## The Chemical and Physico-Chemical Effects of Sodium Carbonate in Soils

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According to the present state of knowledge, the term "sodic alkali soil" refers to soils which, in their solid and liquid phases contain considerable amounts of sodium salts capable of alkaline hydrolysis.

The conditions under which these soils are formed, as well as the nature and manner of soda formation, are various. Such soils may display differences in the degree of alkalization, in the amount of soda accumulated in them, in the distribution of soda among the various horizons, and in the amount and direction of the movement of the soda-containing soil solution.

Regardless of the ways in which soda is formed and of soil genesis processes, even though the latter processes strongly influence the morphological aspect as well as the physical, chemical and colloidal properties of soils, the presence of the sodium salts capable of alkaline hydrolysis affects all soils which are characterized by alkaline reaction. These common chemical features profoundly affect the water uptake and the mineral nutrition of plants growing on such soils, as well as the possibilities of reclaiming affected areas.

The most characteristic effects of the alkaline reaction are the changes in the solubility of salts in the soil solutions. The example given in Fig. 1 shows the "salt profile" of a sodic solonchak-solonetz soil. It can be seen that the accumulated salts are mainly (up to 90 per cent) sodium salts with bicarbonate prevailing. The soil is strongly calcareous, containing almost 40 per cent or more calcium carbonate in some horizons. The alkaline reaction reduces the solubility of calcium and magnesium salts and promotes adsorption by exchange of sodium ions. Even rather diluted solutions of sodium salts, primarily sodium carbonate and sodium hydrocarbonate, may cause considerable alkalization.

An irrigated soil was investigated, where the irrigation water used was of favourable composition, that is it contained little salt and thus had no alkalizing effect. The water table, however, rose in the course of irrigation and came into contact with the upper soil horizons. Since the ground water was alkaline and sodium constituted more than 50 per cent of the cations the alkalinity of the soil (Table 1) and the amount of exchangeable sodium ions (Table 2) increased during the period of observation. It is to be noted that meanwhile no measurable changes occurred in the total soluble salt content of the soil.

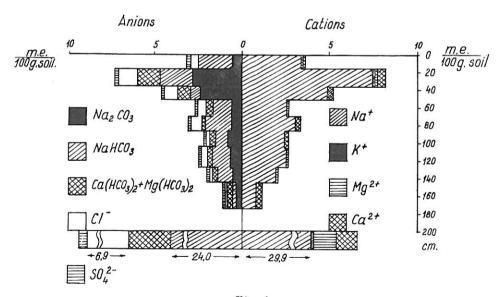
Obviously, the increased amount of exchangeable sodium is related to increases in soil alkalinity and in the relative amount of sodium salts as well as to the alternating movements of the diluted alkaline soil solution. This increase in alkalinity may be, of course, caused also by irrigation waters of

 $Table\ 1.$  Chemical composition of the aqueous extract of soil profile Kopánes 301

Date of sampling	Depth of horizon em.	Dry matter %	Alkalinity			i				
			Alkali metal NuHCO <sub>3</sub>	Alkali earth metal Ca(HCO <sub>3</sub> ) <sub>2</sub>	Total HCO3	CI-	802-	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>
			m, e,/100 g, soil							
	0- 10	0.1550	0.562	0.214	0.778	0.300	1.864	0.409	0.284	1.51
	10 - 20	0.2745	0.616	0.355	0.972	0.380	1.379	0.481	0.267	1.40
	20 - 40	0.1995	0.777	0.256	1.036	0.380	1.477	0.275	0.249	2.00
May 19	40 60	0.2485	0.896	0.376	1.274	0.580	1.664	0.445	0.142	2.05
Ì956	60 - 80	0.3470	0.908	0.279	1.188	0.660	1.962	0.392	0.142	2.43
	80 100	0.3420	1.339	0.256	1.598	0.980	3.855	0.445	0.249	4.79
	100 - 120	0.4050	1.434	0.424	1.858	0.200	3.002	0.424	0.071	4.16
	120 - 140	0.3970	1.456	0.360	1.816	1.740	3.643	0.309	0.169	5.63
August 31	0 - 10	0.3030	1.078	0.882	1.900	0.600	0.929	0.484	0.148	2.72
1956	10 - 20	0.3070	1.056	0.726	1.764	0.580	0.771	0.334	0.123	2.40
	20 - 40	0.2570	1.116	0.766	1.882	0.740	1.256	0.414	0.148	2.67
	40 - 60	0.3100	1.312	0.824	2.136	0.880	1.146	0.429	0.082	3.54
	60 - 80	0.5590	1.686	0.332	2.018	2.040	4.123	0.324	0.148	8.78
	80 - 100	0.5070	1.312	0.472	1.784	2.860	5.306	0.254	0.288	8.46

unfavourable composition which contain carbonate or hydrocarbonate of sodium.

The specific, strongly alkalizing, effect of soda-containing solutions is not limited to the inducement of changes in the solubility of salts. Great importance



 $Fig.\ 1.$  Salt profile of sodic solonehak solonetz soil

must be attached also to the specific colloid-chemical effect of sodium salts capable of alkaline hydrolysis.

On studying these colloid-chemical effects some experiments were carried out with systems of clay mineral/soda solution and soil/soda solution. The clay mineral used was a bentonite specimen from Istenmező, its adsorption capacity being 91 m.e. per 100 g. This capacity was saturated to 60 per cent by Ca<sup>2+</sup>

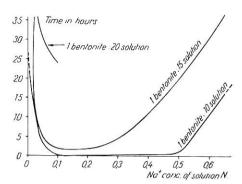


Fig. 2.

Time for the thyxotropic setting of bentonite suspensions treated with Na<sub>2</sub>CO<sub>3</sub> solutions of different concentration

and to 27 per cent by  $\mathrm{Mg^{2+}}$ . According to mineralogical investigation it contained montmorillonite with a high degree of purity. The soil used in our experiments was the A-horizon of a chernozem. Its clay fraction had a comparatively high adsorption capacity of 63.5 m.e. per 100 g., exchangeable  $\mathrm{Ca^{2+}}$  occupying almost 90 per cent of the exchange capacity. On mineralogical examination some poorly crystallized montmorillonite and illite were detected in the sample. In the experiments the ratio of the solid to the liquid phase was 1:10; and seven different concentrations of sodium carbonate solutions were used.

The time necessary for thyxotropic setting and the degree of swelling were determined for the above systems. The results obtained for bentonite are shown in Fig. 2 and Fig. 3. It is evident that by increasing concentrations of sodium carbonate from 0.1 N to 0.3 N the time of thyxotropic setting is greatly shortened. At concentrations greater than 0.5 N it is rapidly increased (Fig. 2).

The graph that shows the change in swelling is almost the reverse of the former, pointing out the fact that under the conditions of this experiment the swelling of the colloid-system reaches maximum values within the concentration range of from 0.05 N to 0.3 N (Fig. 3).

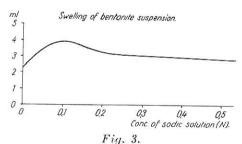
Changes in the state of the colloid-system are also reflected by its adsorption capacity and the nature of its surfaces. The degree of adsorption of the isotope Na<sup>24</sup> by the solid phase as against sodium carbonate concentration was examined in the systems described.

For the sake of comparison, isotope adsorption by the solid phase was also studied in bentonite/sodium chloride systems. The amount of isotope adsorbed on the surfaces, as per cent of the initial activity of the solution,

		Exchangeah	le $Na^+ + K^+$			
Date of sampling	Depth of horizon em.	mg. 100 g. soil	m. e. 100 g. soil	Cation exchange capacity m.e./100 g. soil	ESP	
	0-10	143.29	6.23	21.49	28.9	
May 19 1956	10-20	212.98	9.26	26.32	35.2	
5389 SS 35	20 - 40	246.10	10.70	27.36	39.1	
	40-60	344.08	14.96	24.71	60.0	
	60 - 80	295.09	12.83	22.06	58.1	
	0-10	219.90	9.53		44.4	
lugust 31 1956	10 - 20	289.57	12.59		47.9	
	20 - 40	376.44	16.38		60.0	
	40 - 60	382.72	16.64		67.4	
	60 - 80	358.80	15.60		70.7	

 $Table\ 2.$  Exchangeable Na $^+$  + K $^+$  content of the soil profile No 301

and the distribution quotients of Na<sup>24</sup> between solid and liquid phases were calculated from the experimental data. The calculated values are plotted against the Na<sup>+</sup> concentration in the equilibrium-solutions (Fig. 4, 5).



Swelling of a bentonite suspension

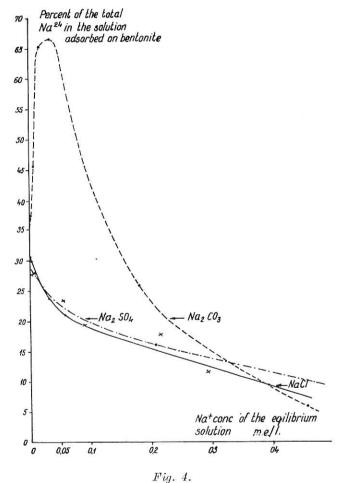
The data obtained show that with sodium chloride solutions the degree of isotope adsorption and the values for distribution quotients calculated from it decrease with increasing concentrations of the sodium ions in the equilibrium solutions. This phenomenon is in accordance with the postulates of the isotope-distribution law.

The situation is not as unequivocal with systems in equilibrium with sodium carbonate solutions. The adsorption of the sodium isotope first increases with increasing concentrations of sodium ions, reaching a maximum at concentrations of 20 m.e./1—40 m.e./l. With concentrations higher than 40 m.e./l. the isotope adsorption of the solid phase decreases (Fig. 4). A similar picture is conveyed by the distribution quotient depending on concentration (Fig. 5).

At concentrations inducing maximum isotope adsorption, swelling also reaches a maximum and the time necessary for thyxotropic setting is the shortest. A similar effect in isotope adsorption was observed with systems of soil/sodium carbonate solution.

All these experiments point toward the necessity of taking into consideration possible changes in the state of soil colloid systems when soils are treated with soda-containing solutions. The experimental data proved that the surface sizes of colloid particles and probably surface charges, too, are subject to change. In order to study ion exchange and laws of ionic adsorption as they relate to the alkalizing or desalkalizing effects of irrigation water and drawing practical conclusions from them, it is obvious that one should start from the equations evolved by Vanselow, Kerr and Gapon. With both theories and calculations of the constants of equilibriums upon which they are based the medium is supposed to contain neutral sodium salts, mainly sodium chloride, and constancy of the surface state of the soil colloids is assumed.

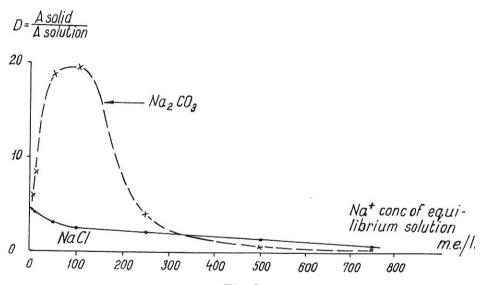
BABCOCK has published some calculations concerning sodium chloride/ clay mineral and sodium sulphate/clay mineral systems. He pointed out that



The activity taken up by bentonite as a percentage of the initial activity plotted as function of the equilibrium Na<sup>+</sup> concentration in bentonite — Na<sub>2</sub>SO<sub>4</sub> and bentonite — Na<sub>2</sub>CO<sub>3</sub> systems

the amount of exchangeable sodium ions was greater with chloride than with sulphate ions under similar conditions. These calculations were based on the Vanselow equation. On calculating ion activity coefficients in the liquid phase, differences in the mean values of activity coefficients of sodium sulphate and sodium chloride, and of calcium chloride and calcium sulphate, respectively, were taken into consideration. It may be assumed, however, that anionic effects are not restricted to the deviations of activity coefficients. In addition to the differences in the degree of dissociation and the mutual electrostatic effects caused by them, an important part is played in the anion effects by the differences in solubility conditions which influence the composition of the soil solution, as well as by the changes in degree of dispersity of soil particles and possibly by changes in the surface charges.

The results of these experiments suggest that, in the presence of sodium salts capable of alkaline hydrolysis, attention should be paid to some complicated correlations between various colloid-chemical actions and interactions. In such systems no constancy either in solubility conditions, or in surface sizes and charges may be expected. That is why special attention must be paid



Distribution quotient of Na  $^{24}$  between solid and liquid phases in bentonite — Na  $_2\mathrm{CO}_3$  systems

not only to the relative amounts of sodium salts, but also to the kind of anions present in the soil solution, when assessing the degree of soil alkalization and determining the alkalizing effect of irrigation waters.

Similar deliberation is required in respect to changes in the colloidal state of the soil, when dealing with soil reclamation, which involves leaching soda and other sodium salts capable of alkaline hydrolysis. These changes are dependent on a number of factors such as nature of clay minerals in the colloid-complex of the soil, organic matter content, degree of alkalization, nature

and amount of soluble salts, etc. For the time being there is no generalized empirical correlation formula available, adequate to characterize the processes in question.

Thus further investigations, involving laboratory experiments and field trials, are necessary to examine the phenomenon observed, in order to formulate the laws regarding the various processes taking place. Such results must be taken into consideration before deciding on practical measures to be taken.

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## Влияние соды на химические и физикохимические свойства почвы

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1. Под содовыми почвами, исходя из современного уровня развития науки, понимаются те почвы, в твердой и жидкой фазах которых в значительных количествах находятся щелочные натриевые соли (сода, гидрокарбонат натрия, силикат натрия).

Общим признаком этих почв является щелочная реакция среды. Этот факт и господствующая роль ионов натрия в жидкой фазе почвы оказывают решающее влияние на физико-химические и коллоидные свойства почв. Вышеуказанные общие химические свойства оказывают влияние на водоснабжение растений, их минеральное питание, а также определяют возможности мелиорации этих почв.

2. Одним из характерных последствий щелочной реакции среды является изменение растворимости веществ. В содово-засоленных почвах уменьшается растворимость солей щелочно-земельных металлов и в почвенном растворе господствующее положение начинают занимать соли натрия, в первую очередь сода и гидрокарбонат натрия.

Эти же обстоятельства способствуют обменной адсорбции ионов натрия и под влиянием относительно разбавленных растворов натриевых солей уже может произойти значительное осолониевание почв.

Подобные явления наблюдаются при орошении в связи с поднятием уровня грунтовых вод, если грунтовые воды и почва содержат значительное количество щелочных солей натрия. Под влиянием, неблагоприятных по химическому составу, содержащих соду, оросительных вод может произойти вторичное осолонцевание почв.

3. Влияние щелочной среды не ограничивается только изменениями условий растворимости, а оказывает большое влияние и на изменение коллоидной фракции почвы. В присутствии растворов, содержащих соду между концентрациями 0,1 н. и 0,5 н. время тиксотропного затвердевания значительно уменьшилось. Вместе с этим при тех же концентрациях увеличилось набухание коллоидов. Опыты были заложены с помощью изотопа натрия—24. Данные опытов показали, что, в присутствии растворов соды, величина изотопной адсорбции показывает некоторую аномалию. При увеличении концентрации карбоната натрия (при исходной концентрации 0,005 н.), параллельно с увеличением концентрации увеличивается и величина изотопной адсорбции твердой фазы, при концентрации раствора 0,1—0,2 н. наблюдается максимум. Максимальная величина изотопной адсорбции совпадает с максимумом набухания коллоидов и с минимумом тиксотропного затвердевания. При более высоких концентрациях, величина изотопной адсорбщии твердой фазы с увеличением концентрации уменьшается. Это явление аналогично тем, которые наблюдались в системах «глинистые минералы — хлорид натрия» и «почва — хлорид натрия» и «почва

Коллоидно-химические изменения и данные по величине изотопной адсорбции показывают, что в щелочных условиях среды необходимо считаться с изменением поверх-

ностных условий коллоидных частичек.

4. При изучении закономерностей и размеров осолонцевания почв необходимо принимать во внимание и влияние анионов. При проведении практических мероприятий надо считаться с изменением состояния коллоидов почвенной системы и степенью адсорбции понов натрия.

Эти изменения являются производными нескольких условий (тип глинистых минералов, присутствующих в коллоидной системе почв, количество органического вещества в почве, характер и величина засоления, количество и качество воднорастворимых солей и т. д.).

На основе уровня современных знаний для характеристики процесса не имеется

даже элементарного обобщающего уравнения.

Поэтому необходимо продолжать исследования вышеописанных явлений, изучать закономерности этих процессов в модельных и полевых опытах и учитывать их при проведении практических мероприятий.