exchange process in soils containing sodium carbonate, the soil solution may be dominated by sodium ions to $90-95$ percent and the solid phase may also be saturated by sodium to a high degree. In many cases of modelling the processes taking place in soils containing sodium carbonate it is more advisable to describe the movement of mobile sodium compounds, than to separate them into soluble and exchangeable forms.

5.2. Interaction in soil solid and liquid phases in the formation and properties of sodic and alkaline soils

The cation exchange phenomena and the adsorption of sodium ions play an important, if not decisive role in the chemistry of sodic and alkaline soils [DARAB 1965; DARAB and RÉDLY 1967; GEDROITZ 1912, 1914, 1925; KELLEY 1948; 'SIGMOND 1929; SZABOLCS 1969].

By ion exchange the reversible process is meant, by which cations and anions are exchanged between solid and liquid phases, if these are in close contact with each other.

Theoretically there are different approaches to express the distribution of ions between the solid and liquid phases at equilibrium [KRISHNAMOORTHY and OVERSTREET 1950; LAGERWERFF and BOLT 1959; LAUDELOUT and VAN BLADEL 1965; DE VAULT 1943]. Formally most of the theories lead to the equations being identical with the so-called mass action relationship:

$$\frac{(A_{ad})^n}{(B_{ad})^m} = K_B^A \frac{(A^{m+})^n}{(B^{n+})^m}$$

(A_{ad}) and (B_{ad}) = the activity of A^{m+} and B^{n+} ions on the adsorbent.
(A^{m+}) and (B^{n+}) = the activity of the same ions in the intermicellar solution
m and n = the valences of cations A and B, respectively.

From the equation applied to characterize the cation exchange equilibria it is evident that the kind and quantity of ions adsorbed on the surface of soil particles depend on:

— the activity ratio of the same cations in the solution
— the valences of cations in the case of non-symmetrical exchange
— the total concentration of the intermicellar solution.

It has been proved in several experiments that the relative replacing power of cations depends on the valences of the adsorbed and counter ions. In the case of non-symmetrical exchange, the relative replacing power of the cations increases with the valence and follows the order $M^+ < M^{2+} < M^{3+}$ ...

The more diluted the soil solution system containing cations with different valences is, the more the equilibrium is displaced in such a direction that the adsorption of cations with higher valence increases and the adsorption of cations with lower valence decreases. On increasing the ionic concentration of the intermicellar solution the equilibrium shifts in favour of cations with lower valences [BABCOCK 1963a; DARAB and RÉDLY 1967].

The effect of the valence of exchangeable and counter ions and the dilution of the intermicellar solution on the sodium saturation is reflected in the data obtained in bentonite-$CaCl_2$-NaCl solution systems (Table 5.4).

In the asymmetrical exchange of sodium and calcium ions, the adsorption shifts in favour of the calcium ions as the ionic concentration of the free solution decreases, because

— the Na^+ concentration decreases much faster during dilution than the Ca^{2+}, if the ratio of the exchanger to the solution is kept constant,

— the activity coefficients are influenced by the valences and sizes of the ions and by the total ionic concentration of the solution. The ratio of the activity coefficients of sodium and calcium ions decreases much faster in the free electrolyte solution during the dilution of suspension than it does on the exchanger,

— the dilution effect can be achieved either by decreasing the ionic concentration of the intermicellar solution, by decreasing the ratio of the solution

The amount of exchangeable sodium in bentonite-NaCl-CaCl₂ solution systems
The ratio of bentonite to solution 1 : 100

I mole/l	[Na⁺]	[Ca²⁺]	$\frac{[Na^+]}{[Ca^{2+}]}$	$\frac{[Na^+]^2}{[Ca^{2+}]}$	$\frac{[\gamma_{Na}^+]^2}{[\gamma_{Ca}^{2+}]}$	Exchangeable Na⁺	CEC	ESP
	$10^4 \cdot$ mole/l					me/100 g		
$5.0 \cdot 10^{-3}$	4.6	0.14	32.62	0.15	1.179	16.03	96	16.7
$7.5 \cdot 10^{-3}$	7.1	0.23	31.21	0.22	1.223	23.00		23.9
$1.0 \cdot 10^{-2}$	9.2	0.28	32.91	0.30	1.262	28.00		29.4
$2.5 \cdot 10^{-2}$	21.9	0.71	30.95	0.68	1.444	38.07		39.7
$5.0 \cdot 10^{-2}$	41.3	1.52	27.26	1.12	1.682	50.85		53.0
$2.5 \cdot 10^{-3}$	1.89	0.11	18.60	0.03	1.123	8.5	96	8.9
$5.0 \cdot 10^{-3}$	4.31	0.18	24.70	0.10	1.179	12.0		12.5
$7.5 \cdot 10^{-3}$	7.04	0.26	26.90	0.19	1.223	15.15		15.8
$1.0 \cdot 10^{-2}$	9.09	0.35	25.70	0.24	1.262	16.45		17.1
$2.5 \cdot 10^{-2}$	21.90	1.06	20.70	0.45	1.444	25.15		26.2
$2.5 \cdot 10^{-3}$	2.06	0.11	18.60	0.04	1.123	4.23	96	4.4
$5.0 \cdot 10^{-3}$	4.31	0.23	18.90	0.08	1.179	7.70		8.0
$7.5 \cdot 10^{-3}$	6.52	0.34	18.90	0.13	1.223	9.78		10.2
$1.0 \cdot 10^{-2}$	8.26	0.51	16.40	0.13	1.262	11.82		12.3

to the adsorbent, or by increasing the cation exchange capacity of the adsorbent (Table 5.5).

In all these cases the increase in the preference of calcium ion adsorption over that of sodium ions is due to an increase in the difference in the concentration of the micellar and intermicellar solutions and to an increase in the potential differences between the surface of the adsorbent and the free solution. The preference of sodium ion adsorption comes to the fore as the concentration of free electrolytes increases, the solution-adsorbent ratio increases, or the cation exchange capacity of the adsorbent decreases [DARAB and RÉDLY 1967].

The total ionic concentration of the soil solution varies through a wide range [International Source Book 1967; KOVDA 1946; KOMAROVA and KRJUKOV 1959]. In non-saline soils it is relatively low and does not usually exceed 0.01 mole/l. In salt affected soils, depending on the chemistry and degree of salinization and/or alkalization, the salt concentration can be as high as 0.1 — 5 mole/l, or even more (Table 5.6).

In solutions with high concentration of salts, a special electrolyte "structure" is formed, due to the electrostatical interaction of the ions [DAVIES 1962; MINKIN et al. 1977; RAO et al. 1968; TANJI 1969]. This interaction has an effect on the concentration of ions with free valences and as a result of the formation of the electrolyte "structure", it influences several properties of the electrolyte, including the degree of dissociation of the dissolved salts and the ratio of ion activities in the solution [ADAMS 1971; BENNETT and ADAMS 1972, 1976; NAKAYAMA 1968; NAKAYAMA and RASNICK 1967; RAO et al. 1968]. The ion-pair formation model is one of the approaches to describe the electrolyte "structure" formed under the interaction of ions with opposite charges [ADAMS 1971].

The amount of exchangeable sodium at different concentrations of bentonite and different ionic concentrations of solution in bentonite-NaCl-CaCl₂ solution suspensions

I mole/l	Bentonite: solution	$[Na^+]$	$[Ca^{2+}]$	$\dfrac{[Na^+]}{[Ca^{2+}]}$	Exchangeable Na⁺		CEC	ESP
		$10^2 \cdot$ mole/l			me/100 g	me/l		
1.14 · 10⁻²	1 : 50	8.17	0.16	51.6	14.4	3.10	18.7	16.6
	1 : 75	8.34	0.16	52.2	18.1	2.30	11.8	19.5
	1 : 100	8.34	0.16	52.2	19.4	2.00	9.6	21.2
	1 : 200	8.34	0.15	57.6	29.8	1.30	4.0	32.9
1.0 · 10⁻²		6.95	0.69	10.1	5.98	0.60		6.2
5.0 · 10⁻²	1 : 10	34.30	3.69	9.3	16.83	1.68		17.5
1.0 · 10⁻¹		86.90	7.88	11.0	40.35	4.03		42.0
1.0 · 10⁻²		7.83	0.39	20.1	11.03	0.44		11.5
5.0 · 10⁻²	1 : 25	38.70	1.50	25.8	31.36	1.25		32.7
1.0 · 10⁻¹		100.01	4.45	22.5	66.81	2.67		69.6
1.0 · 10⁻²		8.17	0.16	51.1	14.30	0.29		14.9
5.0 · 10⁻²	1 : 50	40.40	0.79	51.1	50.00	1.00		52.1
1.0 · 10⁻¹		105.20	2.30	45.7	97.17	1.94		100.0

The average of CEC for bentonite: 90.5 me/100g

Solutions of sodium carbonate and sodium bicarbonate (Table 5.7) and saturation extracts of sodium carbonate solonchak (Profile No. 1.) and solonchak solonetz (Profile No. 2.) and sulphate-containing solonetz soils (Profiles Nos. 7 and 109) (Table 5.8) were analysed to evaluate the applicability of the ion-pair formation model to characterize the electrochemical behaviour of mixed salt solutions. The well-known method of iteration was applied to calculate the $NaCO_3^-$ and $NaHCO_3^0$ ion pair concentrations in the sodium carbonate and bicarbonate solutions (Fig. 5.1).

Applying the same programme for the computation of ion-pair concentrations in saturation extracts, negative ion concentrations are obtained as intermediary values in 50 percent of the cases. The method of calculation is modified by the formation of weighted averages for the ion concentrations after each iterative step.

The deviation of the function of concentration from the abscissa is expressed by the introduction of an error function containing the ratio of the sum of ion-pair concentrations to the analytical concentration of the ion. The concentration of the ion "i" in the "nth" step of iteration is given by the relationship:

$$C_{i\,(iterated)} = \frac{C_{i(n-1)}\,EF + C_{i(n)}}{EF + 1} \tag{5.7}$$

C_i = the concentration of the ion "i", mole/l

EF = error function

$EF = 1$ the concentration function is convergent if the original method using differences in concentration is applied.

7

Table 5.6

**The concentration ranges of soil solutions at different degrees of salinization
(calculated values)**

Total salt content g/100 g	Moisture content at		Salt concentration of soil solution at			
	Field capacity	Wilting point	Field capacity	Wilting point	Field capacity	Wilting point
	g/100 g		g/l		mole/l	
0.1	35	17 26 31	2.86	5.88 3.85 3.23	$4.77 \cdot 10^{-2}$	$9.8 \cdot 10^{-2}$ $6.42 \cdot 10^{-2}$ $5.38 \cdot 10^{-2}$
0.2	35	17 26 31	5.72	11.76 7.70 6.46	$9.53 \cdot 10^{-2}$	$19.60 \cdot 10^{-2}$ $12.80 \cdot 10^{-2}$ $10.80 \cdot 10^{-2}$
0.5	35	17 26 31	14.30	29.40 19.25 16.15	0.24	0.49 0.32 0.27
1.0	35	17 26 31	28.6	58.80 38.50 32.30	0.48	0.98 0.64 0.54
1.5	35	17 26 31	42.9	88.20 57.75 48.45	0.72	1.47 0.96 0.81
2.0	35	17 26 31	57.2	117.60 77.00 64.60	0.96	1.96 1.28 1.08

Table 5.7

Chemical composition of sodium carbonate and bicarbonate solutions

Ratio of dilution	pH 24 °C	Concentration of			I	Activity of Na^+	γ_{Na^+}	
		Na^+	CO_3^{2-}	HCO_3^-			a	b
		$10^3 \cdot$ mole/l						
Standard solution	10.04	552.20	188.60	193.15	749.85	270.00	0.488	0.641
1 : 5	10.09	110.40	37.24	39.51	149.60	77.00	0.697	0.750
1 : 10	10.07	55.22	18.07	20.85	74.18	41.00	0.742	0.797
1 : 25	10.02	22.39	7.40	7.53	29.76	17.50	0.781	0.851
1 : 50	9.97	10.78	3.57	4.51	14.79	9.40	0.872	0.886
1 : 100	9.54	5.22	1.73	2.42	7.28	4.60	0.881	0.915
1 : 500	9.73	1.04	0.28	0.60	1.38	0.87	0.837	0.960

a) Calculated from the measured activity and concentration of sodium

b) Calculated from the DEBYE and HÜCKEL equation: $-\lg \gamma_i = \dfrac{Z_i^2 A \sqrt{I}}{1 + Bv_i \sqrt{I}}$;

z_i = the valence of ion "i"; v_i = the diameter of the hydrated ion; A, B = constants.

Table 5.8

Chemical composition of saturation extract of salt affected soils

Profile Nos. and depth of sampling cm	pH	Ca^{2+}	Mg^{2+}	Na^+	CO_3^{2-}	HCO_3^-	SO_4^{2-}	Cl^-	I
		$10^3 \cdot$ mole/l							
No. 1									
0—3	9.35	0.25	0.35	95.30	4.75	38.10	17.05	17.70	120.30
3—10	10.15	0.32	0.28	81.50	8.90	38.80	4.90	15.80	96.84
10—20	9.70	0.36	0.45	66.70	7.20	30.00	5.45	17.80	84.15
20—30	9.90	0.11	0.07	39.70	4.45	15.40	2.30	14.40	48.10
30—40	9.55	0.54	0.36	33.50	2.65	11.30	3.70	9.60	41.69
40—50	9.75	0.62	0.30	36.00	3.05	14.60	2.90	5.55	41.80
No. 2									
3—10	10.10	0.54	0.29	88.50	8.90	44.60	7.05	11.20	105.70
10—20	10.40	0.42	0.26	82.80	3.55	56.70	5.15	9.35	93.16
20—30	10.40	0.33	0.75	68.70	5.60	45.10	3.15	8.63	80.86
40—50	9.75	0.53	0.40	19.50	3.55	8.90	1.35	5.30	28.50
50—60	9.40	1.05	0.53	17.70	1.10	8.60	4.25	4.50	29.25
No. 7									
10—20	6.87	1.48	1.33	45.09	—	8.44	21.70	0.00	75.78
20—40	6.44	3.50	3.55	102.17	—	2.82	57.55	1.37	182.40
40—60	6.75	6.61	5.76	133.40	—	1.89	76.30	3.10	246.50
60—80	7.64	11.27	9.17	186.64	—	1.53	104.34	3.17	345.20
80—100	7.61	2.29	2.17	64.60	—	7.71	33.03	3.88	113.10
100—200	7.94	0.95	1.08	84.75	—	4.64	44.75	3.55	140.00
120—140	8.22	0.90	0.65	63.11	—	7.09	31.23	3.38	102.30
No. 109									
0—10	6.75	1.11	1.11	9.66	—	5.22	2.22	0.00	16.32
20—40	6.80	0.95	1.56	18.22	—	6.16	4.72	9.30	31.23
40—60	7.10	0.90	3.62	31.34	—	3.93	11.75	15.58	57.96
60—80	7.75	1.08	3.85	35.13	—	4.21	11.23	17.23	60.58
80—100	7.83	0.68	2.53	25.58	—	3.35	7.03	13.67	41.75
100—120	7.50	0.63	1.85	18.92	—	5.37	6.93	10.74	36.32
120—140	7.49	0.69	1.14	10.12	—	6.60	2.52	5.46	19.77

EF > 1 the new iterated value of the weighted average of the concentration shifts towards the previous one and the value of the error function approaches 1 with an increasing number of iterative steps. The calculation is taken to be complete if the difference between the concentrations in two subsequent steps of iteration is less than 1 percent and the value of the error function is equal to 1 (Fig. 5.2).

Computation carried out with the data of sodium carbonate and bicarbonate solutions and with soil saturation extracts verified that the modified programme of iteration, i.e. the introduction of weighted averages for the ion concentrations and the correction of the matrix effect of the solution compounds with an error function, can be applied for electrolytes of any concentration and composition.

The applicability of the ion-pair formation model to characterize the electrolyte properties is proved by comparing the activities of sodium ions calculated by subtracting the sum of ion-pair concentrations with those measured with an ion-selective electrode. The calculated and measured values of ion activities agree both in the case of sodium carbonate and bicarbonate solutions and for saturation extracts (Table 5.9).

7*

Table 5.9

Sodium ion activity in sodium carbonate and bicarbonate solution and in saturation extracts of sulphatic solonetz soils

Ratios of dilution	Sodium ion activity ($10^3 \cdot$ mole/l)		Profile No 7 depth of sampling cm	Sodium ion activity ($10^3 \cdot$ mole/l)		Profile No 109 depth of sampling cm	Sodium ion activity ($10^3 \cdot$ mole/l)	
	measured	calculated		measured	calculated		measured	calculated
Standard solution	270.00	289.90	10—20	43.40	35.30	0—10	6.30	8.50
1 : 5	74.00	74.30	20—40	72.50	72.70	20—40	15.60	15.30
1 : 10	41.00	40.70	40—60	87.90	92.20	40—60	22.70	25.30
1 : 25	15.50	18.20	60—80	119.50	124.60	60—80	28.00	28.30
1 : 50	9.40	9.30	80—100	49.10	48.70	80—100	18.70	21.20
1 : 100	4.60	4.70	100—120	64.40	62.20	100—120	13.50	15.80
1 : 500	0.84	1.00	120—140	43.90	47.80	120—140	9.01	8.80

The degree of ion-pair formation, in accordance with other data published [ADAMS 1971; DAVIES 1962], depends on the valences, sizes and concentrations of the ions in the solution (Table 5.10).
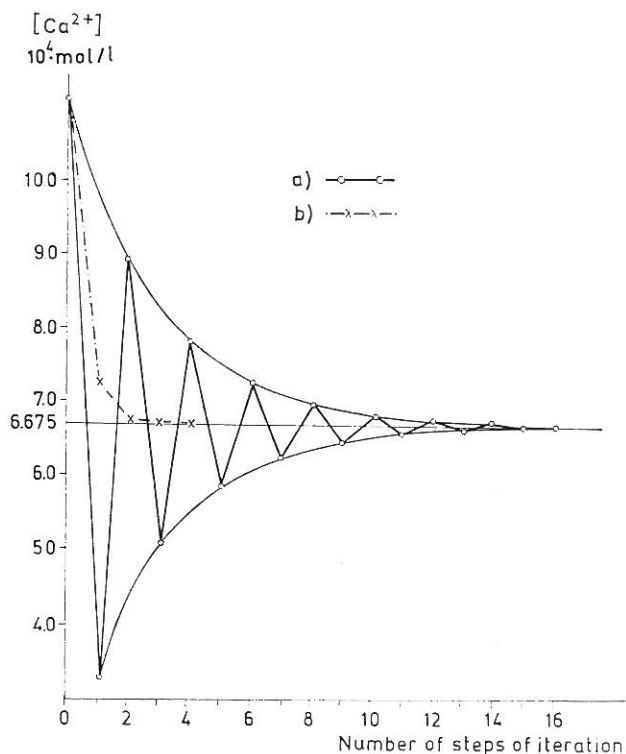

Fig. 5.1

Ca^{2+} concentration in soil saturation extracts after each step of the iteration. a) using the arithmetic means of the concentrations; b) by the formation of a weighted average of the ion concentration

Among the cations 15—75% of the magnesium ions, 15 – 65% of the calcium ions and 2 – 25% of the sodium ions form ion pairs (Table 5.11, Figs. 5.3, and 5.4).

The decisive role of the sodium ions in the soil solution is strengthened by the different ability of cations to form ion-pairs. The different degree of ion-pair formation in the case of sodium, calcium and magnesium ions raises the SAR value in the soil solution. The increase in the SAR value due to the ion-pair formation becomes more important as the ionic concentration of the soil solution increases and it shifts the balance of exchangeable cations in favour of sodium (Table 5.12).

The ratio of exchangeable cations depends on the kind of anions present. The effect of the anion is due to the following:

— The ratios of ion activities in solution, which are included in all the ion exchange equations are different, and depend upon the kind of anions present [BABCOCK 1963b]. This is the case if we compare systems which are identical except that the sodium and calcium salts are present as chlorides in one of the series and as sulphates in the solutions of other systems (Table 5.13). A comparison of the data in bentonite-NaCl-CaCl$_2$ solution and bentonite-Na$_2$SO$_4$-CaSO$_4$ solution systems indicates that the degree of sodium saturation of the adsorbent is influenced only slightly by the activity of the anions (in the case of chloride and sulphate ions). In general, the adsorption of sodium
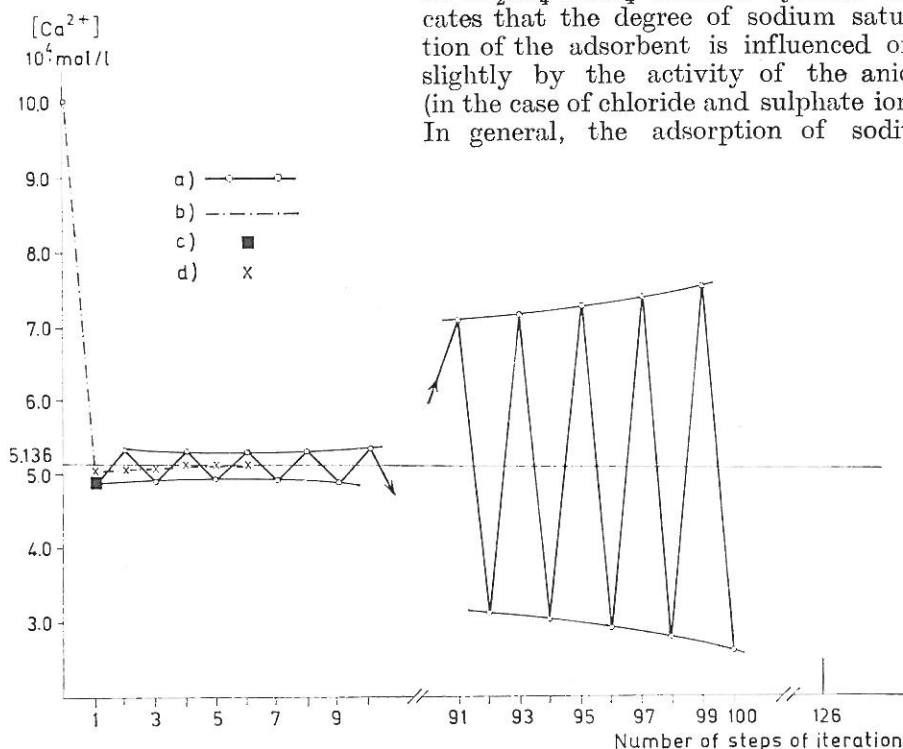

Fig. 5.2
Ca^{2+} ion concentration after each step of iteration. a) The calculation by the original method is divergent. b) The calculation is convergent using weighted averaging. c) The negative value found in the first step is shifted into the positive area by arithmetic averaging. d) The points obtained by weighted averaging

Table 5.10

The concentration of free charged ions and ion-pairs

Profile Nos. (and depth of sampling cm	Ca^{2+}	$CaCO_3^0$	$CaHCO_3^+$	$CaSO_4^0$	Mg^{2+}	$MgCO_3^0$	$MgHCO_3^+$	$MgSO_4^0$
				$10^3 \cdot mole/l$				
No. 1								
0—3	0.11	0.07	0.02	0.04	0.13	0.15	0.02	0.05
3—10	0.11	0.17	0.03	0.01	0.07	0.19	0.01	0.01
10—20	0.13	0.18	0.02	0.02	0.12	0.28	0.02	0.02
20—30	0.05	0.06	0.005	0.004	0.02	0.04	0.002	0.002
30—40	0.27	0.20	0.02	0.04	0.15	0.18	0.01	0.02
40—50	0.30	0.25	0.03	0.04	0.12	0.16	0.01	0.01
No. 2								
3—10	0.19	0.27	0.05	0.03	0.08	0.18	0.02	0.01
10—20	0.20	0.12	0.07	0.03	0.11	0.11	0.11	0.03
20—30	0.14	0.14	0.04	0.01	0.25	0.42	0.06	0.02
40—50	0.22	0.28	0.02	0.02	0.12	0.26	0.01	0.01
50—60	0.65	0.20	0.05	0.02	0.29	0.15	0.02	0.06
No. 7								
10—20	0.86	—	0.05	0.58	0.79	—	0.04	0.51
20—40	1.76	—	0.03	1.72	1.77	—	0.02	1.76
40—60	3.24	—	0.03	3.34	2.77	—	0.02	2.97
60—80	5.38	—	0.03	5.86	4.23	—	0.02	4.92
80—100	1.25	—	0.05	0.98	1.20	—	0.04	0.93
100—120	0.49	—	0.01	0.45	0.55	—	0.01	0.51
120—140	0.49	—	0.02	0.39	0.35	—	0.01	0.2S
No. 109								
0—10	0.93	—	0.05	0.13	0.95	—	0.04	0.12
20—40	0.74	—	0.04	0.17	1.24	—	0.05	0.27
40—60	0.63	—	0.02	0.25	2.57	—	0.06	1.00
60—80	0.77	—	0.02	0.29	2.79	—	0.07	1.00
80—100	0.52	—	0.01	0.15	1.96	—	0.04	0.54
100—120	0.47	—	0.02	0.15	1.39	—	0.05	0.41
120—140	0.57	—	0.04	0.09	0.96	—	0.05	0.13

ions in chloride-containing systems is higher than in sulphate-containing suspensions at a low concentration of intermicellar solution, whereas a higher sodium saturation is found in sulphate-containing systems when the ionic strength of the solutions increases.

— In non-equilibrium systems the solubility of calcium-sodium exchange products has an influence on the ionic composition of the solution and on the ratio of exchangeable cations. A reverse relation exists between the solubility of compounds forming in the course of ion exchange, the calcium concentration ratio and the degree of sodium saturation of the adsorbent. Equilibrium is reached in the chloride-containing system at a relatively low degree of sodium saturation. The presence of calcium sulphate causes a relatively stable concentration of calcium ions in the free solution of sulphate-containing systems and the ratio of sodium to calcium ions in the intermicellar and micellar solution depends on the changes in the total ionic concentration of the free electrolyte solutions.

Saturation extracts of sulphate-containing solonetz soils were prepared and they were saturated by the addition of gypsum.

in the saturation extracts of salt affected soils

Na^+	$NaCO_3^-$	$NaHCO_3^0$	$NaSO_4^-$	CO_3^{2-}	HCO_3^-	SO_4^{2-}	Cl^-	I
				$10^3 \cdot mole/l$				
91.23	1.43	1.12	1.52	3.10	36.96	15.44	17.70	112.00
77.49	2.58	1.01	0.42	5.97	37.75	4.46	15.80	88.26
63.79	1.84	0.66	0.41	4.90	29.29	5.00	17.80	76.90
38.41	0.95	0.21	0.13	3.41	14.18	2.16	14.40	45.31
32.71	0.46	0.14	0.19	1.82	11.12	3.44	9.60	38.42
35.08	0.56	0.20	0.16	2.08	14.36	2.69	5.55	38.24
84.00	2.63	1.24	0.62	5.82	43.29	6.38	11.20	95.84
79.80	1.03	1.53	0.45	2.30	55.08	4.66	9.35	87.43
65.99	1.43	1.04	0.25	3.61	43.97	2.87	8.63	73.90
19.02	0.43	0.07	0.05	2.58	8.88	1.28	5.30	25.25
17.41	0.10	0.06	0.13	0.65	8.47	3.91	4.50	26.35
43.94	—	0.13	1.16	—	8.24	19.59	0.00	69.58
97.67	—	0.08	4.40	—	2.70	49.66	1.37	159.50
126.90	—	0.07	6.42	—	1.78	63.57	3.10	208.30
176.50	—	0.07	10.02	—	1.41	83.54	3.17	281.90
62.60	—	0.16	2.09	—	7.47	29.26	3.88	102.10
81.63	—	0.12	3.38	—	4.51	40.77	3.55	131.10
61.15	—	0.15	2.05	—	6.93	28.73	3.38	96.53
9.60	—	0.02	0.04	—	5.11	1.93	0.00	15.09
17.95	—	0.04	0.14	—	6.03	4.16	9.30	29.11
30.86	—	0.04	0.47	—	3.81	10.06	15.58	52.03
34.61	—	0.05	0.49	—	4.07	9.49	17.23	54.46
25.30	—	0.03	0.26	—	3.27	6.10	13.67	38.50
18.69	—	0.04	0.20	—	5.26	6.18	10.74	33.63
10.05	—	0.03	0.05	—	6.49	2.25	5.46	18.67

The solubility product of $CaSO_4$ calculated from the analytical data of these extracts increases with increasing ionic concentration in these solutions, regardless of whether the total or the iterated values of the concentrations of calcium and sulphate ions are taken. The thermodynamic solubility products do not depend on the ionic concentration of the electrolyte. Taking into account the ion pair formation, the standard deviation of the solubility products is low and the average is the same as that published by NAKAYAMA [1971]; MEITES and PODE [1966]; and THOMAS [1965] (Table 5.14).

In carbonate-containing systems the sodium ions dominate in the inter-micellar solutions as a result of the poor solubility of calcium carbonate and the adsorbent has a high degree of sodium saturation even if the ionic concentration of the liquid phase is low. In these systems the pH value of the medium determines the solubility of calcium carbonate and consequently, it has an effect on the cation-exchange equilibria of soil-solution systems. The activity of calcium ion in solution can be calculated from the thermodynamic solubility products of calcium carbonate:

$$lg\ (Ca^{2+}) = lg\ K_{CaCO_3} - lg\ (CO_3^{2-}) \qquad (5.8)$$

Quantity of ions with free valences in the percentage of the total concentration of the same ion in the saturation extracts of salt-affected soils

Profile Nos and depth of sampling cm	Ca²⁺	Mg²⁺	Na⁺	CO₃²⁻	HCO₃⁻	SO₄²⁻
No. 1						
0—3	44.33	36.47	95.73	65.29	96.94	90.56
3—10	35.08	25.54	95.08	67.07	97.29	91.04
10—20	37.37	27.70	95.63	67.99	97.65	91.79
20—30	40.77	30.47	96.76	76.52	98.50	94.03
30—40	50.51	40.92	97.65	68.60	98.43	93.08
40—50	48.13	38.31	97.45	68.22	98.34	92.75
No. 2						
0—3			no convergence			
3—10	35.56	26.26	94.92	65.39	97.07	90.53
10—20	48.92	41.21	96.38	64.76	97.14	90.47
20—30	42.04	32.65	96.05	64.45	97.49	91.08
30—40			no convergence			
40—50	41.23	31.01	97.54	72.77	99.72	94.68
50—60	62.09	56.04	98.37	58.84	98.52	92.06
No. 7						
10—20	58.25	59.19	97.46	—	97.67	90.27
20—40	50.35	49.87	95.60	—	95.56	86.29
40—60	49.02	48.04	95.14	—	94.11	83.31
60—80	47.72	46.14	94.59	—	92.15	80.07
80—100	54.86	55.20	96.90	—	96.93	88.59
100—120	51.40	51.28	96.32	—	97.23	91.12
120—140	54.49	54.91	96.90	—	97.74	92.01
No. 109						
0—10	84.12	85.61	99.38	—	97.97	86.93
20—40	78.45	79.91	99.04	—	97.88	88.16
40—60	69.96	71.04	98.45	—	97.02	85.64
60—80	71.53	72.55	98.54	—	96.72	84.54
80—100	76.25	77.44	98.91	—	97.47	86.85
100—120	73.87	75.32	98.78	—	98.03	89.23
120—140	82.73	84.30	99.29	—	98.36	89.62

The activity of the carbonate ions depends on the pH of the solution:

$$\lg (CO_3^{2-}) = \lg K_{d_1} K_{d_2}(H_2CO_3) + 2pH \qquad (5.9)$$

K_{d_1} and K_{d_2} = the first and second dissociation constants of carbonic acid
(H_2CO_3) = the activity of carbonic acid in the solution.

From the data of sodium carbonate and bicarbonate solutions it is found that the product of the two dissociation constants and the activity of carbonic acid is a linear logarithmic function of the square root of the ionic concentration in the solution:

$$\lg [K_{d_1} K_{d_2}(H_2CO_3)] = a + b\sqrt{I} \qquad (5.10)$$

The activity of carbonate ions depends on the pH value and ionic concentration of the solution, as follows:

$$\lg (CO_3^{2-}) = a + b\sqrt{I} + 2pH \qquad (5.11)$$

Table 5.12

Sodium adsorption ratio in saturation extracts of salt affected soils

Profile Nos. and depth of sampling cm	SAR calculated from				Profile Nos. and depth of sampling cm	SAR calculated from			
	total	iterated	total	iterated		total	iterated	total	iterated
	cation concentration		cation activities			cation concentration		cation activities	
No. 1					No. 7				
0—3	123.54	186.22	148.70	221.96	10—20	26.90	34.26	31.81	40.23
3—10	105.66	182.65	124.51	215.14	20—40	38.48	52.03	46.99	63.11
10—20	74.57	125.10	87.63	146.24	40—60	37.94	51.79	46.88	63.64
20—30	94.90	150.66	115.61	183.48	60—80	41.29	56.95	51.60	57.47
30—40	35.41	50.47	41.11	58.37	80—100	30.61	39.95	36.71	48.02
40—50	37.64	54.79	43.69	64.09	100—120	59.56	80.04	71.45	97.17
					120—140	50.77	66.52	60.69	79.73
No. 2					No. 109				
3—10	97.44	163.18	117.36	197.49	0—10	6.48	6.99	7.20	7.73
10—20	101.16	143.33	120.18	167.60	20—40	11.48	12.74	13.05	14.40
20—30	66.26	107.05	77.63	123.93	40—60	14.75	17.26	17.05	19.87
40—50	20.28	33.44	23.09	37.53	60—80	15.83	18.39	18.31	21.12
50—60	14.10	17.91	16.08	20.33	80—100	14.30	16.10	16.37	18.30
					100—120	12.01	13.70	13.68	15.48
					120—140	7.49	8.14	8.38	9.03

where $a = -22.9458$; $b = 1.821$.

To prove the validity of this relationship, carbonate ion activities in the saturation extracts of sodium carbonate solonchaks were computed by the modified iteration method and calculated from equation (5.11). The averages of carbonate ion activities after subtracting the concentrations of the $MgCO_3^0$, $CaCO_3^0$ and $NaCO_3^-$ ion-pairs, and calculated from the pH values of the extracts, were $1.23 \cdot 10^{-3}$ mole/l and $1.52 \cdot 10^{-3}$ mole/l respectively.

The calcium ion activity may be calculated by combining the equations (5.8) and (5.11):

$$\lg Ca^{2+} = a' - b \sqrt{I} - 2pH \qquad (5.12)$$

where $a' = +22.9458 + \lg K_{CaCO_3}$

The activity ratio of exchangeable cations depends on the sodium-calcium activity ratio and on the pH value of the intermicellar solution in the case of salt affected soils containing sodium carbonate:

$$\lg \frac{(RNa)^2}{(RCa)} = \lg K_{Ca}^{Na} + \lg a_{Na^2} - \lg a_{Ca} = \lg K_{Ca}^{Na} + (pCa - 2pNa) \quad (5.13)$$

$$\lg \frac{(RNa)^2}{(RCa)} = \lg K_{Ca}^{Na} - a' + b \sqrt{I} + 2(pH - pNa) \qquad (5.14)$$

K_{Ca}^{Na} = the exchange constant of calcium-sodium ion exchange
RNa, RCa = the activities of exchangeable sodium and calcium ions
pNa, pCa = the negative logarithm of the sodium and calcium ion activity in the intermicellar solution

Table 5.13

The amount of exchangeable sodium in bentonite-Na$_2$SO$_4$-CaSO$_4$ solution systems

I mole/l	[Na$^+$]	[Ca^{2+}]	$\dfrac{[Na^+]}{[Ca^{2+}]}$	$\dfrac{[Na^+]^2}{[Ca^{2+}]}$	$\dfrac{[\gamma Na^+]^2}{[\gamma Ca^{2+}]}$	Exchangeable Na$^+$	CEC	ESP
	mole/l · 10^3					me/100 g		
5.0 · 10^{-3}	2.60	0.10	25.7	6.7 · 10^{-2}	1.165	11.8	96	12.3
7.5 · 10^{-3}	3.94	0.18	22.4	8.8 · 10^{-2}	1.208	13.8		14.4
1.0 · 10^{-2}	5.48	0.26	21.3	11.7 · 10^{-2}	1.332	21.7		22.6
2.5 · 10^{-2}	13.30	0.61	21.9	29.2 · 10^{-2}	1.416	26.5		26.5
7.5 · 10^{-3}	3.94	0.13	31.0	12.2 · 10^{-2}	1.205	20.9	96	20.9
1.0 · 10^{-2}	5.30	0.18	30.3	16.1 · 10^{-2}	1.242	21.7		22.6
2.5 · 10^{-2}	13.90	0.48	29.0	40.3 · 10^{-2}	1.421	33.8		35.2
5.0 · 10^{-2}	30.40	0.98	31.0	94.3 · 10^{-2}	1.678	51.9		54.1

and
$$\lg \frac{(RNa)^2}{(RCa)} = a'' - b \sqrt{I} + 2(pH - pNa) \tag{5.15}$$

The approaches used to calculate the exchange constant or the ratios of exchangeable cations differ in the way in which the activity of exchangeable cations is expressed. VANSELOW [1932] supposes that the adsorbent behaves as an ideal mixture of solid solutions so that the activity of exchangeable cations can be calculated by their molar fractions. THOMAS [1965] uses the equivalent fractions as a measure of the activity of the cations adsorbed. LAUDELOUT [1965] takes the monoionic form of the soil-solution suspension at a large ratio of diluted solution to the solid adsorbent as the standard state of soil-electrolyte solution systems.
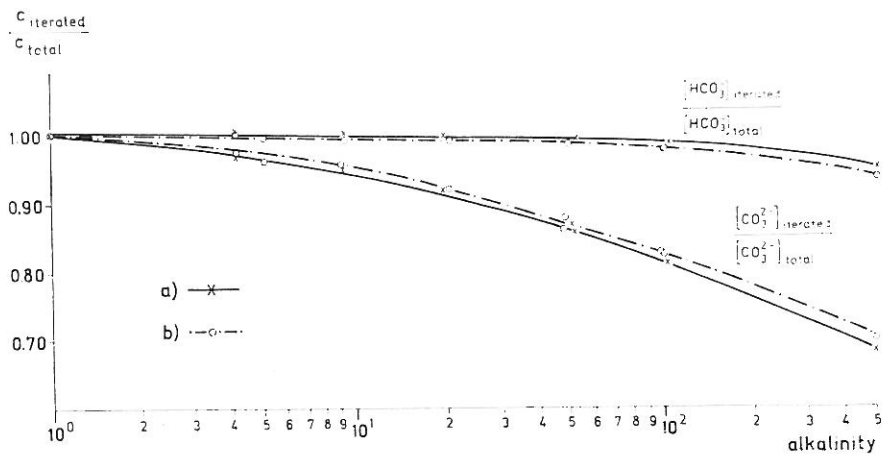

Fig. 5.3
Dependence of calculated and total ion concentration ratio on the alkalinity of the solution. a) determined in the absence of NaCl; b) determined in the presence of NaCl

Table 5.14

The solubility product of CaSO$_4$ determined in saturation extracts saturated with gypsum

Depth of sampling cm	I_x $10^3 \cdot$ mole/l		Solubility product $10^4 \cdot$ (mole/l)^2		Thermodynamic solubility product $10^5 \cdot$ (mole/l)^2	
	a	b	a	b	a	b
40—60	230.5	173.9	7.33	2.92	5.81	2.83
60—80	147.6	115.8	4.78	2.11	5.19	2.71
80—100	143.9	111.5	4.80	2.11	5.31	2.77
100—120	115.0	89.3	3.69	1.71	4.77	2.60
120—140	103.5	79.9	3.10	1.46	4.28	2.39
				Average	5.07	2.67

$S_x = 5.78 \cdot 10^{-6}$ $S_x = 1.49 \cdot 10^{-6}$
$\overline{S}_x = 2.59 \cdot 10^{-6}$ $\overline{S}_x = 6.65 \cdot 10^{-7}$

a) Calculated from original concentrations of ions
b) Calculated from iterated concentrations of ions
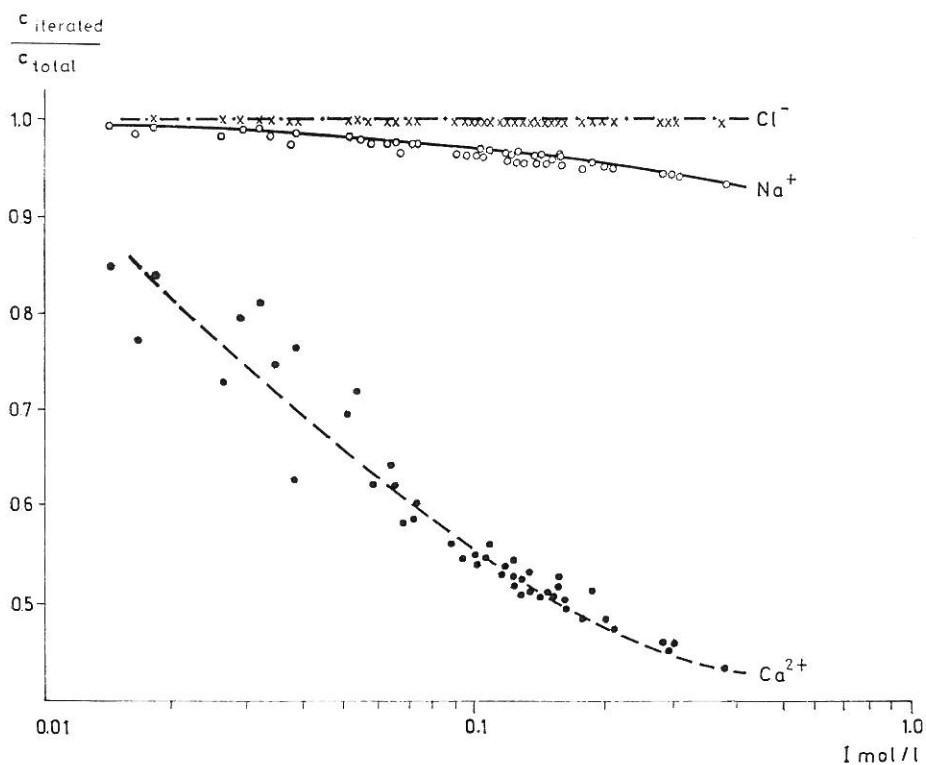
Fig. 5.4
Dependence of iterated and total ion concentration ratios on the ionic concentration of saturation extracts

Table 5.15

The quantities and ratio of components contributing to the cation exchange capacity of some salt affected soils

Soil type	Organic matter	CaCO₃	Clay	Silt	Cation exchange capacity in the investigated samples				
					Clay	Silt	Organic matter	CaCO₃	Total
	%				me/100 g soil				
Solonetz soil									
horizon "B"	2.25	2.92	22.2	11.6	11.2	1.02	4.60	—	16.8
horizon "C"	0.22	25.00	24.8	10.8	15.0	1.26	—	9.73	26.0
Solonetzic meadow soil									
horizon "B"	2.34	—	39.8	15.1	22.5	2.74	9.63	—	34.87
horizon "C"	0.33	8.5	45.3	24.9	22.6	4.47	—	3.31	30.38

The GAPON equation is based on the misciple displacement of foliar water on the surface of the adsorbent [KELLEY 1948]. The DONNAN, ERIKSSON [cit: BABCOCK 1963] and BOLT equations are based on the model of a diffuse double layer [BOLT and PAGE 1965; LAGERWERFF and BOLT 1959].

The systems do not always correspond to the conditions applied during the calculations of exchangeable cation activity and the "exchange constant" varies more or less with the total electrolyte concentration of the solution and the molar or equivalent fractions of the adsorbed ions. The variation of the "exchange constant" is the greater the more unequal the sizes and charges of the adsorbed and counter ions are and the higher the selectivity of the adsorbent is to any of the ions. For natural exchangers there are only limited concentration ranges where the exchange constant proved to be fairly constant.

The ability of soils to adsorb cations in an exchange form is related to the free negative charges of soil particle surfaces and it is composed of the following components:

— the cation exchange capacity of the layer silicates in the clay fraction of the soils,
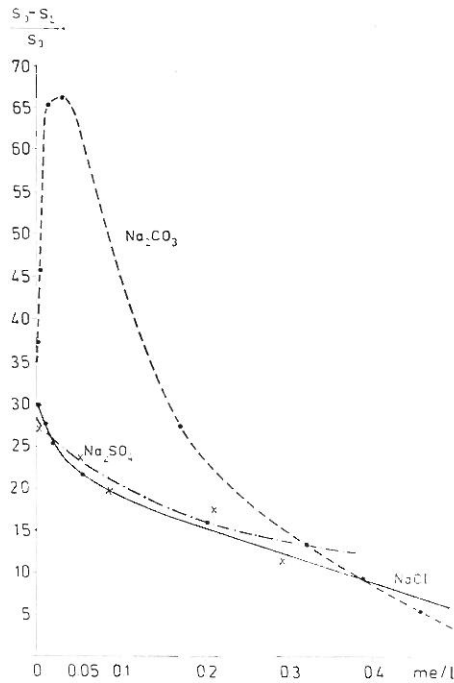

Fig. 5.5

Dependence of bentonite Na-24 activity as a percentage of the total Na-24 activity on the equilibrium Na⁺ concentration in bentonite-NaCl, Na₂SO₄ and Na₂CO₃ solution systems Horizontal axis: Na⁺ concentration of the equilibrium solution (me/1). Vertical axis: S_0 = total Na-24 activity; S_L = activity of the equilibrium solution

The amount of exchangeable sodium in bentonite-Na₂CO₃ solution and illite-Na₂CO₃ solution suspensions

Exchanger	Solution	I mole/l	pH	Alkalinity	$[Na^+]$ me/l	$\dfrac{[\gamma_{Na^+}]^2}{[\gamma_{Ca^{2+}}]}$	Exchangeable Na⁺ me/l
Bentonite	Na₂CO₃	$2.2 \cdot 10^{-3}$	8.9	1.03	1.04	1.1144	0.73
		$5.0 \cdot 10^{-3}$	9.4	3.93	3.56	1.1787	5.38
		$6.2 \cdot 10^{-3}$	9.3	5.70	5.22	1.2006	12.10
		$7.9 \cdot 10^{-3}$	9.6	6.95	6.95	1.2301	19.05
		$2.1 \cdot 10^{-2}$	10.0	20.52	16.54	1.4041	46.13
		$4.7 \cdot 10^{-2}$	10.1	39.75	38.26	1.6503	89.76
Illite	Na₂CO₃	$1.0 \cdot 10^{-3}$	7.8	1.03	0.95	1.1609	0.34
		$5.0 \cdot 10^{-3}$	9.6	4.36	4.43	1.1795	3.36
		$7.4 \cdot 10^{-3}$	10.0	6.44	6.26	1.2218	9.30
		$9.8 \cdot 10^{-3}$	10.0	8.31	9.13	1.2581	10.71
		$2.5 \cdot 10^{-2}$	10.2	22.39	20.86	1.4402	14.84
		$5.3 \cdot 10^{-2}$	10.4	45.19	44.34	1.7107	16.76

— the cation exchange capacity of the compounds in the silt fraction of the soils,

— the cation exchange capacity of the organic matter in the soils,

— the cation exchange capacity of salts sparingly soluble in water.

In the case of soils it depends on the texture, mineralogy and chemistry of soil compounds and on the degree of dispersion of particles with the ability to adsorb cations in an exchangeable form (Table 5.15).

Investigations carried out with phase-equilibrium systems show that the influence of the pH value on soil colloid systems manifests itself not only in the change in solubility of poorly soluble salts, but also influences the degree of dispersion, the cation exchange capacity and the surface charge density of the adsorbent too [DARAB 1965]. The distribution quotient of Na-24 decreases as a rule with an increase in the concentration of solutions containing chlorides and sulphates. It increases and reaches a maximum value if sodium salts capable of alkaline hydrolysis are present in the free electrolyte solution of phase equilibrium systems labelled with Na-24 (Fig. 5.5). From the material balance of the system it follows, that if there is an increase in the isotope distribution quotient in spite of the increase in sodium ion concentration in the solution this indicates an increase in the cation exchange capacity of the adsorbent:

$$\frac{S_0 - S_L}{S_L} \cdot C_{Na} V_s = M N_{Na} \qquad (5.16)$$

S_0 = activity of the solution used for labelling, imp/min/ml

S_L = activity of the free solution at equilibrium, imp/min/ml

C_{Na} = sodium ion concentration in the intermicellar solution at equilibrium, mole/l

V_s = volume of free electrolyte corresponding to 1 g of adsorbent

M = CEC of adsorbent, me/g

N_{Na} = equivalent fraction of exchangeable sodium.

Table 5.17

Isotope exchange of sodium and calcium ions

Salt	Concentration N	Isotope	Rate constant of exchange			Rate of exchange		
			K_1	$\bar{K}_2$ sec.$^{-1}$	K_3	v_1	v_2 g atom sec.$^{-1}$	v_3
CaCl$_2$	$5 \cdot 10^{-3}$	Ca-45	$0.5 \cdot 10^{-2}$	$1.0 \cdot 10^{-3}$	—	$1.5 \cdot 10^{-5}$	$1.7 \cdot 10^{-7}$	—
CaCl$_2$	$1 \cdot 10^{-2}$	Ca-45	$1.1 \cdot 10^{-2}$	—	$1.8 \cdot 10^{-4}$	$3.1 \cdot 10^{-5}$	—	$7.7 \cdot 10^{-8}$
CaCl$_2$	$5 \cdot 10^{-2}$	Ca-45	$2.0 \cdot 10^{-2}$	$2.9 \cdot 10^{-3}$	$2.1 \cdot 10^{-4}$	$5.2 \cdot 10^{-5}$	$2.3 \cdot 10^{-6}$	$12.9 \cdot 10^{-8}$
NaCl	$5 \cdot 10^{-3}$	Ca-45	—	$2.9 \cdot 10^{-3}$	$0.4 \cdot 10^{-4}$	—	$6.8 \cdot 10^{-6}$	$2.9 \cdot 10^{-8}$
NaCl	$5 \cdot 10^{-3}$	Na-22	$2.5 \cdot 10^{-2}$	$0.8 \cdot 10^{-3}$	—	$1.0 \cdot 10^{-5}$	$3.6 \cdot 10^{-7}$	—
Na$_2$CO$_3$	$5 \cdot 10^{-3}$	Ca-45	—	$1.1 \cdot 10^{-3}$	$1.9 \cdot 10^{-4}$	—	$1.9 \cdot 10^{-6}$	$5.0 \cdot 10^{-8}$
Na$_2$CO$_3$	$5 \cdot 10^{-3}$	Na-22	$1.0 \cdot 10^{-2}$	—	$0.5 \cdot 10^{-4}$	$2.3 \cdot 10^{-5}$	—	$2.2 \cdot 10^{-8}$

Amount of exchangeable cations corresponding to the part processes

Salt	Concentration N	Isotope	Ca_1^{2+}	Na_1^+	Ca_2^{2+} me/100 g	Na_2^+	Ca_3^{2+}	Na_3^+
CaCl$_2$	$5 \cdot 10^{-3}$	Ca-45	65.6	—	3.3	—	8.5	—
CaCl$_2$	$1 \cdot 10^{-2}$	Ca-45	58.8	—	—	—	12.6	—
CaCl$_2$	$5 \cdot 10^{-2}$	Ca-45	58.8	—	1.6	—	14.0	—
NaCl	$5 \cdot 10^{-3}$	Ca-45	—	—	46.0	5.5	—	—
NaCl	$5 \cdot 10^{-3}$	Na-22	—	5.05	—	—	6.1	—
Na$_2$CO$_3$	$5 \cdot 10^{-3}$	Ca-45	—	—	37.3	—	—	—
Na$_2$CO$_3$	$5 \cdot 10^{-3}$	Na-22	—	26.9	—	—	—	5.6

The increase in the exchange capacity can be either apparent or actual. By determining the sodium ion concentration and pH value of the equilibrium solution and measuring the amount of exchangeable sodium, the product of the selectivity coefficient and the cation exchange capacity can be calculated if it is assumed that the activities of the exchangeable cations are related to their equivalent fractions:

$$\frac{N_{Na}^2}{N_{Ca}} = \frac{[RNa]^2}{T[T-RNa]} = K\,{}_{Ca}^{Na} \cdot \frac{[Na^+]^2}{[Ca^{2+}]} \tag{5.17}$$

$$[Ca^{2+}] = num\ lg\ (15.5872 - b\ \sqrt{I} - 2pH) \tag{5.18}$$

taking the value of the thermodynamic solubility product for $CaCO_3$ to be that measured by NAKAYAMA [1968, 1969].

Taking the CEC value of the adsorbent to be constant, the selectivity coefficient of sodium-calcium ion exchange depends on the sodium saturation of the adsorbent. This dependence can be expressed as a second rate function between the natural logarithm of the selectivity coefficient of cation exchange and the equivalent fraction of exchangeable sodium (Table 5.16). Integrating this function, practically the same values are obtained for the exchange constant in the case of bentonite and illite:

$$\ln K_{Ca}^{Na} = \int_0^1 \ln K'\ dN_{Na} \tag{5.19}$$

$$\ln K_{Ca}^{Na} = -0.86044 \text{ for bentonite}$$

$$\ln K_{Ca}^{Na} = -1.1153 \text{ for illite.}$$

In the case of calcium-sodium exchange, the surface properties of the adsorbent may change with the increase in its sodium saturation. In the case of montmorillonite the degree of hydration and the amount of adsorbed OH^- increases, while the degree of crystallization decreases with an increase in sodium saturation [DARAB 1965, 1974].

The changes in the colloid properties and in the degree of crystallization of the solid phase also influence the activities of the exchangeable cations, the selectivity of the adsorbent to the sodium ions and the mobility of the cations adsorbed. According to the kinetics of Ca-45 isotope adsorption in a bentonite-$CaCl_2$ solution equilibrium system, three part processes characterized by rate constants of exchange differing in their order of magnitude may be distinguished (Table 5.17). In systems of Ca- and Na-bentonite prepared with sodium chloride and sodium carbonate solutions, different ion adsorption part processes exist. Usually each of the part processes is dominated by one of the cations taking part in the ion exchange.

The different values of the exchange rate constants of calcium and sodium ions in the systems indicate that the distribution of exchangeable sodium and calcium ions in the double layer and on the surface is not stochiometrically homogeneous. At a low degree of sodium saturation the sodium ions occupy sites with low energy and they are more mobile than the calcium ions which are adsorbed on places with higher energy. As the sodium saturation increases, the alkalinity of the medium and the degree of dispersion also increase, and the sites with low mobility become accessible to the exchange of sodium.

The existence of exchangeable cations with different mobility means that the equilibrium of the cation exchange is influenced by the interaction between the intermicellar and micellar solution, the diffusibility of cations in the diffuse double layer and the mobility of ions on the surface of the adsorbent.

The equilibrium of cation exchange, as is mentioned above, is determined by the concentration and chemistry of the liquid phase and the composition and surface properties of the solid phase. The equilibrium state of cation exchange in soils can only be characterized on the basis of detailed and exact data related to the chemistry, physico-chemistry and mineralogy of the soils investigated. If these soil properties change during the soil formation the cation exchange can only be characterized as a process leading to a momentary quasi equilibrium state between the solid and liquid phase of the soil.

When modelling the chemistry of soil salinization and/or alkalization, measurable values such as ion activities in solution and calculable functions or values such as the dependence of carbonic acid dissociation constants on the ionic concentration of the solution, the thermodynamic solubility products of sparingly soluble salts and the influence of ion-pair formation on the value of the sodium adsorption ratio can be taken into account. Many of the factors affecting the regime of salts and mobile sodium compounds must be simplified. First of all, in the models it is taken for granted that the surface properties do not change with changes in the sodium saturation of the soil. Consequently, it is assumed that the selectivity coefficient of cation exchange is constant. Further investigations are necessary if accurate information is to be obtained on the variation of surface properties with variations in the degree of soil salinity and sodicity.

Several works [BOWER, GARDNER and GOERTZEN 1957; BROOKS, GOERTZEN and BOWER 1958; FILEP 1969, 1974; LAI and JURINAK 1971; RIBLE and DAVIS 1955] have been published on the modelling of the vertical movement of water and salts in soils. The fundamental point of this model is the application of chromatographic equations to the description of the accumulation and leaching processes in soil columns.

5.3. Ion transport in column models

The regularities of ion exchange processes in soils are usually studied under static conditions.

In nature, exchange reactions are accompanied by the movement of soil moisture. Because of the presence of different readily dissociable inorganic and organic salts, the liquid phase of the soil (soil solution) is characterized by the properties of strong electrolytes.

In the vertical transport of solutions through soils, a dynamic interaction occurs between the ions of the solution and those adsorbed on the surface of the solid phase.

The vertical transport of ions *in situ* is a complex process, the result of downward and upward solution movements.

Ion transport occurs by means of mass flow (ions move together with the water stream), diffusion (ions move due to the concentration gradient) or both. Diffusion, together with other factors such as reactions with the ex-

change complex of the soil, hydrodynamic disturbances, tortuosity, etc., eventually causes a considerable dispersion. Dispersion, the physical properties of the soil (e.g. the pore volume) and the variable solution flux determine the flow rates occurring in the soil profile. At high values of flow rate, transport by diffusion is negligible compared with transport by mass flow, whereas at low flow rates, transport by diffusion may be the dominant process.

The salt concentration of the soil solution is also a variable factor. It influences the equilibrium between adsorbed and non-adsorbed ions and thus the rate of the transport process in the soil.

Transport phenomena are usually described with reference to column models. The soil is considered as a system consisting of a non-moving porous solid phase with a considerable surface area and a moving liquid phase. The material uptake and release governed by the interactions between the two phases can be described by the equations found for ion exchange chromatography. However, the theories valid when chromatography column operation is applied in the ionic separation processes of homogeneous synthetic ion exchanger resins can only be used for ion exchange processes in soil systems if certain simplifications and approximations are made. Therefore, the validity and applicability of chromatography models and theories for the particular transport problem must be checked by soil column experiments under well-defined conditions. On the other hand, soil column experiments also have their technical difficulties, because of the changes in the physical, physico-chemical and colloid properties of the solid phase of the soil during percolation and consequently (e.g. in the case of percolation with Na^+-containing salt solutions), due to the gradual decrease in the flow rate. Therefore, some simplifications (e.g. the use of soil-sand mixtures) are necessary [FILEP 1969; POELSTRA and FRISSEL 1965; RÉDLY 1975].

The column process. — When a column of exchanger saturated with one kind of cation "A" is eluated with a solution containing a second ionic species "B", the "B" ions present in the influent solution will gradually replace the ions originally present in the column. As this percolation will cause a repeated adsorption and desorption of ions, the replacement of "A" by "B" will proceed from the top to the bottom. Thus, after the process has been operative for some time, the following three zones may be distinguished:

1. A zone where all "A" ions have been replaced by "B".
2. A transition zone, where ions "A" and "B" occur together and where the relative amount of "A" increases with depth.
3. A zone where it is still only "A" ions which are present.

The depth of the appearance of the different zones and their thickness is greatly affected by the ion exchange power of the interacting cations [FILEP 1972; VAN DER MOLEN 1957].

The changes in the amount of adsorbed cations may be graphically represented in the following ways:

1. By isochrones, giving the change in the distribution of adsorbed cations with depth at a fixed time. Isochrones referring to the ions displaced from the column are known as rear boundaries, whereas those referring to the influent ions are denoted as front boundaries.

2. By isoplanes giving the change in adsorbed cations with eluate volume (or in the case of steady flow, with time) at a fixed depth.

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3. In the same way the variations in solution composition may be given. The isoplane of the solution corresponding to the bottom of the columns gives a picture of the changes in the composition of the effluent; if the isoplane refers to the influent ion, it is generally known as the break-through curve.

4. The relation between adsorbed ions and the ions in the solution may be given in the usual way by adsorption isotherms. The distribution of the various cation pairs at equilibrium and the shape of the isotherm (in the case of cations with different valences) depends on whether the cation of higher valence or that of lower valence is the exchangeable or the counter ion at the beginning of the process.

The shape of the break-through curve is affected mainly by the character of the ion exchange, the flow rate and concentration of the solution, the rate of ion exchange and the length of the column.

The use of chromatography theories allows:

a) the prediction of a component in the effluent,

b) the calculation of the amount and distribution of the component adsorbed on the solid phase within the column,

c) the calculation of the concentration and distribution of the same component in the liquid phase.

Theories of column operation. — When using chromatographic transport theories, it is necessary to select the proper theory, because when a theory derived for a given situation is applied to a problem connected with a different situation, no acceptable agreement between theory and experiment can be expected [FRISSEL and POELSTRA 1967].

The chromatography theories applied in soil science can be divided according to the presence or absence of the following simplifying characteristics of the system:

a) The existence of an instantaneous, local equilibrium between the adsorbed ions and those in the solution phase.

b) The validity of the linear adsorption (or exchange) isotherm.

c) The consideration of convection only (ignoring diffusion and fluid dispersion flux).

1. The presence of all three simplifications, a), b) and c) is the simplest case and can justly be termed "chromatography". In this case an adsorption band does not change shape even in homogeneous material; for soils this combination does not reflect the true situation.

2. The absence of b) and the presence of simplifications a) and c) is also very unlikely, as diffusion dispersion processes are usually involved in the soil. Only at high liquid velocities can the diffusion process be ignored, but in this case the existence of the exchange reaction may be doubtful.

3. The presence of b) and the absence of a) and c) is probably the right combination in many cases (e.g. for transport of herbicides, microelements and radioactive tracers), because of the validity of the linear adsorption curve. This will not be the case for certain macroelements, so for the transport of these,

4. the absence of any of the above simplifications would be the right solution.

The theoretical approach, however, is very complex in this case, so most of the theories are only applicable to case 3.

Two distinct approaches to cation transport based on the treatment of the rate of cation exchange are recognized in the literature: the equilibrium approach and the kinetic approach. The first model applied by RIBLE and DAVIS [1955] to ion exchange in soil profiles was proposed by DE VAULT [1943]. It requires that a dynamic equilibrium should exist between the ions in solution and in the adsorption phase. The theory was developed for ion exchange chromatography in ideal columns in which the thickness of the theoretical plates was assumed to be infinitesimal. The effect of diffusion, dispersion, channelling and turbulent flow are ignored.

The theory starts with the material balance over a cross-sectional layer of the column of thickness ∂z [DE VAULT 1943]:

$$\frac{\partial c}{\partial z} + \omega \frac{\partial c}{\partial V} + \frac{\partial q}{\partial V} = 0 \qquad 5.20)$$

where $c =$ local concentration of the given ion in the solution phase
   $q =$ local concentration of the given ion in the solid phase
   $z =$ distance from the top of the column
   $\omega =$ pore fraction
   $V =$ volume of solution fed into the column.

The general solution of this equation is:

$$z = S(c) + \frac{V}{\omega + \varphi f'(c)} \qquad (5.21)$$

where $\varphi =$ the amount of adsorber per unit of length
   $f'(c) =$ the derivate of $f(c)$ with respect to c
   $f(c) =$ the adsorption isotherm defined in such a way that $q = \varphi f(c)$
   $S(c) =$ any function determined by the initial distribution of the solute through the column.

DE VAULT [1943] shows that adsorption isotherms with positive curvature eventually give diffuse front boundaries, whereas negative curvatures give front boundaries which remain constant or even become sharp. Rear boundaries show the opposite situation. With a linear isotherm the shape of the boundaries remains unchanged as the boundary moves.

RIBLE and DAVIS [1955] have used DE VAULT's theory in soils with varying degrees of success. They derived the adsorption isotherm for the equilibrium constant of an ion exchange system. FILEP [1969] used the above-mentioned theory for the calculation of break-through curves in Ca soil columns percolated by Na-containing salt solutions. He showed that the theory could be adapted only when assuming complete equilibrium between the two phases and for the exchange of only two cations. The main limitation of DE VAULT's theory is, that in practice (e.g. in the soil) not only isotherms with positive curvature, but also linear isotherms and those with negative curvatures give diffuse boundaries. Apparently the ideal case of infinitesimal plate thickness

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is not fulfilled in actual columns in which disturbing factors such as finite grain size, diffusion in the solution and non-equilibrium are operative.

These disturbing factors may be taken into account by introducing a finite plate thickness using the MARTIN and SYNGE [1941] chromatography model. In applying the plate concept, the column is assumed to consist of a series of independent plates of equal height, in which an equilibrium is established between the components of the two phases. MARTIN and SYNGE [1941] show that the distribution of a solute obeys the laws of probability.

When a substance originally present only at the top of the column is eluated, the binomial (BERNOULLI) distribution is obtained. After a large amount of liquid has passed through a large number of theoretical plates, the distribution approaches the curve of error. If initially the column was evenly loaded with solute, the terms of the Bernoulli distribution should be summated; when a large number of plates has been passed, the error curve should be integrated into the error function. In this case, the point at which the concentration has decreased to half of its original value, is travelling downward with constant speed, and at the same time the boundary is gradually broadening. GLUECKAUF [1955] has used the plate concept in the evaluation of saturation curves, elution separations, etc. For the case of a linear adsorption isotherm, local equilibrium and continuous flow, GLUECKAUF's general equation is

$$\left[\frac{\partial f(Q)}{\partial V}\right]_X + \left[\frac{\partial C}{\partial X}\right]_V - k\left[\frac{\partial^2 C}{\partial X^2}\right]_V = 0 \qquad (5.22)$$

where k represents half the thickness (in g/cm^2) of the theoretical unit from the plate theory.

For non-equilibrium cases another differential equation was obtained.

The solution of the equation for the eluation of columns with homogeneous salt profiles was given by GLUECKAUF [1955] in the following way:

$$C = \frac{C_0}{2}\left[\operatorname{erfc}\frac{p-1}{\sqrt{2p}}\sqrt{N} - e^{2N}\operatorname{erfc}\frac{p+1}{\sqrt{2p}}\sqrt{N}\right] \qquad (5.23)$$

C = the concentration of the component in the liquid phase of the column (layer), mg/ml

C_0 = the initial concentration of the component in the liquid phase of the column (layer), mg/ml

$f(Q)$ = total amount of the component, mg/g dry material

V = the volume of eluating solution, ml/cm^3

X = the weight of the adsorbent per surface unit of the column, dry material g/cm^2

$2k$ = the thickness of theoretical plates ($N = 1/2\,k$)

$\overline{V}$ = the volume of the liquid phase at the given depth of column, ml/cm^2

p = $\dfrac{V}{\overline{V}}$ the ratio of the volume of the eluating solution to that of the liquid phase.

The error function:

$$\text{erfc } n = 1 - \frac{2}{\sqrt{\pi}} \int_0^n e^{-u^2} \, du \qquad (5.24)$$

In the case of $N > 4$

$$C = \frac{C_0}{2} \text{ erfc } \frac{p-1}{\sqrt{2p}} \sqrt{N} \qquad (5.25)$$

The theory was applied by VAN DER MOLEN [1956, 1957] to calculate the desalinization of Dutch soils and satisfactory agreement was found between the theoretical and experimental values. With certain modifications, the solution of the general equation is also possible in some cases of non-linear adsorption, e.g. the replacement of an ion by another with greater adsorption power, such as the exchange of Na^+ by Ca^{2+}. In the reverse case, e.g. when strongly adsorbed Ca^{2+} ions are replaced by less strongly adsorbed Na^+ ions, no theoretical description of the phenomena is available.

Since the above-mentioned equilibrium theories assumed convection to be the dominant effect in the ion transport, the chromatography model of LAPIDUS and AMUNDSON [cit: FRISSEL and POELSTRA 1967] involves the fluid dispersion effect. The model considers the case of a linear exchange isotherm. The equation based on the material balance over a layer Δz is:

$$D \frac{\partial^2 C}{\partial z^2} - \bar{v} \frac{\partial C}{\partial z} = \frac{\partial C}{\partial t} + \frac{\varrho}{\omega} \frac{\partial S}{\partial t} \qquad (5.26)$$

where

C = the concentration of the counter cation in the solution, me/cm^3
S = the amount of cation adsorbed per unit weight of the exchanger, me/g
z = the depth of the column along the direction of flow, cm
t = time, in hours
D = the fluid dispersion coefficient, $cm^2/hour$
$\bar{v}$ = the average pore velocity, cm/hour
ϱ = bulk density, g/cm^3
ω = pore fraction.

In some particular cases analytical solutions may exist for linear exchange isotherms but in general numerical solutions with defined initial and boundary conditions are applied both to linear and, with some modifications in the material balance equation, to non-linear exchange isotherm conditions [LAI and JURINAK 1971].

The chromatography model originally developed by THOMAS and extended by HIESTER and VERMEULEN [1952] is a kinetic approach. The kinetics of second order reactions are applied to the rate of adsorption. This model also considers convection to be the dominant effect in ion transport processes.

The ion exchange between the non-moving solid phase and the moving liquid phase is characterized by two partial differential equations. Firstly:

$$-\left[\frac{\partial C_A}{\partial l}\right]_V = \varrho\left[\frac{\partial q_A}{\partial V}\right]_l + f\left[\frac{\partial C_A}{\partial V}\right]_l \qquad (5.27)$$

This equation expresses the fact that any loss of ion "A" from the solution flowing through an infinitesimally thin section must be equal to the gain of "A" in the solid phase.

The other differential equation expresses the ratio between the cations in the solution and those on the exchanger.

For ions of equal valencies the following approximation can be made:

$$\left[\frac{\partial q_A}{\partial t}\right]_l = k_{\text{kin}}\left[C_A q_A - \frac{1}{K} q_A C_B\right] \qquad (5.28)$$

In the case of equilibrium $\frac{\partial q_A}{\partial t} = 0$ and the equation will be of the mass action type.

C_A, C_B = the concentration of ion "A" or "B" in the liquid phase at the given depth of column, me/cm³

l = length of column, cm

q_A = the concentration of ion "A" in the solid phase

ϱ = bulk density, g/cm³

V = the volume of solution fed into the column, ml/cm²

f = the ratio of the solution to the total volume of the column (dimensionless).

K = the ion exchange constant (dimensionless)

k_{kin} = ion exchange rate constant, ml/me/min.

The adsorption equation can also be used as the starting point. The theory is also valid for non-linear adsorption isotherms. For each type of adsorption isotherm the front becomes increasingly diffused in time.

On the basis of the above two equations a series of dimensionless parameters are defined during the derivation. In order to simplify the calculations HIESTER and VERMEULEN [1952] gave break-through curves in the form of graphs as a function of any of the above parameters. Numerical solutions are also evaluated. The validity of the kinetic theory of HIESTER and VERMEULEN was proved by BOWER et al. [1957] for the calculation of the effluent composition in the case of Mg-Ca and Na-Ca ion exchange in homoionic and biionic soil systems. A fair agreement between the theoretical and experimental data was obtained. FILEP [1969, 1974] also found a good agreement between experimental break-through curves and calculated ones on the basis of the HIESTER and VERMEULEN [1952] kinetic approach.

When modelling ion transport care must be taken to select a proper model which makes it possible to take into account most of the factors determining the mass transport in soil columns.

In most cases, the differential equations describing the rate of movement of the solvent and the solute have no general solutions. Numerical approaches must be employed with determined boundary conditions.

The computation of this kind of solution provides greater possibilities for the quantitative description of soil processes.

List of Symbols

(A_{ad})	the activity of exchangeable "A" cation
(B_{ad})	the activity of exchangeable "B" cation
C	the local concentration of the counter ion in the solution phase of the column [me/ml]
C_i	the concentration of the ion "i" [mole/l]
C_0	the initial concentration of the counter ion in the solution phase of the column [me/ml]
C_{Na}	sodium ion concentration in the intermicellar solution in equilibrium [mole/l]
EF	the error function
I	ionic concentration of the electrolyte [mole/l]
K	exchange constant
K_B^A	the thermodynamic exchange constant
K_{CA}	the solubility product of the salt $C\nu_A \cdot A\nu_B$
K_{Ca}^{Na}	thermodynamic exchange constant of Ca^{2+}-Na^+ exchange
K_{CaCO_3}	the solubility product of $CaCO_3$
K', K''	the first and second constants of carbonate ion hydrolysis
K_{d_1}	the first dissociation constant of carbonic acid
K_{d_2}	the second dissociation constant of carbonic acid
K_w	the ion activity product of water
K'	selectivity coefficient of Na^+-Ca^{2+} exchange
K_1, K_2, K_3	exchange rate constant in the 1st, 2nd, 3rd part processes [sec^{-1}]
M	CEC of the adsorbent [me/g]
N	the number of plates [$N = 1/2\,k$]
N_{Na}	equivalent fraction of exchangeable sodium
(RCa)	the activity of the exchangeable Ca
(RNa)	the activity of the exchangeable Na
S	the amount of cation adsorbed per unit weight of the solid phase [me/g]
$S(c)$	any function determined by the initial distribution of solute through the column
S_L	activity of the free solution in equilibrium [imp/min/ml]
S_0	activity of the solution used to label the system with Na-24 [imp/min/ml]
T	CEC of the adsorbent [me/100 g]
V	volume of the solution fed into the column [ml/cm^2]
V_s	volume of free electrolyte per 1 g of adsorbent
$\bar{V}$	the volume of the liquid phase at a given depth of the column [ml/cm^2]
X	the weight of the solid phase per surface unit of the column [dry material g/cm^2]
a	constant
b	constant
f	ratio of the solution to the total volume of the column [dimensionless]
$f(c)$	the adsorption isotherm defined in such a way that $q = \varphi f(c)$
$f'(c)$	the derivate of $f(c)$ with respect to c
$f(Q)$	the total amount of the ion [mg/g dry material]

$2k$	the thickness of the theoretical plates
k_{kin}	ion exchange rate constant $[\sec^{-1}]$
l	length of the column $[cm]$
m	the valence of the cation
n	the valence of the anion
(n)	the number of steps of iteration
$p = \dfrac{V}{\overline{V}}$	the ratio of the volume of the eluating solution to that of the liquid phase
pCa	$-\lg(Ca^{2+})$
pNa	$-\lg(Na^{+})$
$q(q_A, q_B)$	local concentration of the ion (A, B) adsorbed on the solid phase $[me/layer]$
t	time $[hours]$
v_1, v_2, v_3	rate of exchange in the 1st, 2nd, 3rd part processes $[g\ atom\ \sec^{-1}]$
$\overline{v}$	average pore velocity $[cm/hour]$
z	distance from the top of the column along the direction of flow $[cm]$
γ	the activity coefficient of the ion
ν_A	the number of cations in the salt
ν_B	the number of anions in the salt
ϱ	bulk density $[g/cm^3]$
φ	the weight of the solid phase per unit length of column $[g/cm^3]$
ω	pore fraction (dimensionless)
$(\ )$	activity of ions in the solution $[mole/l]$
$[\ ]$	concentration of ions in the solution $[mole/l]$