

## **The Role of Sodium Compounds in the Formation and Properties of Salt Affected Soils**

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Salt affected soils may be found with a great diversity of physical, chemical and biological properties under a wide range of environmental conditions. Salt affected soils may occur in closed basins, river deltas and terraces with moderate climates in North and South America, Europe, Australia, Asia [23]. Large areas in semiarid and arid regions are covered with soils having increased quantities of water soluble salts and/or poor water physical properties (in the Near and Middle East, Central Asia, North Africa, etc.).

In spite of the deviations in their origins and physical, chemical and biological properties, all of these soils have the common feature that an increased amount of salts plays and/or has played a decisive role in their formation, and water soluble salts are responsible directly or indirectly for their low fertility.

The soluble salt content of soils is usually low and the various salts accumulate in reverse sequence of their solubility (Table 1.).

The total ionic concentration of soil solutions has a wide range. In non-saline soils the concentration of dissolved salts is relatively low and does not usually exceed 0.01 mole/l. In salt affected soils containing 0.2–10 g/100 g of salts soluble in water, the concentration of the soil solution can be as high as 0.1–5 mole/l [4].

The formation of salt affected soils has two preconditions:

1. The contact of the soil layer with the sources of soluble salts.
2. Conditions ensuring that salt accumulation prevails periodically or permanently over leaching.

Under non-saline soil conditions the amount of soluble salts is low and in the non-saline soils of the temperate zone calcium and magnesium hydrocarbonates are dominant among the soluble salts. With an increase in the salt content, salts with better solubility will be dominant. Calcium sulphate, magnesium sulphate and calcium chloride may accumulate if the soil layer does not contain free carbonate, and saline soils with this type of salinization can form. The increasing salinity of the soil is usually combined with an increased ratio of sodium salts. This phenomenon is clearly demonstrated in the chemistry of salt accumulation in different types of hydromorphic soils from the Hungarian Lowland (Table 2).

The main sodium salts accumulating in soils are sodium carbonate, sodium bicarbonate, sodium sulphate and sodium chloride.

*Table 1*  
**Characteristics of accumulation processes in Eurasia,  
 in relation to natural conditions [14]**

Conditions	Residual salinization of sedimentary rocks	Maximum mineralization of waters (in g/l)			Max. quantity of soluble salts in top horizons of solonchaks, %	Typical compounds	Salinization of irrigated soils
		river	ground	lake			
Desert	common	20—90	200—350	350—400	25—75	NaCl KNO <sub>3</sub> NaNO <sub>3</sub> MgCl <sub>2</sub> MgSO <sub>4</sub> CaSO <sub>4</sub> CaCl <sub>2</sub>	Wide-spread
Semi-desert	frequent	10—30	100—150	300—350	5—8	NaCl Na <sub>2</sub> SO <sub>4</sub> CaSO <sub>4</sub> MgSO <sub>4</sub>	Often found
Steppes	rare	3—7	50—100	100—250	2—3	Na <sub>2</sub> SO <sub>4</sub> NaCl Na <sub>2</sub> CO <sub>3</sub> NaHCO <sub>3</sub>	Rarely found
Forest steppes	none	0.5—1.0	1—3	10—100	0.5—1.0	NaHCO <sub>3</sub> Na <sub>2</sub> CO <sub>3</sub> Na <sub>2</sub> SO <sub>4</sub> Na <sub>2</sub> SiO <sub>3</sub>	Un-known
Forests	none	0.1—0.2	0—1	none	none	R <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub>	None

Among the sodium salts, sodium chloride is the most mobile of the soluble salts. It has a high solubility and the concentration of a sodium chloride saturated solution does not depend on the temperature (Fig. 1). This facilitates the accumulation of this salt, but at the same time it can easily be leached out, either by natural or artificial drainage.

This salt is partly of magmatic origin and partly the product of the weathering of crystalline rocks. Sodium chloride occurs in saline ground waters, lakes, sediments and soils in desert and semi-desert regions. It is the main compound in sea water, in salts accumulated on sea shores and in marine deposits. Due to the high solubility of chloride salts, their quantities increase with an increase in soil salinity. Sodium chloride, together with sodium sulphate and magnesium sulphate, is the most common component of saline soils. Sodium chloride is exceptionally toxic to plants due to its high solubility. The chloride part of the salts moves freely with water. The leaching out of sodium chloride saline soils is fairly easy if the soils contain gypsum.

Sodium sulphate is usually a product of the weathering of crystalline rocks, but the possibility of magmatic origin cannot be neglected. Sodium sulphate is easily dissolved in water. The saturation concentration of sodium sulphate is 185 g/l at 25°C and depends very much on the temperature (Fig. 1). It is a typical compound of saline soils, saline groundwaters, lakes and muds in desert and semi-desert regions and in waters, sediments and soils of dry regions.

Table 2

The chemical composition of saturation extracts of hydromorphic soils in Hungary

Soil	Depth of sampling cm	Soluble salts %	Ca <sup>++</sup>	Mg <sup>++</sup>	Na <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>-</sup>
			me/l					
Meadow soil	7—17	0.10	5.25	0.98	0.87	0.64	3.90	0.55
	58—72	0.30	14.80	12.60	6.10	1.46	12.80	6.60
	90—110	0.35	22.50	12.10	4.80	0.88	5.30	27.00
	126—136	0.22	17.80	9.80	7.60	1.00	5.60	22.90
Solonetz-like meadow soil	5—17	0.01	2.40	2.80	0.97	0.25	2.00	0.50
	30—42	0.06	2.50	5.30	1.60	3.00	2.50	1.30
	56—76	0.10	3.75	3.60	1.60	1.60	0.72	2.60
Meadow solonetz	89—100	0.55	17.40	16.00	21.30	1.40	1.10	31.40
	8—16	0.06	4.3	6.00	6.40	3.10	4.40	1.40
	26—37	0.12	4.5	3.70	10.00	3.50	3.40	4.30
	45—55	0.20	4.0	3.40	18.20	4.80	4.60	4.10
	75—85	0.75	15.1	41.70	37.70	1.50	1.70	37.80
	97—105	0.75	15.5	34.80	34.30	1.40	1.30	43.50
	117—126	0.25	3.1	8.30	24.50	3.30	2.70	8.30

Sodium sulphate may also accumulate in waters, sediments and soils in the temperate zone, if the hydrogeochemical conditions are in favour of sulphatic accumulation. In this case the degree of sulphate accumulation is less than usual under a dry climate (Tables 3 and 4).

The dependence of sodium sulphate solubility on temperature has a great influence on the movement of this salt. In dry, warm periods the dissolution of sodium sulphate increases with an increase in the air temperature. The soil moisture moves upwards and the sodium sulphate containing solution rises to the surface of the soil together with the other most soluble salts. In the cool, rainy season the solubility of sodium sulphate decreases with the decreasing temperature. It is not leached out with other easily soluble salts. The bulk of it remains in the top layers of the soils. In the temperate zone the sources of soil salinization are less saline, and the intensities of accumulation and leaching processes are closer to each other even when the accumulation process prevails. Under these conditions the water regime, as well as the interaction between the ions of the electrolyte solution and the solid phase of sediments and soils regulate the sodium sulphate regime during the soil forming processes.

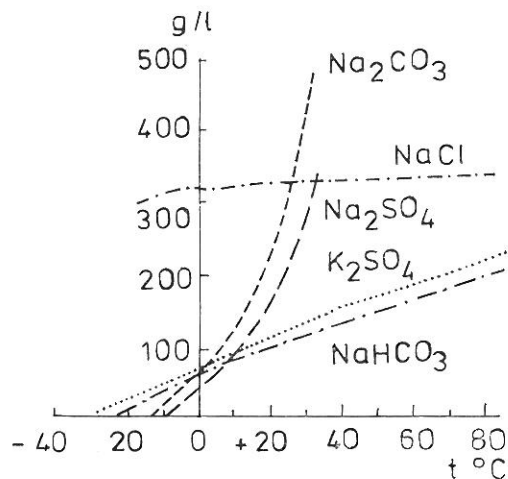


Fig. 1

Salt solubility as a function of temperature [4]

Table 3

The chemical composition of soluble salts of a meadow solonchak in the northern part of the Kyzylkum Desert, determined from 1 : 5 aqueous extracts [4]

Depth of sampling, cm	Dry residue	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup> + K <sup>+</sup>
	%							
0— 2	21.73	0.04	traces	1.85	11.36	2.63	0.36	5.68
2— 6	16.00	0.04	traces	1.46	8.62	2.52	0.33	4.18
10— 15	4.41	0.02	∅	1.05	1.61	0.33	0.18	0.74
25— 30	3.52	0.02	∅	1.09	1.04	0.11	0.16	0.79
40— 45	3.23	0.01	∅	0.89	1.04	0.13	0.12	0.71
120—125	1.24	0.01	∅	0.20	0.58	0.12	0.04	0.19
190—195	1.94	0.02	∅	0.18	1.04	0.18	0.05	0.32

Sodium carbonate is a highly soluble compound. The solubility of sodium carbonate and sodium bicarbonate depends very much on the temperature (Fig. 1). As a result of hydrolysis, a solution containing sodium carbonate always has an alkaline reaction up to pH 12. Because of its high solubility and strong alkalinity, a sodium carbonate solution is always very harmful to plants and causes the peptization of soil colloids, low water permeability and poor water physical properties in the soil.

Sodium carbonate may occur in surface and groundwaters, in deposits and soils in every region [4, 14, 22]. The main source of the accumulating sodium carbonate is the weathering of crystalline rocks in carbon dioxide containing water, but it may form in smaller quantities due to chemical reactions [13], ion exchange [12] and biological processes [2] as well. In waters and soils with a medium degree of salinization sodium carbonate is usually the dominant compound among the dissolved salts. The reaction of a solution containing sodium carbonate is regulated by the partial pressure of carbon dioxide and the total ionic concentration [10, 14, 15].

The soil solution can always be considered as a solution of mixed salts. In a solution containing dissociable salts the electrostatic interaction of the ions results in a special arrangement in the electrolyte [1]. This interaction decreases the concentration of ions with free valences and influences several properties of the solution, including the equivalent conductivity of the electrolyte [25], the solubility of poorly water soluble salts [3, 20], the degree of dissociation of the dissolved salts [18] and the ratios of ion activities in the solution [1, 17]. The elaboration of a model of ion pair formation is one approach to the description of the non-ideal behaviour of real solutions in saline soils [7, 8].

This model assumes that due to the electrostatic interaction of ions having opposite charges, ion associations may form with no valency or be partly neutralized in the electrolyte solution. The stability of ion pairs is characterized by their relative dissociation constants (Table 5). By considering the analytical concentrations of the ions and the dissociation constants of the ion pairs, the actual ionic concentrations and ion activities may be computed by the method of successive approximation in the case of a simple electrolyte solution containing three or four ions.

Table 4

Chemical compositions of the saturation extracts of solonetz soils

Depth of sampling, cm	pH	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	"T"
		10 <sup>-4</sup> · mole/l						
Profile 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—120	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	31.21	3.38	102.30
Profile 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	18.12	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
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

For a mixed salt solution it must be taken into account, that a cation may form ion pairs with a number of anions in the electrolyte. The same holds true of the anions present in the salt solution. In an effort to overcome the difficulties caused by the matrix effect of the ions, the computation programme was modified for mixed salt solutions by calculating the weighted averages of ion concentrations after each iterative step, with the introduction of a function representing the ratio of the sum of ion pair concentrations to the analytical concentration of the related ion:

$$(C_i)_{n \text{ red}} = \frac{[(C_i)_{(n-1)} \cdot EF] + (C_i)_n}{[EF + 1]}$$

if:

$C_i$  = the concentration of the ion "i" (mole/l)

$n$  = the number of steps in the iteration

$$EF = \frac{\sum_{j=1}^y (C_i A_j)}{(C_i)}$$

$EF$  = error function

$(C_i A_j)$  = the concentration of ion pairs formed by ions  $C_i$  and  $A_j$

Table 5

Dissociation constants of ion pairs to be expected in solutions of salt affected soils

Ion pair	$K_d$
CaCO <sub>3</sub> <sup>0</sup>	6.3 · 10 <sup>-4</sup>
CaHCO <sub>3</sub> <sup>+</sup>	5.5 · 10 <sup>-2</sup>
CaSO <sub>4</sub> <sup>0</sup>	5.25 · 10 <sup>-3</sup>
MgCO <sub>3</sub> <sup>0</sup>	4.0 · 10 <sup>-4</sup>
MgHCO <sub>3</sub> <sup>+</sup>	6.9 · 10 <sup>-2</sup>
MgSO <sub>4</sub> <sup>0</sup>	5.88 · 10 <sup>-3</sup>
NaCO <sub>3</sub> <sup>-</sup>	5.35 · 10 <sup>-2</sup>
NaHCO <sub>3</sub> <sup>0</sup>	1.78
NaSO <sub>4</sub> <sup>-</sup>	2.4 · 10 <sup>-1</sup>

The computation carried out for the data of sodium carbonate and sodium bicarbonate solutions and saturation extracts of salt affected soils clearly indicated that the modified programme may be applied over a wide range of concentrations and compositions of electrolytes [7, 8, 20].

Table

## The concentration of free charged ions and

Soil and depth of sampling, cm	Ca <sup>++</sup>	CaCO <sub>3</sub> <sup>0</sup>	CaHCO <sub>3</sub> <sup>+</sup>	CaSO <sub>4</sub> <sup>0</sup>	Mg <sup>++</sup>	MgCO <sub>3</sub> <sup>0</sup>	MgHCO <sub>3</sub> <sup>+</sup>	MgSO <sub>4</sub> <sup>0</sup>
	10 <sup>4</sup> · mole/l							
<b>Sodium carbonate solonchak soils</b>								
Profile 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
<b>Solonchak-solonetz soils</b>								
Profile 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
<b>Sulphatic solonetz soils</b>								
Profile 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	0.28
Profile 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

The degree of ion pair formation depends on the valences, sizes and concentrations of the ions. It was found that 15—75% of magnesium ions, 15—65% of calcium ions and 2—5% of sodium ions formed ion pairs (Fig. 2.). According to the chemistry of the saturation extracts of the soils, NaHCO<sub>3</sub><sup>0</sup>, NaHCO<sub>3</sub><sup>+</sup>, NaSO<sub>4</sub><sup>-</sup> have the highest concentration in sodium carbonate solonchak and solonchak-solonetz soils (Table 6). The order of ion pair concentrations in the saturation extracts of the solonetz soils investigated were NaSO<sub>4</sub><sup>-</sup> > CaSO<sub>4</sub><sup>0</sup> > MgSO<sub>4</sub><sup>0</sup> and MgSO<sub>4</sub><sup>0</sup> > NaSO<sub>4</sub><sup>-</sup> > CaSO<sub>4</sub><sup>0</sup> respectively (Table 6).

Ion pair formation results in a lesser decrease in total ion concentration in the saturation extracts of sodium carbonate containing soils than in those of sulphate containing solonetz soils.

The soil solution interacts with both the solid phase of the soil and the plant roots.

6

on pairs in the saturation extracts of salt affected soils

Na <sup>+</sup>	NaCO <sub>3</sub> <sup>-</sup>	NaHCO <sub>3</sub>	NaSO <sub>4</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	I
10 <sup>3</sup> · 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	9.10	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 interaction between the soil solution and the solid phase of the soil can be further divided into:

- a) the dissolution and precipitation of poorly soluble salts in soils,
- b) the ion exchange between cations of the micellar and intermicellar solutions.

Both of these processes are highly influenced by the total ionic concentration and the chemistry of the soil solution. The solubility of poorly soluble salts increases as the total ionic concentration of the solution increases and it decreases if the solution contains ions which are identical with the cation or with the anion of the poorly soluble salts (Fig. 2). The change in the dissolution of poorly soluble salts with changes in the concentration and chemistry of the soil solution means that the increase or decrease of the soil moisture content in soils affects not only the total concentration of dissolved salts, but also

Table 7

The solubility product of gypsum calculated from the concentrations and from the ionic activities of  $\text{CaSO}_4$  saturated soil saturation extracts

Ionic strength of the solution		Solubility product calculated from		Thermodynamic solubility product calculated from	
total	reduced	total	reduced	total	reduced
$10^3 \cdot \text{mole/l}$		ion concentrations		ion activities	
230.5	107.7	$7.33 \cdot 10^{-4}$	$2.92 \cdot 10^{-4}$	$5.81 \cdot 10^{-5}$	$2.85 \cdot 10^{-5}$
147.6	114.0	$4.78 \cdot 10^{-4}$	$2.12 \cdot 10^{-4}$	$5.19 \cdot 10^{-5}$	$2.74 \cdot 10^{-5}$
143.9	109.9	$4.80 \cdot 10^{-4}$	$2.12 \cdot 10^{-4}$	$5.39 \cdot 10^{-5}$	$2.81 \cdot 10^{-5}$
114.5	89.3	$3.69 \cdot 10^{-4}$	$1.72 \cdot 10^{-4}$	$4.76 \cdot 10^{-5}$	$2.62 \cdot 10^{-5}$
103.5	78.9	$3.10 \cdot 10^{-4}$	$1.46 \cdot 10^{-4}$	$4.28 \cdot 10^{-5}$	$2.39 \cdot 10^{-5}$
				$\bar{K}_{sp} = 5.07 \cdot 10^{-5}$	$2.68 \cdot 10^{-5}$
				$\bar{S} = 2.59 \cdot 10^{-6}$	$8.24 \cdot 10^{-7}$
				$CV = 11.4\%$	$6.87\%$

has an influence on the chemical composition of the liquid phase of the soil. The concentration of the solution and the degree of ion pair formation increase with decreasing soil moisture content. The coefficient of ion activities decreases and the ratio of the monovalent ions increases if the soil dries up. If the soil moisture content increases or decreases, the changes in the dissolution of poorly soluble salts can be calculated from the changes in the soil moisture, the total content of easily soluble salts and the thermodynamic solubility product of poorly soluble salts (Table 7).

In solutions containing free carbonate the dissolution of  $\text{CaCO}_3$ , and consequently the concentration of  $\text{Ca}^{2+}$  ions, are regulated by the pH value and the partial pressure of  $\text{CO}_2$  in the soil solution:

$$-\lg(\text{Ca}^{2+}) = -\lg K_{\text{CaCO}_3} + \lg K_{d_1} \cdot K_{d_2}(\text{H}_2\text{CO}_3)^* + 2 \text{pH} \quad (1)$$

The first ( $K_{d_1}$ ) and second ( $K_{d_2}$ ) dissociation constants and the activity of carbonic acid ( $\text{H}_2\text{CO}_3$ ) depend on the total ion concentration of the solution and can be expressed by the following function

$$\lg K_{d_1} \cdot K_{d_2}(\text{H}_2\text{CO}_3) = a + b\sqrt{I} \quad (2)$$

where:

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

Substituting equation (2) into equation (1) the concentration of the calcium ion can be expressed as:

$$-\lg(\text{Ca}^{2+}) = -\lg K_{\text{CaCO}_3} + a + b\sqrt{I} + 2 \text{pH}$$

$$\text{pCa} = \lg K' + b\sqrt{I} + 2 \text{pH} \quad (3)$$

where:

$$\text{pCa} = -\lg(\text{Ca}^{2+})$$

$$\lg K' = \lg K_{\text{CaCO}_3} + a$$



Table 8

Chemical composition of saturation extracts after treatment with CaSO<sub>4</sub> anhydrite

Depth of sampling cm	pH	Ca <sup>2+</sup>	CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	"I" 10 <sup>3</sup> · mole/l	Thermodynamic solubility product	
		me/l					CaSO <sub>4</sub>	CaCO <sub>3</sub>
2—8	8.25	39.75	2.06	6.54	141.30	266.3	4.635 · 10 <sup>-5</sup>	2.2346 · 10 <sup>-8</sup>
8—17	8.10	29.01	2.16	3.79	139.30	251.0	3.582 · 10 <sup>-5</sup>	0.7867 · 10 <sup>-8</sup>
17—32	8.13	29.68	1.26	3.64	154.67	272.9	3.743 · 10 <sup>-5</sup>	0.8906 · 10 <sup>-8</sup>
32—42	7.85	29.42	1.34	3.52	140.24	250.9	3.631 · 10 <sup>-5</sup>	0.2544 · 10 <sup>-8</sup>
42—63	7.75	30.19	1.18	3.34	100.24	180.1	3.520 · 10 <sup>-5</sup>	0.1916 · 10 <sup>-8</sup>
63—79	7.80	34.43	0.98	1.99	70.90	136.3	3.703 · 10 <sup>-5</sup>	0.3251 · 10 <sup>-8</sup>
79—90	7.75	25.65	0.59	2.21	63.40	124.8	3.725 · 10 <sup>-5</sup>	0.2839 · 10 <sup>-8</sup>
							$\bar{X} = 3.791 \cdot 10^{-5}$	$\bar{X} = 0.7096 \cdot 10^{-8}$
							$\bar{S} = 3.81 \cdot 10^{-6}$	$\bar{S} = 0.2747 \cdot 10^{-8}$
							$\bar{S} = 1.44 \cdot 10^{-6}$	
							$CV = 9.74\%$	

$$\lg K_{CaCO_3} = \lg (Ca^{2+}) + 2 \text{pH} + \lg [K_1 \cdot K_2(H_2CO_3)]$$

$$\lg K_{CaSO_4} = \lg (Ca^{2+}) + \lg (SO_4^{2-})$$

Equation (3) expresses the function of the calcium ion activity on the total concentration and the reaction of the solution. The numerical values of constants *a* and *b* were calculated from the analytical data of model solutions of sodium carbonate and sodium bicarbonate. The thermodynamic solubility products of calcium sulphate and calcium carbonate were calculated from the data of saturation extracts saturated with CaCO<sub>3</sub> and CaSO<sub>4</sub> (Table 8).

The other reaction between the liquid and solid phases of the soil is the cation exchange.

It is well known that the equilibrium between the cations of intermicellar and micellar solutions depends on the total ion concentration and the ratio of cations in the intermicellar solution. There are also data in the literature referring to the influence of the type of anion on the cation exchange equilibrium [6, 7, 21, 22]. It is true that under the same conditions the degree of sodium saturation is the highest if the solution is dominated by carbonate and bicarbonate ions. This is followed by the ESP values of soils where sodium sulphate prevails, while equilibrium is reached at a relatively low degree of sodium saturation in systems dominated by sodium chloride [2 15]. With an increase in soil salinity, the ratio of sodium ions increases and it becomes more and more dominant. An increase in total salt concentration, the valency effect or an increase in SAR values may result in a high degree

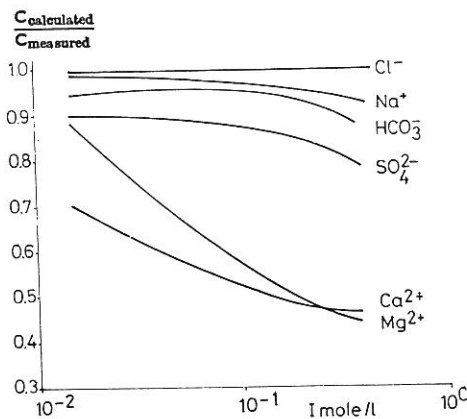


Fig. 2  
Function of calculated and measured ionic concentration ratios versus the ionic strength in saturation extracts of sulphate containing solonetz soils

Table 9  
Data obtained from analysis of soil solutions [16]

Depth of sample, cm	Total salt content, g/l	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup> + K <sup>+</sup>	SAR
		me/l						
2— 8	256.5	2.0	4304	104	65	426	3918	250
8— 17	151.4	2.2	2470	126	80	177	2341	204
17— 33	112.7	2.6	1827	106	60	163	1712	162
33— 51	107.8	2.6	1720	144	74	291	1502	111
51— 80	105.1	3.8	1675	134	77	233	1496	120
80—120	113.6	4.5	1840	135	75	339	1565	109
120—145	88.3	6.6	1382	134	74	321	1120	80
145—180	86.1	6.6	1366	132	67	328	1109	79

of sodium saturation even for the accumulation of sodium salts which dissociate with a neutral reaction. As examples, the chemical composition of the soil solution of a chloridic solonchak from the Kuru Araxes Depression in the Soviet Union is given in Table 9, and that of a sulphatic solonchakized solonetz from the Hungarian Lowland in Table 10. The SAR value at the top of the solonchak soil is over 200 and decreases as the salt content decreases in the soil profile. The soil is apparently saturated with sodium to a remarkable degree, but in the presence of a high concentration of sodium chloride the reaction of the media remains neutral and the soil colloids are flocculated due to the negligible difference between the concentrations of the micellar and intermicellar solutions. In the present state the low fertility of this soil is connected with the high concentration of the soil solution, which causes a physiological drought. The low concentration of calcium ions indicates the absence of calcium

Table 10  
The chemistry of the soil solution of a solonchakized solonetz soil in Hungary

Depth of sample, cm	Moisture %	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	SAR
		me/l							
0— 20	33.9	9.2	1.2	11.6	141.6	6.0	3.0	124.6	58.7
20— 40	26.5	1.5	1.2	8.4	142.8	2.4	2.2	151.1	99.6
40— 60	23.3	6.3	0.9	10.8	229.8	2.5	2.5	178.1	112.6
60— 80	20.7	7.2	0.9	10.9	140.3	1.8	5.1	144.1	77.6
80—100	21.4	6.9	1.8	9.3	51.2	0.7	0.6	64.8	80.4
100—120	22.8	9.1	1.6	9.1	26.1	0.7	0.2	43.2	64.4
120—140	25.7	8.4	1.8	6.3	35.7	0.4	0.1	65.9	131.8

salts in the soil. The insufficiency of calcium salts may indicate the danger of solonetz formation if the soil is ameliorated by leaching without the application of chemical amendments.

In the case of sulphatic solonchakized solonetz, the soil solution is less concentrated than the solution of the previous profile (Table 10). Among the soluble salts the sulphates are dominant. The soil has a neutral or slightly alka-

Table 11

Sodium—hydrogen potential and ESP values in the sodium carbonate solonchak and solonchak solonetz soils

Depth of sampling, cm	(pH - pNa)	Exchangeable Na <sup>+</sup> me/100 g	CEO	K <sub>g</sub>	ESP		
					measured	calculated	
						a	b
Profile No 1.							
0—3	8.197	5.10	7.82	0.604	66.37	64.41	63.26
3—10	8.934	6.30	6.96	0.579	90.52	60.72	89.68
10—20	8.405	7.41	10.95	0.447	67.67	52.10	71.15
20—30	8.402	6.60	8.70	0.779	75.86	58.11	68.16
30—40	7.987	3.90	8.70	0.419	44.83	33.76	44.27
40—50	8.218					35.17	57.45
Profile No 2.							
3—10	8.916	10.22	13.50	0.192	75.70	58.76	89.54
10—20	9.190	10.53	16.50	0.067	63.82	39.67	93.98
20—30	8.614	9.30	17.15	0.712	54.22	49.10	46.72
40—50	7.964	7.50	13.40	0.960	55.97	22.27	41.06
50—60	7.574					16.35	22.25

*a* = calculated from SAR-ESP function [11]; *b* = calculated from equation [9]

line reaction, the SAR value in the soil solution is fairly high and the degree of sodium saturation is also remarkable. The soil has a well developed columnar structure in the accumulation horizon, which indicates the increased dispersion of soil colloids. In this case, both the increased concentration of the soil solution and the poor water physical properties of the soil contribute to low fertility. The total ionic concentration of the soil solution is over 7 g/l in the *A* and *B* horizons. This concentration of salts can be toxic to most plants, but the solution is not concentrated enough to flocculate the sodium saturated colloids.

Table 12

Mineral composition of cotton plants at different phases of vegetation [14]

Condition of plant	Vegetation phase	Mineral sub- stances	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	Na <sup>2+</sup>	Mg <sup>2+</sup>		
			% of absolute dry weight							SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup> + Mg <sup>2+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>
Normal	sprouting	16.10	1.54	3.83	3.35	0.81	0.41	0.54	0.076	0.27	0.40		
	budding	11.50	0.78	2.83	3.01	0.68	0.13	0.37	0.028	0.10	0.40		
	ripening	10.60	0.40	3.23	3.95	0.35	0.04	0.17	0.008	0.06	0.15		
Depressed	sprouting	17.00	1.56	2.03	1.83	0.87	0.54	1.04	0.144	0.33	0.78		
	budding	16.40	1.97	3.47	3.89	0.94	0.40	0.77	0.064	0.23	0.40		
	ripening	8.20	0.81	1.72	2.28	0.57	0.19	0.64	0.052	0.18	0.41		
Strongly depressed	sprouting	20.73	2.84	3.05	1.26	1.10	1.22	1.30	0.32	0.51	1.65		
	budding	17.14	2.04	5.94	2.10	1.47	0.63	0.50	0.12	0.23	1.15		
	ripening	11.78	0.81	3.06	1.97	1.15	0.43	0.36	0.09	0.19	0.96		

In carbonate containing systems the sodium ions dominate in the intermicellar solution and the adsorbent has a high degree of sodium saturation even if there is a low ionic concentration in the liquid phase. In such systems the pH values of the media, as was shown in equation (3), determine the solubility of calcium carbonate and, consequently, influence the equilibrium of the cation exchange.

The activity ratios of exchangeable cations and the ratios of cations in the intermicellar solution are in linear correlation. The case of sodium—calcium ion exchange is given in equation (4):

$$\lg \frac{(RNa)^2}{(RCa)} = \lg K_{Ca}^{Na} + (pCa - 2pNa) \quad (4)$$

where:

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

In salt affected soils containing free carbonate, the logarithm of the activity ratio of exchangeable cations is determined by the sodium—hydrogen potential as derived from equations (3) and (4):

$$\lg \frac{(RNa)^2}{(RCa)} = \lg K'' + b \sqrt{I} + 2(pH - pNa) \quad (5)$$

if:

$$\lg K'' = \lg K_{Ca}^{Na} - \lg K_{CaCO_3} + a \approx -14.8$$

In the case of a system containing  $Ca^{2+}$ ,  $Mg^{2+}$  and  $Na^+$  ions, equation (5) may be written as follows:

$$\lg \frac{(RNa)^2}{\sqrt{(RCa) \cdot (RMg)}} = \lg \frac{\sqrt{K_{Ca}^{Na} \cdot K_{Mg}^{Na}}}{\sqrt{K_{CaCO_3} \cdot K_{MgCO_3}}} + a + b \sqrt{I} + 2(pH - pNa)$$

A proper thermodynamic treatment of a system containing  $Ca^{2+}$ ,  $Mg^{2+}$  and  $Na^+$  ions requires more information about the behaviour of  $Mg^{2+}$  in ion exchange processes than is available at present [5].

The Gapon equation, assuming a miscible displacement between the micellar and intermicellar solutions, gives a plot of the ratio of exchangeable mono- and divalent ions against the cation adsorption ratio in the soil solution that appears to be linear:

$$\frac{RNa}{(CEC - RNa)} = K_G \frac{a_{Na}}{\sqrt{a_{Ca} + a_{Mg}}} \quad (6)$$

The activities of calcium and magnesium ions ( $a_{Ca}, a_{Mg}$ ) can be expressed by their solubility products:

$$(a_{Ca} + a_{Mg}) = \frac{1}{(CO_3^{2-})} (K_{CaCO_3} + K_{MgCO_3}) = \frac{(K_{CaCO_3} + K_{MgCO_3}) \cdot (H^+)^2}{K_{d_1} K_{d_2} (H_2CO_3)} \quad (7)$$

Table 13

Classification of saline soils by degree and type of salinity in relation to field crops [14]

Condition of agricultural crops with medium salt resistance	Degree of soil salinity	Type of salts dominating in soils						
		Soda	Chloridic soda and soda chloridic	Sulphatic soda and soda sulphatic	Chloridic	Sulphatic Chloridic	Chloridic Sulphatic	Sulphatic
		Content of salts soluble in water in the horizon of maximum salt accumulation within the stratum 0-60 cm (in %)			Average content of salts soluble in water for the 0-100 cm stratum (in %)			
Good growth and development (no bare patches, crop normal)	Practically non-saline (or only very slightly saline)	0.10	0.15	0.15	0.15	0.20	0.25	0.30
Slight withering (bare patches and decrease of crop by 10-20%)	Slightly saline	0.10-0.20	0.15-0.25	0.15-0.30	0.15-0.30	0.20-0.30	0.25-0.40	0.30-0.60
Medium withering (bare patches and decrease of crop by 20-50%)	Medium saline	0.20-0.30	0.25-0.40	0.30-0.50	0.30-0.50	0.30-0.60	0.40-0.70	0.60-1.0
Marked withering (bare patches and decrease of crop by 50-80%)	Strongly saline	0.30-0.50	0.40-0.60	0.50-0.70	0.50-0.80	0.60-1.0	0.70-1.20	1.0-2.0
A few scattered plants survive (virtually no crop)	Solonchaks	>0.50	>0.60	>0.70	>0.80	>1.0	>1.20	>2

Substituting equation (3) and converting equation (7) into logarithmic form, we get:

$$-\lg(a_{Ca} + a_{Mg}) = pCa + pMg = -\lg(K_{CaCO_3} + K_{MgCO_3}) + a + b \sqrt{I} + 2pH \quad (8)$$

Applying the logarithmic form of the Gapon equation and combining it with equation (8) we get the following function:

$$\lg \frac{RNa}{(CEC - RNa)} = \lg K_G - \frac{1}{2} - \lg(K_{CaCO_3} + K_{MgCO_3}) + \frac{1}{2}a + \frac{1}{2}b \sqrt{I} + (pH - pNa) \quad (9)$$

and

$$\lg \frac{RNa}{(CEC - RNa)} = \lg K'' + \frac{b}{2} \sqrt{I} + (pH - pNa) \quad (10)$$

The value of  $\lg K''$  in equation (10) was calculated from the analytical data related to samples of sodium carbonate solonchak and solonchak-solonetz soils. The mean of the calculated values was  $-8.427$  and the standard deviation of the mean was  $0.13$ .

Calculating the ESP values with the mean of  $\lg K''$  leads to a better agreement between the calculated and measured values than by applying the ESP-SAR function (Table 11).

The toxicity of sodium ions for plants depends on the kind of anion dominating in the soil solution. The data in the literature referring to the toxicity

of different kinds of sodium salts are very diverse. The diversity of the data may be traced back to the fact that the toxicity of sodium and other salts depends on the total concentration and the chemistry of the soil solution, as well as on the vegetation phase of the plants (Table 12).

The ion uptake of cotton plants, as is demonstrated in Table 10, increases with an increase in soil salinity, and the ratios of ions in the dry matter shift in favour of chloride, magnesium and sodium ions as the solution becomes more concentrated.

On studying the interaction of the soil solution with the solid part of soils and plants, the conclusion has been reached that when evaluating soil salinity and sodicity, not only the total salt concentration and the ratio of the cation concentrations in the soil solution should be taken into consideration, but the anionic composition

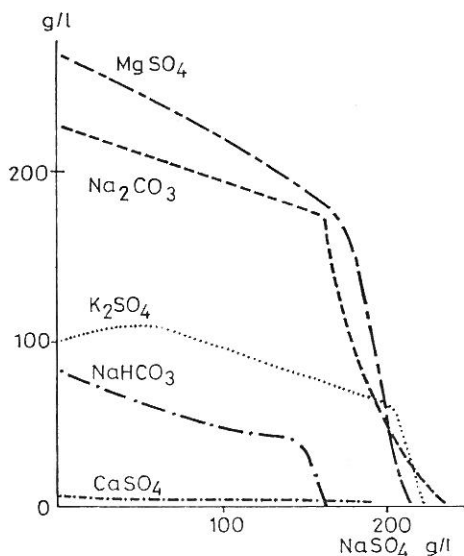


Fig. 3  
Solubility of salts as a function of  $\text{Na}_2\text{SO}_4$  concentration

of the salts as well, because it also has a decisive influence on the formation and properties of salt affected soils (Table 13).

### Summary

Salt affected soils may form if accumulation processes prevail over leaching processes.

In the process of salt accumulation the solubility of salts plays a decisive role and the salts accumulate in the reverse sequence of their solubility.

The total ionic concentration of the soil solution has a wide range. In non-saline soils the concentration of the dissolved salts does not usually exceed  $0.01$  mole/l. In salt affected soils containing  $0.2$  to  $10$  g/100 g of soluble salts, the concentration of the soil solution can be as high as  $0.1$  to  $5$  mole/l with  $20\%$  moisture. The influence of the accumulated salts on the soil properties depends on the total quantity and chemistry of the dissolved salts. A soil solution containing dissociable salts can be considered as an electrolyte solution of mixed salts. The ions of the solution interact:

a) with the other ions in the solution, having opposite electrostatic charges. A model for ion pair formation and its applicability to the soil saturation extracts are discussed.

b) with the solid part of the poorly soluble salts in the soils. The thermodynamic solubility product of calcium carbonate and calcium sulphate is calculated, taking into account the ion pair concentrations, coefficients of activities of ions and the dependence of the sodium carbonate dissociation constant on the total ionic concentration of the solution.

c) with the cations of the micellar solution. The ion exchange process can be described in terms of the sodium—calcium and sodium—hydrogen ion potential of the soil solution. The ion potential of the intermicellar solution is directly related to the standard free energy of the cation exchange.

In the light of the interactions of the solution with the solid part of the soils and with the plant roots, the conclusion has been reached that when the limit values of soil salinity are calculated, the chemistry of the accumulated salts should be taken into consideration.

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### Discussion

SINGH, N. T.

In view of changes in the solubility of sulphates and carbonates with temperature, do you think that soil samples should be removed at a particular time of the year and the saturation extract obtained at a given temperature for diagnostic purposes?

DARAB, K.

All of the analytical methods of soil investigation are standardized methods. The dissolution of  $\text{CaSO}_4$  and  $\text{CaCO}_3$  during the preparation of saturation extracts is determined by the temperature of the laboratory and it is usually not influenced by the air temperature at the time of collecting the soil samples.

GIRDMAR, I. K.

One of the Tables of your lecture indicates that the soil is having low pH, low  $\text{CO}_3 + \text{HCO}_3$  and high ionic strength with dominate salt of  $\text{SO}_4 + \text{Cl}$ . Why have you classified this soil under solonetz not under solonchak?

DARAB, K.

The name solonetz refers to the morphological features of soils. We classify those soils under solonetz which have columnar B horizon and whose fertilities are determined by the poor water regime of the B horizon. In the case of solonchak soils the determining feature is a high quantity of soluble salts on the surface and in the upper layer causing physiological drought to the plants. In solonetz soils the pH value of the soil suspension can be slightly alkaline if the chemistry of soluble salts is chlorid-sulphatic. The limiting feature of the investigated soil has been the columnar structured B horizon. This is the reason why this soil is classified under solonetz.

GIRDHAR, I. K.

Have you any data to show the effect of different anionic composition on the solubility of  $\text{CaCO}_3$  and  $\text{MgCO}_3$ ?

DARAB, K.

I have some data but the dependence of the dissolution of  $\text{CaCO}_3$  on the concentration and ionic composition of salt solution is well known and several data referring to the  $\text{Ca}^{2+}$  ion concentrations of solutions saturated with  $\text{CaCO}_3$  are published in the literature.

GIRDHAR, I. K.

Your results show that the solubility of  $\text{CaCO}_3$  and  $\text{CaSO}_4$  is more or less the same. Why? Because the literature indicates that the solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is higher than  $\text{CaCO}_3$ .

DARAB, K.

It is clearly demonstrated in Table 8. that the thermodynamic solubility products of  $\text{CaSO}_4$  and  $\text{CaCO}_3$  differ from each other in four magnitudes. It means that the contribution of  $\text{CaSO}_4$  to the calcium ion concentration in the saturation extracts was nearly  $3.5 \times 10^3$  higher than that of  $\text{CaCO}_3$ .