The Evaluation of Physico-Chemical Processes from the Point of View of Alkali Soil Amelioration

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The amelioration of sodic soils with gypsum involves the neutralization of salts capable of alkaline hydrolysis and the replacement of exchangeable sodium by calcium. The basic principles are well known [1, 7, 11], but when calculating the quantity of gypsum required and predicting the ameliorative effect of the amendment, the physico-chemical processes affecting the movement and distribution of $CaSO_4$ in the soil profile are generally ignored. Even the possibilities of an approximative description of these processes have not been fully investigated.

Data are already available concerning the effect of the degree of $CaSO_4$ dissolution on the rate of changes in the soil properties and the factors affecting solubility [4, 5, 6].

The dissolution of $CaSO_4$ in the soil solution is influenced by the concentration and composition of the salts, as well as by the characteristic composition of the mixed electrolyte solution [6, 9]. The results of investigations carried out usually in soil-water extracts are valid only for the given experimental conditions and the characteristics of the movement of Ca compounds with the flow of solutions are not taken into account.

Model experiments were carried out to study the vertical distribution of Ca^{2+} and Na^+ ions in the solid and liquid phases and to describe the changes in the properties of the ameliorated soil layer of alkali soil columns treated with gypsum.

Materials and methods

The 0.5—2 mm particle size fraction of the B_1 horizon (4—16 cm) of an alkali soil was used for the model experiments. The chemical and physical characteristics of the soil and the parameters of the soil columns are given in Table 1. The preparation of the soil columns, the solution treatment, and the simplifications taken into account in the boundary conditions of the column models have been reported elsewhere [8, 10].

The way in which the soil columns were treated with gypsum and the parameters of the percolating solutions are given in Table 2.

Table 1

**Chemical and physical characteristics of the soil sample and
soil column parameters**

$pH_{(H_2O)}$	8.1	Column length, cm	10
$CaCO_3$ %	0.74	Column diameter, cm	4.65
Salt content, %	1.40	Weight of model soil sample, g	180
Exchangeable Na, me/100 g	15.58	Bulk density, g/cm³	1.3
CEC, me/100 g	23.48	Pore fraction, dimensionless	0.56
ESP	66.39		
Saturation percentage	64.00		

1. Saturation (1st part of the experiment)

The soil columns, without or after the previous treatment with gypsum, were saturated in a capillary way with 0.01 N Na_2SO_4 solutions. Every saturation with sodium sulphate solution was carried out in four replications. One of the parallel columns was used for analysing the process of saturation and three of them for leaching.
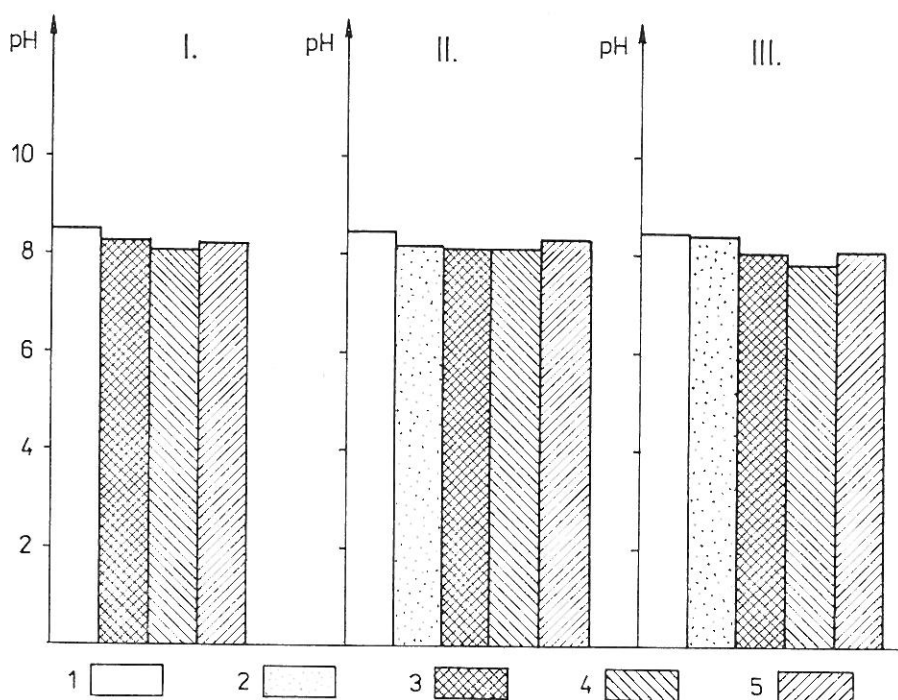

Fig. 1

Changes in the pH values of solutions extracted from the soil column layers in experiments I, II and III. 1. Saturation with 0.01 N Na_2SO_4 solution; 2. Saturation with 0.01 N Na_2SO_4 in soil previously mixed with gypsum; 3. Leaching of columns 1 and 2 with distilled water; 4. Leaching of columns 1 and 2 with 0.01 N Na_2SO_4 solution; 5. Leaching of columns 1 and 2 with 0.1 N Na_2SO_4 solution

Table 2

The treatment of soil columns; percolating solution parameters

Experiment No. treatment with gypsum	Parallel samples of columns	1st part of the experiment (saturation)				2nd part of the experiment (leaching)				Volume of solution percolated through the column, ml
		water capacity of the column, g/kg	Na$^+$	SO$_4^{2-}$	I	Na$^+$	Ca^{2+}	SO$_4^{2+}$	I	
			concentration, me/l		mole/l	concentration, me/l			mole/l	
			of the saturating solution			of the solutions used for leaching				
I No pretreatment	1	46.72	12.24	11.95	$2.31 \cdot 10^{-2}$	Cut into sections and analysed after saturation				
Percolation of CaSO$_4$ 2 H$_2$O saturated solutions	2	48.27	12.24	11.95	$2.31 \cdot 10^{-2}$	—	26.75	28.08	$5.48 \cdot 10^{-2}$	840
	3	46.67	12.24	11.95	$2.31 \cdot 10^{-2}$	13.04	23.20	35.41	$6.51 \cdot 10^{-2}$	620
	4	49.26	12.24	11.95	$2.31 \cdot 10^{-2}$	89.13	17.40	115.5	$2.22 \cdot 10^{-1}$	980
II Percolation of solutions through soil sample pre-treated by mixing with 9 g CaSO$_4$ 2 H$_2$O	1	65.13	9.3	10.12	$1.94 \cdot 10^{-2}$	Cut into sections and analysed after saturation leached with distilled water				
	2	62.71	9.3	10.12	$1.94 \cdot 10^{-2}$					180
	3	67.83	9.3	10.12	$1.94 \cdot 10^{-2}$	9.3	—	10.12	$1.94 \cdot 10^{-2}$	280
	4	68.22	9.3	10.12	$1.94 \cdot 10^{-2}$	95.7	—	98.6	$1.92 \cdot 10^{-1}$	240
III Percolation of solutions through soil sample pre-treated by applying 9 g CaSO$_4$ 2 H$_2$O to the top of the column	1	43.88	10.86	10.45	$2.13 \cdot 10^{-2}$	Cut into sections and analysed after saturation leached with distilled water				
	2	57.77	10.86	10.45	$2.13 \cdot 10^{-2}$					810
	3	63.33	10.86	10.45	$2.13 \cdot 10^{-2}$	10.86	—	10.45	$2.13 \cdot 10^{-2}$	790
	4	56.83	10.86	10.45	$2.13 \cdot 10^{-2}$	95.70	—	98.60	$1.92 \cdot 10^{-1}$	850

2. Leaching of soil columns (2nd part of the experiment)

a) In the case of soil columns without previous treatment with gypsum, the leaching solutions were saturated with gypsum.

b) In the case of soils pretreated with gypsum, the leaching solutions were: distilled water, 0.01 N and 0.1 N Na_2SO_4 solutions. The flow rate was controlled at 3 mm/h. The Na^+, Ca^{2+} and SO_4^{2-} ion concentrations in the effluent solutions were continuously controlled. In the experiment where leaching was carried out with $CaSO_4$ saturated solutions, the steady state was reached with respect to Na^+ and Ca^{2+} ion concentrations when 600—900 ml solution was percolated. In the experiments where gypsum was previously mixed with the soil or was applied to the top of the column, leaching was carried out until the effluent was saturated with gypsum.

Once the steady state was reached in the effluent after the given treatments, the columns were cut into 1 cm sections. The soil solution in each section was separated by centrifugation and the soil was air-dried. The pH and the ionic concentrations in the soil solutions were determined using standard methods [12]. CO_3^{2-} and HCO_3^- concentrations were determined from the pH, the concentrations of the other ions in the soil solution and the 2nd dissociation constant of carbonic acid using an iteration procedure. The electrolyte compositions (ion pair concentrations, ion concentrations and activities, taking into account the ion pair formation) were calculated with the computation programme elaborated by DARAB, CSILLAG and PINTÉR [5, 6].

The exchangeable Na^+ and Ca^{2+} ions were determined by the isotope dilution method using Na-22 and Ca-45 [2, 3, 4]. The amount of exchangeable
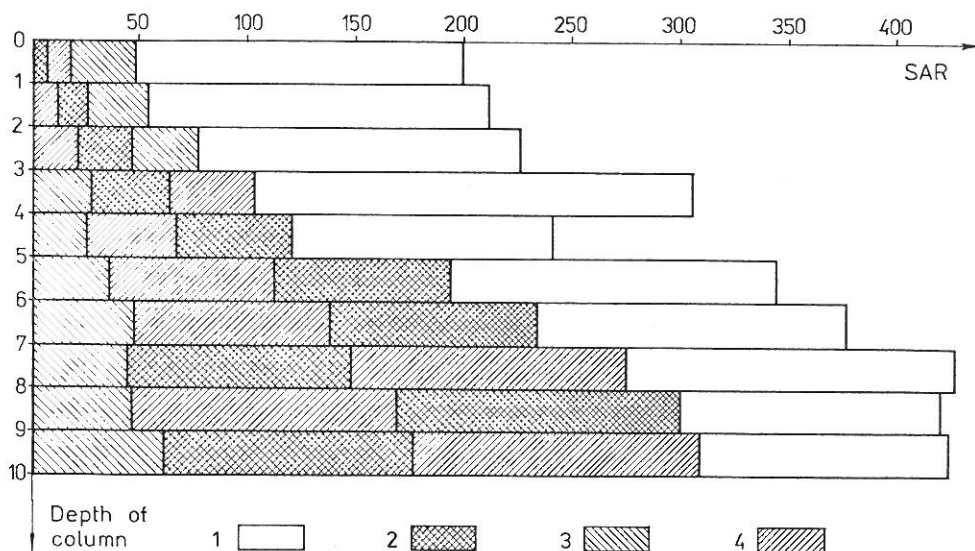

Fig. 2

Changes in the SAR values in solutions extracted from 1 cm layers. 1. Saturation with 0.01 N Na_2SO_4 solution; 2. Leaching of column 1 with $CaSO_4$ saturated water; 3.Leaching of column 1 with $CaSO_4$ saturated 0.01 N Na_2SO_4 solution; 4. Leaching of column 1 with $CaSO_4$ saturated 0.1 N Na_2SO_4 solution

Table 3

**Average Ca²⁺ concentrations, the amount of dissolved CaSO₄ and
the thermodynamic solubility product of gypsum in solutions extracted from
1 cm thick sections of the soil columns**

Treatment[a]		Ca^{2+} me/l	Dissolved $CaSO_4 \cdot 2 H_2O$ g/kg	K_{sp}
I	1	3.75		$4.89 \cdot 10^{-6}$
	2	3.76	0.004	$7.14 \cdot 10^{-7}$
	3	3.81	0.024	$9.02 \cdot 10^{-7}$
	4	3.77	0.008	$1.13 \cdot 10^{-5}$
II	1	11.35	0.41	$1.10 \cdot 10^{-5}$
	2	9.43	0.29	$4.88 \cdot 10^{-6}$
	3	6.68	0.18	$5.49 \cdot 10^{-6}$
	4	5.42	0.15	$5.43 \cdot 10^{-6}$
III	1	10.28	0.52	$1.63 \cdot 10^{-5}$
	2	17.93	0.66	$1.08 \cdot 10^{-5}$
	3	12.55	0.49	$1.08 \cdot 10^{-5}$
	4	17.77	0.49	$1.04 \cdot 10^{-5}$

* For treatments, see Table 2.

Mg^{2+} was calculated from the values of exchangeable Na^+ and Ca^{2+}, assuming that the CEC is constant.

Results and discussion

The equilibrium concentration of Ca^{2+} ions in the solution extracted from the 1 cm sections of the soil columns increases after treatment with gypsum. The changes in the Ca^{2+} ion concentrations are within the error of analysis in
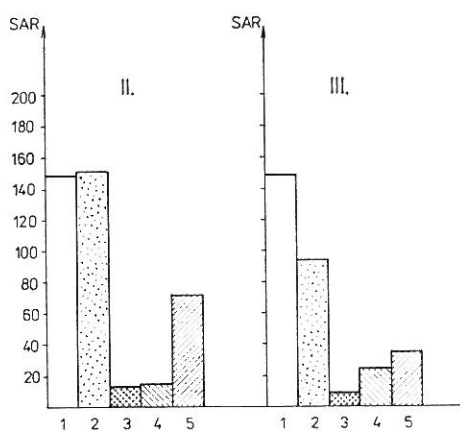

Fig. 3
Changes in the average SAR values of solutions extracted from soil columns previously treated with gypsum in experiments II and III. 1—5, see Fig. 1

the case when solutions saturated with gypsum are percolating through untreated soil columns (Treatment No. I), but if the soil column is previously treated with gypsum, the equilibrium Ca^{2+} concentrations are 3—5 times greater than those measured in the solution of the column prepared from untreated soil samples.

The amount of dissolved gypsum is the highest in the case of columns treated with gypsum on the top, and the maximum can be found in the upper 3 cm layer (Table 3).

The average values of the thermodynamic solubility product (i. e. the product of the activities of Ca^{2+} and SO_4^{2-} ions in the solutions) are generally
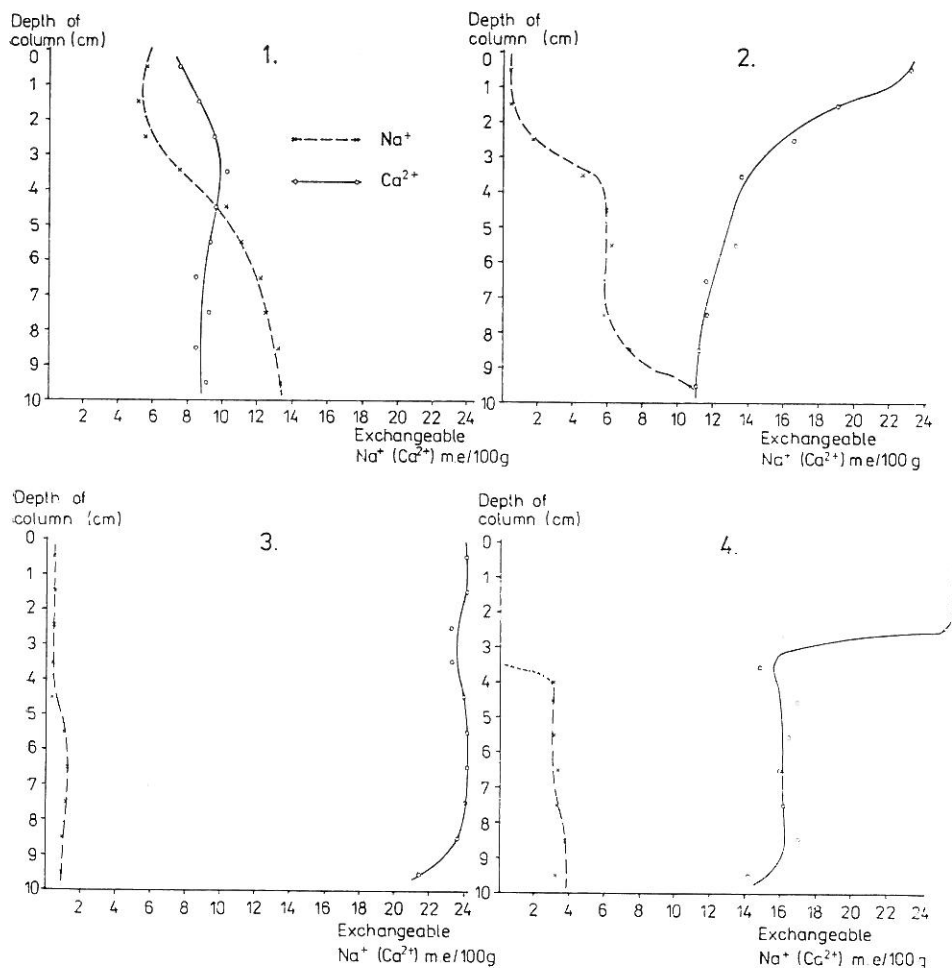

Fig. 4

The vertical distribution of exchangeable Na^+ and Ca^{2+} ions in soil columns after different treatments with gypsum. 1. Original soil saturated with 0.01 N Na_2SO_4 solution; 2. Leaching of column 1 with $CaSO_4$ saturated distilled water; 3. Soil column 1 mixed with 9 g gypsum and leached with distilled water; 4. 9 g gypsum applied to the top of column 1 and leached with distilled water

low and they approximate only in a few cases the solubility product of $CaSO_4 \cdot 2 H_2O$ found in the literature. The soil solutions were saturated with gypsum only in the upper $3-4$ cm layers of soil columns where gypsum was applied to the top.

This means that even under the conditions of the given soil column model experiment, where a much larger amount of the amendment was used in comparison with field conditions, the solutions percolating in the soil are not saturated with gypsum.

The pH values of the solutions are usually lower after treatment with gypsum than they were before gypsum application, but the change in the pH values exceeds the error of analysis only in the case of a few samples (Fig. 1).

In the case of percolation with $CaSO_4$ saturated solutions, a considerable change in the SAR values of the solutions — due to the dissolution of gypsum — can only be found in the upper 3 cm layer of the soil columns (Fig. 2).

After pretreatment of the soil with gypsum (Experiments No. II and No. III), even the average SAR values show a considerable decrease (Fig. 3).
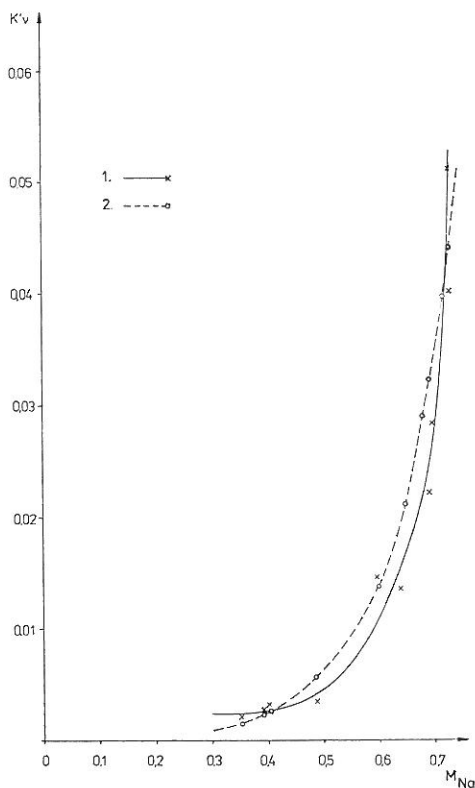

Fig. 5
The correlation between the Vanselow selectivity coefficient and the mole fraction of exchangeable Na^+. (From the data of soil columns saturated with 0.01 N Na_2SO_4 solution.)
1. Experimental data; 2. Calculated from the exponential equation:
$$K' = 8.0 \cdot 10^{-5} \cdot e^{8 \cdot 615} M_{Na}$$

The vertical distribution pattern of the exchangeable Ca^{2+} and Na^+ ions corresponds to the chromatographic distribution of ions in the column of ionic exchangers (Fig. 4). With the percolation of $CaSO_4$ saturated solutions, a fairly sharp rear boundary of Na^+ ions develops, in accordance with the unfavourable (concave) adsorption isotherm of sodium. In the 3—4 cm top layer, a considerable decrease in the exchangeable Na^+ values was observed.

A similar, even more characteristic picture can be observed in those soil columns where $CaSO_4 \cdot 2\,H_2O$ was applied to the top. In the upper layers the Ca^{2+}—Na^+ ion exchange is practically complete. The exchangeable Na^+ and Ca^{2+} values in the 2 cm top layer are only estimated, because the surface conditions in the presence of the high amount of gypsum in this layer disturb the exact determination of Na-22 and Ca-45 isotope exchange.

When the soil was previously mixed with gypsum, leaching with distilled water leads to a drastic decrease in exchangeable sodium in the whole soil column.

The experimental results show that there are differences in the distribution patterns of exchangeable Na^+ and Ca^{2+} ions in the soil columns, when gypsum saturated solutions are percolated or when the soil is previously treated with gypsum.

The shape of the distribution pattern also depends on the different Na : Ca ratios of the leaching solutions. With an increase in the Na : Ca ratio, a lower decrease of sodium ions was found.

The correlation between the Vanselow selectivity coefficient and the mole fraction of sodium on the adsorbent can be represented by an exponential equation (Fig. 5). After reaching the value of 0.5 of the mole fraction (ESP > 33), the value of the selectivity coefficient suddenly increases, proving the non-ideal ion exchange behaviour of the solid phase of the soil.

The Na—Ca ion exhange isotherm based on the data of the experimental system is given in Fig. 6. The equivalent fractions of sodium in the solutions (X_{Na}) are plotted against the equivalent fractions on the adsorbent (Y_{Na}). Under the given experimental conditions, X_{Na} is generally high (in most cases > 0.9) and the majority of the measured values can be found on the steeply rising part of the isotherm. Consequently, even a very small decrease in the relative amount of Na^+ ions in the solution can lead to a considerable decrease in the degree of sodium saturation. The experimental values found on the horizontal part of the isotherm correspond to the "ameliorated" soil layers, where the solution is nearly saturated with gypsum. The shape of the isotherm plotted using the ionic activity data of the solution, represents a more concave character than that based on ionic concentrations. This may prove the conclusions based on previous experiments concerning the over-estimation of the selectivity of the adsorbent for sodium, when the concentration of ions is used for the characterization of ion exchange processes in the soil.

Conclusions

The ameliorative effect of $CaSO_4$ amendment is influenced by the physicochemical processes occurring during the flow of solutions in soils treated with gypsum.
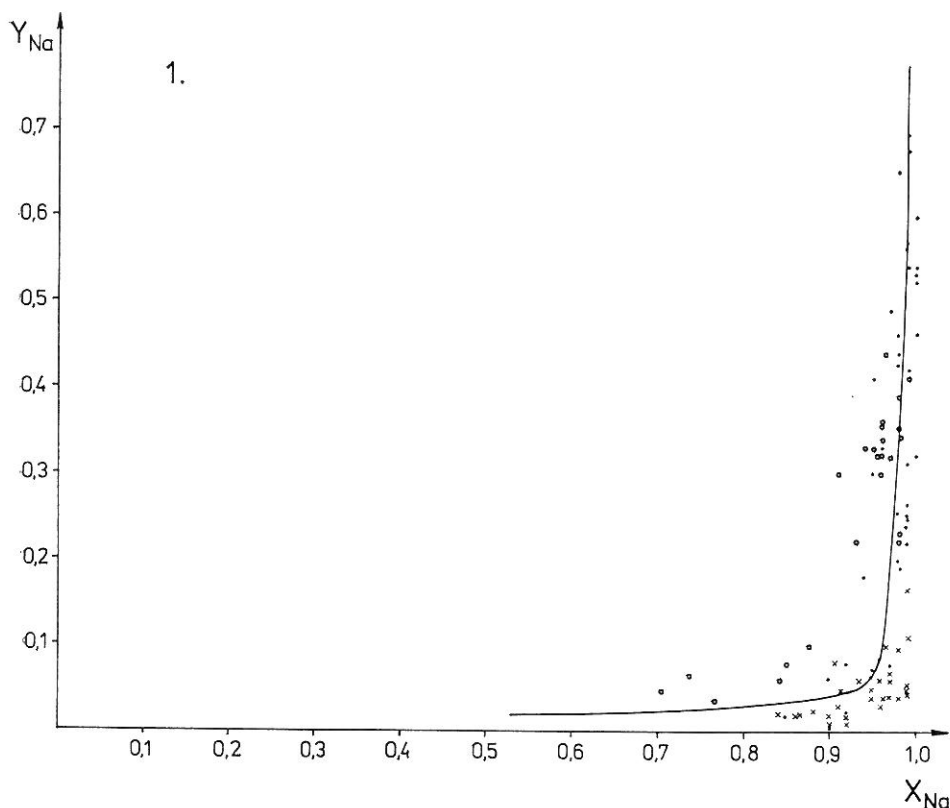
The Na—Ca ion exchange isotherm based on the experimental data. 1. X_{Na} calculated
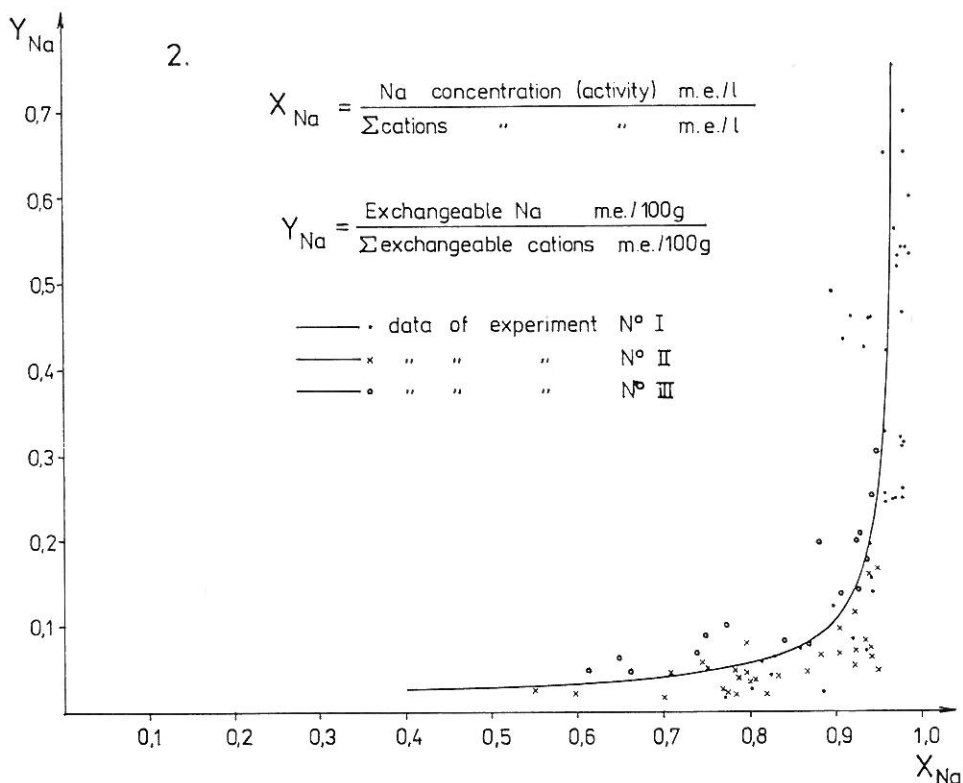
Under field conditions, the solutions percolating in the soil are not saturated with gypsum even after the chemical amelioration of sodic soils. It is the cation exchange process between the micellar and intermicellar solutions, which determines the changes in the soil properties and the increase in the amount of mobile Ca compounds in the given soil layer to be ameliorated. The rate of dissolution of $CaSO_4$, influenced by the ionic concentration and composition of the soil solution, has an effect on the ion exchange.

The experimental data and the calculations used make it possible to approximately describe the mechanism of chemical reclamation under dynamic conditions and to predict the ameliorative effect of $CaSO_4$-containing amendments.

On the basis of the experimental data the following practical conclusions may be drawn:

— Differences between improving the quality of irrigation water containing residual carbonate and the amelioration of soils containing salts capable of alkaline hydrolysis must be taken into account.

— The saturation of the irrigation water with gypsum can serve to prevent the development of secondary sodic soils.

$$X_{Na} = \frac{Na \text{ concentration (activity)} \quad m.e./l}{\Sigma \text{cations} \quad \text{''} \quad \text{''} \quad m.e./l}$$

$$Y_{Na} = \frac{Exchangeable \ Na \quad m.e./100g}{\Sigma \text{exchangeable cations} \quad m.e./100g}$$

—————· data of experiment N° I
—————×   ''   ''   ''   N° II
—————∘   ''   ''   ''   N° III

6

from ionic activities; 2. X_{Na} calculated from ionic concentrations

— When the amelioration of a sodic soil is carried out by the application of gypsum combined with the use of leaching water, a greater effect can be achieved if the amendment is first mixed into the soil layer to be ameliorated, and afterwards leaching is carried out.

Summary

The amelioration of sodic soils with gypsum involves the neutralization of salts capable of alkaline hydrolysis and the replacement of exchangeable sodium by calcium.

In spite of the fact that the basic principles are well known, the possibilities of describing the movement and distribution of $CaSO_4$ containing amendment in the soil profile and determining the rate of the changes in the soil properties influenced by the degree of $CaSO_4$ dissolution, have not been fully investigated. These are the further steps in the understanding of the mechanism of chemical reclamation, and the basis of more exact calculations of the gypsum requirement.

Model experiments were carried out to study the vertical distribution of Ca^{2+} and Na^+ ions in the solid and liquid phases of alkali soil columns treated with gypsum. The percolation of $CaSO_4$ saturated solutions and the elution of $CaSO_4$ applied to the top of the soil column, by water and by Na_2SO_4 solutions of different concentrations, were the techniques used.

The ionic concentration and composition of the soil solution and the amount of exchangeable cations were determined in 1 cm thick sections of the soil columns.

The changes in the ion exchange equilibria due to $CaSO_4$ dissolution were determined.

The solubility of $CaSO_4$ in the soil solution was characterized by the thermodynamic solubility product, i.e. the product of the activities of Ca^{2+} and SO_4^{2-} ions.

The characteristics of the chromatographic distribution of exchangeable Ca^{2+} and Na^+ ions in the columns and the extent of increase in the mobile Ca compounds in the ameliorated soil layer were determined.

Based on the experimental data and the calculations used, it is possible to approximately describe the process of chemical reclamation under dynamic conditions and to predict the ameliorative effect of $CaSO_4$ containing amendments.

References

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Discussion

VÁRALLYAY, G.
What is your opinion about the applicability of the models presented in your paper [in the case of unsaturated conditions?
RÉDLY, M.
Theoretically both the physical model (the study of chromatographic distribution of ions in soil column s) and the mathematical model based on the mathematical chromatography and used for our previous investigations (see: „Modelling of soil salinization and alkalization" Agrokémia és Talajtan, Suppl. 1979.) can be used also for unsaturated soil conditions. The limitations are:
— the technical difficulties in extracting the solution from the sections of the soil columns;
— the limited validity of our computation programme in solutions with ionic concentrations >0.1 mole/l.