

## Investigation on the Effect of Anions on Na—Ca Ion Exchange in Soils with Radio-Active Tracers

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The exchangeable cations, particularly the sodium ions, have a considerable influence on the physical, chemical and biological properties of soils. In alkali soils the detrimental effect of the exchangeable sodium ions is responsible for the disadvantageous soil properties. When these soils are ameliorated for the purpose of agricultural utilization, one of the most commonly used methods is the exchange of Na-ions with Ca-ions.

The degree of the sodium ions' adsorption depends not only on the kind of the adsorbent, on the composition of the exchangeable cations, on the concentration of the soil solution and on the composition of cations in the soil solution but also on the kind of anions present in the soil solution. Experiments have proved that the adsorption of sodium ions is higher in the presence of sodium salts capable of alkaline hydrolysis than when the soil solution contains neutral sodium salts under the same conditions otherwise. Therefore, in many cases the formation of sodic soils is not coupled with a considerable increase in the amount of soluble salts in the soils. Many experiments prove that even in the case of a relatively lower concentration of sodium ion in the soil solution, the organic-mineral complex of the soil is saturated with it to a large extent. According to experimental data, in the presence of soda, a total salt concentration as low as 0,05 N is already sufficient in order to have the colloid-complex of the soil saturated with Na-ions to 60—70 per cent of the total exchange capacity.

The effect of the kind of anions present in the soil solution on the exchange of sodium ions may be traced back to several factors:

1. The average activity coefficients of sodium salts of various anions are different in the solution.
2. The solubility of calcium compounds, forming in the course of exchange between calcium and sodium ions or accumulated in the soil owing to other reasons, is different.
3. The differences shown in the degree of dispersion of the mineral fraction of the soil.
4. The changes occurring in the colloid-chemical state of the highly dispersed fraction of the soil as a function of the soil solution's concentration and of the kind of anions present in the soil solution.
5. The possible changes occurring in the properties and in the fine-structure of the adsorbent.

1. The difference caused by the different activity values of sodium salts of various anions appears in each case where the valences are different. This difference manifests itself in connection with sodium chloride — sodium sulphate solutions, for example. In this line BABCOCK [2] established that, under the same conditions otherwise, the "VANSELOW'S constant", corrected with the corresponding activity coefficients, is approximately the same to 50 ESP value in salt solution—soil systems of NaCl and Na<sub>2</sub>SO<sub>4</sub>, and it does depend on the molar concentration of the solution.

2. In connection with chloride and sulphate ions, the differences originating in the solubility of calcium compounds manifest themselves mainly at higher concentrations in the course of ion exchange and they can be calculated in the light of the solubility product of gypsum.

From the viewpoint of soil formation, alkalization or dealkalinization (degradation), the moderate solubility of gypsum is important because it results in rather limited mobility of this compound. That is why gypsum, remaining at the place of its formation or accumulation, maintains a relatively favourable Na : Ca ratio in the soil solution. Owing to its chemical reaction, it prevents the medium getting alkaline. In the course of the leaching of the more mobile sodium salts, gypsum provides the calcium ions to exchange the adsorbed sodium ions.

In the case of carbonates or other sodium salts capable of alkaline hydrolysis, the difference caused by the solubility of calcium compounds is considerably greater and, from the viewpoint of alkalization, it is just of the opposite tendency. When the medium becomes alkaline with a concomitant rise in its pH, the solubility of calcium carbonate is reduced to the minimum and the sodium ions play almost an exclusive role in the soil solution. It is not unusual for instance, that in alkaline medium the sodium salts present in the soil solution amount to 85—95 per cent of its total salt concentration.

In cases like these, in all probability, the degree of the sodium ions' adsorption depends only on the sodium ion concentration in the soil solution. GAPON, taking into account the low solubility of calcium carbonate, expresses the calcium ion concentration and the equilibrium constant together in the case of calcium-sodium ion exchange taking place in alkaline medium and states his equation accordingly as follows:

$$\frac{1}{c_{\text{Na}}} \cdot \frac{RNa}{RCa} = \frac{K}{\sqrt{c_{\text{Ca}}}} = K'$$

where  $c_{\text{Na}}$  = sodium ion concentration in the solution, mole/l

$c_{\text{Ca}}$  = calcium ion conc. in the solution, mole/l

$RNa$  = amount of exchangeable Na ions, meq/100 g soil.

$RCa$  = amount of exchangeable Ca ions, meq/100 g soil.

$K$  = Gapon's constant of ion exchange

$$K' = \frac{K}{\sqrt{c_{\text{Ca}}}}$$

3. Differences shown in the dispersity of the soil's mineral part. Here it is also the increase of the degree of dispersion, occurring in alkaline medium, which mainly deserves attention from the viewpoint of the formation and properties of alkali soils. The presence of sodium salts capable of alkaline

hydrolysis, rendering the medium more alkaline, increases the degree of dispersion and consequently the exchange capacity of the mineral part also increases.

The examinations carried out by ANTIPOV-KARATAEV [1] in soil—soda solution system pointed to the above phenomenon. In the course of his examinations, he noted that, diluted soda solution acted towards increasing significantly the percentage amount of soil particles belonging to the colloid-order.

Under natural conditions, the increase of the percentage amount of the clay fraction and that of the cation exchange capacity may be observed in the "B" horizon of solonetz soils.

4. Of the changes occurring in the colloid-chemical properties of the soil's finely dispersed fraction, the change in the degree of hydration, the increase of the swelling ability and the rise of the sol-gel state's reversibility in alkaline medium should be mentioned. The increase of the  $\xi$  potential and, accordingly, that of the particles' surface charge in the presence of sodium salts capable of alkaline hydrolysis should also be considered.

5. Changes occurring in the properties and in the texture of the adsorbent. From among these the most prominent, which may be observed in each case, is the dissolution of the organic part of the soil's adsorbing complex in alkaline medium and, as a consequence, the decrease in the soil's cation exchange capacity.

Certain changes may also take place in the fine structure of the system's mineral part. For example the increase of the distance between the latticelayers of certain clay minerals, and the increase of the amount of the so-called "textural water" in alkaline medium.

Under natural conditions, effects lasting for longer periods may result in the degradation of the organic-mineral complex, in the dissolution of the organic part and in the decomposition of the mineral part.

According to the above mentioned facts, four phenomena from among the above listed ones are in close connection with the change in the medium's pH value and with that whether there are sodium salts capable of alkaline hydrolysis in the soil—solution system or not, and if so, in what quantities.

In each case though, in different forms but all the changes are in connection with the change in the cation exchange capacity or rather they may occasion the latter.

We have relatively few numerical data at our disposal in the soil science literature concerning the study of the effect of anions, especially that of sodium salts capable of alkaline hydrolysis. Therefore, the widening of our findings concerning ion exchange was deemed advisable.

During our examinations it was kept in view that, under different conditions, the presence of sodium salts capable of alkaline hydrolysis, the pH of the medium getting alkaline presumably bring forth an apparent or actual change in the properties and in the exchange capacity of the adsorbent.

The change in the exchange capacity of the adsorbents can be observed in the case of synthetic exchangers, too. SCHAY and co-workers [5, 6] observed for instance, that the distribution quotient between the solid and liquid phases of a given ion increased to a certain value along with an increase in the concentration of the solution, then it decreased, and in a well definable concentration range it showed a maximal value.

In the same experiments the equilibrium constant (the quantity of the exchangeable Na ions was expressed in mole fraction, the Na ion concentration of the solution in mol/l) showed a change in the order of magnitude when the total concentration of the solution increased.

This change was traced back to the apparent change in the exchange capacity caused by the change in the adsorbed ions' activity coefficient, as well as to the increase of the absolute value of capacity, and both were calculated together.

In certain cases, during alkalinization processes, the increase of the exchange capacity may occur and that the change in the capacity occasioned by the processes taking place especially that of alkaline hydrolysis initiated by sodium salts capable of that, may be expected in the case of soils, too.

### *Some essential lines of examination*

1. For the examination of the mineral part, it is practical to chose a model material of homogeneous composition because the colloid-chemical effects occurring in alkaline medium may be observed correctly with it.

2. In the course of the examinations, a wide range should be assured for the drift of the proportion of the calcium-sodium ions in the liquid phase, and it should include also proportions corresponding to the concentration conditions prevailing in the liquid phase of sodic soils.

3. In the course of the examinations, attention should be paid to the changes occurring in the colloid-chemical state of the system with the condition that the concentration range must be relatively wide. A few examinations should be carried out in order to find out whether a certain change may be detected in the structure of the clay mineral chosen as model material under the relatively very simplified conditions of the model experiments.

4. Comparative examinations should be carried out with systems containing neutral sodium salts and when evaluating the analytical data, attention should be paid to that in what degree are the changes occurring in the relative quantity of the exchangeable cations and the alkaline medium or rather the effect of sodium salts capable of alkaline hydrolysis responsible for the measured differences.

### **Materials and methods**

In accordance with the above mentioned conditions, the following model materials were chosen:

Bentonite from Istenmező, Hungary. According to the chemical and mineralogical examinations (differential thermal-analysis, X-ray diffraction analysis, determination of exchange capacity and of the composition of the exchangeable cations measured by the Melich method at a pH value of 8.5), it contains montmorillonite in high purity. The fractions smaller than  $2 \mu$  in diameter were separated by sedimentation from the water-suspension of the material, and were used for the examinations.

## Examinations

### 1. Kinetic examinations

1 : 5 aqueous suspension of the bentonite's separated fraction (containing particles smaller than  $2 \mu$  in diameter) was diluted with Na-chloride solution of corresponding concentration, so that the ratio of bentonite and solution was 1 : 10 in the suspension. The suspension was labelled with  $\text{Na}^{24}$  isotope and, under constant mixing, samples were taken in the 2nd, 15th, 30th minutes and in the 1st, 2nd, 4th, 6th, 24th, 48th, 96th and 120th hours, after the labelling. The samples were centrifuged immediately and the activity of the solution and the concentration of the Na ion were determined. The aim of the examinations was to determine the time which is necessary to reach the phase-equilibrium of the active and inactive ions.

### 2. Examinations with phase-equilibrium systems

Bentonite was equilibrated with solutions of various ionic strength, where, in the case of the same ionic strength, the concentrations of the calcium and sodium ions were different.

The ratios of the concentrations of the sodium and calcium ions in the solutions were the following: 15,4; 11,6; 9,0;

The values of ionic strength were

in the case of 15,4 ratio of the  $\text{Na}^+ - \text{Ca}^{2+}$  ion concentration: 0,05; 0,025; 0,01; 0,0075; 0,005 moles/l

in the case of 11,6 ratio of the  $\text{Na}^+ - \text{Ca}^{2+}$  ion concentration: 0,25; 0,01; 0,0075; 0,005; 0,0025 moles/l

in the case of 9,07 ratio of the  $\text{Na}^+ - \text{Ca}^{2+}$  ion concentration: 0,01; 0,0075; 0,005; 0,0025 moles/l.

In the case of sodium sulphate systems, the ionic strengths were identical and the ratios of the  $\text{Na}^+ - \text{Ca}^{2+}$  ion concentrations were: 17,1; 14,3; 11.

Concentration ratios like the formers could not be set in the case of systems containing sodium carbonate because in the equilibrium solution the sodium ions predominated from the beginning and, for example, when the ionic strength was 0,05 moles/l, the exchange capacity of the bentonite became completely saturated due to the effect of a single treatment. When the ionic strength was  $7 \times 10^{-3}$  moles/l the bentonite became saturated with sodium ions more gradually and the complete saturation of the exchange capacity was achieved only after 4–5 repeated treatments.

In view of the above mentioned facts, two series were set in with systems containing sodium carbonate, in order to examine phase-equilibrium systems:

1. The ionic strength of the solution was approximately constant, about  $7 \times 10^{-3}$  moles/l and the concentration ratio of the Ca—Na ions had six different values.

2. The concentration ratio of the Ca—Na ions in the solution was approximately constant, and the ionic strengths were  $1,9 \times 10^{-3}$ ;  $3 \times 10^{-3}$ ;  $5 \times 10^{-3}$ ;  $8 \times 10^{-3}$  moles/l. The ratio of the solid phase to the liquid one was 1 : 100 in all cases.

Having the above described systems isotopically labelled, we allowed them to stand for 48 hours. The solid and liquid phases were separated by the

dialysis method. The systems containing sodium chloride and sodium sulphate were labelled with  $\text{Na}^{24}$ . In systems containing sodium carbonate, where the concentration ratio of the Ca—Na ions was constant but the ionic strengths were different, labelling with  $\text{Ca}^{45}$  and  $\text{Na}^{24}$  was done. The systems containing sodium carbonate, where the concentration ratios were different but the ionic strength remained the same, were labelled also with  $\text{Na}^{24}$ . The  $\text{Ca}^{45}$  and  $\text{Na}^{24}$  activities, the Na and Ca ion concentrations, the anion concentration depending on the kind of anions in the system and the pH value of the dialysate were measured.

Assuming that the exchange capacity is constant, on the basis of the measured data the value of the selectivity coefficients corresponding to Vanselow's equation was calculated.

### 3. *Examinations carried out in systems with bentonite, and sodium sulphate, sodium chloride and sodium carbonate solutions of different concentration*

The bentonite, chosen as model material, was equilibrated with given sodium salt solutions of different concentration. In the case of NaCl and  $\text{Na}_2\text{SO}_4$  solutions, the systems were labelled with  $\text{Ca}^{45}$  and  $\text{Na}^{24}$ , while systems containing  $\text{Na}_2\text{CO}_3$  were labelled with  $\text{Na}^{24}$ . The ratio of the solid and liquid phases was 1 : 10 in bentonite—NaCl solution, bentonite— $\text{Na}_2\text{SO}_4$  solution systems. In the case of bentonite— $\text{Na}_2\text{CO}_3$  solution systems, three ratios — 1 : 100; 1 : 50; 1 : 10 —, were chosen for each concentration. The solid and liquid phases of the 1 : 50 and 1 : 100 suspensions were separated by dialysis, while the 1 : 10 suspensions were centrifuged. From the dialysates and centrifugates the activity of  $\text{Ca}^{45}$  and  $\text{Na}^{24}$ , the Na and Ca concentrations in the solutions, the concentration of the corresponding anion as well as the pH value were determined.

### 4. *Colloid-chemical examinations*

The following colloid-chemical examinations were carried out.

a) The determination of the rate of swelling (volumetrically) in bentonite—sodium carbonate systems.

b) Measurement of the time of thixotropic setting.

c) Determination of the value of the  $\xi$  potential as a function of the concentration of the  $\text{Na}_2\text{CO}_3$  solution. In the course of the pretreatment, seven equilibrium systems of different concentration were prepared in the concentration range of 0,005 N and 0,5 N. The ratio of the solid and liquid phases was 1 : 100 in systems used for measuring the  $\xi$  potential and 1 : 10 in systems used for the determination of the time of thixotropic setting.

The determination of the  $\xi$  potential was made with an equipment by Nernst, by measuring the electroforetic migration velocity. In the equipment the direct current (D.C.) voltage was 127,5 V, the distance between the electrodes was 33,2 cm and the fall of potential was 3,82 V/cm. The ultra filtrate of the suspension's clear part was layered over the suspension. The electrokinetic potential was calculated from the electroforetic migration velocity on the basis of the following equation:

$$\zeta = \frac{6 \pi \eta \cdot v \cdot 300^2}{H D}$$

where  $v$  = electroforetic migration velocity, cm/sec  
 $H$  = fall of potential, V/cm  
 $D$  = dielectric constant  
 $\eta$  = coefficient of internal friction.

### 5. Micro-mineralogical examinations

The bentonite suspensions, prepared with water or  $\text{Na}_2\text{CO}_3$  solutions of different concentration, were centrifuged in order to separate their solid phases from the liquid phases, and the obtained samples were kept in desiccator, over 50 per cent sulphuric acid until they reached the state of constant weight. Afterwards the curve of the samples' loss of weight, as well as the DTA and DTG graphs were plotted on a Paulik—Erdey derivatograph. The determinations were made from 350 mg material, with 100 minutes' heating up, and aluminium oxide was the inert material. From the curve of the loss of weight we determined the quantities of water lost on different degrees of temperature. The samples were heated to 1000 Celsius degrees, and on the basis of the following intervals: 100—300°C; 300—760°C; 760—1000°C.

After centrifuging and drying the samples treated with sodium carbonate solution, X-ray exposures were taken with the Debey—Scherrer powder-method, using a Micrometa-type fine-structure apparatus. For the 12 hours' exposure  $\text{FeK } \alpha$  rays without filter were used in a camera which was 114 mm in diameter, the intensity of the current was 8 mA, and the voltage was 34 kV. The determination of the  $d$  Å distance was made by measuring the 001 line intensity and the place of the base-reflection with a Zeiss photometer.

## Discussion of the analytical data

### 1. Kinetic examinations

The values obtained in the course of the kinetic examinations showed that when plotting the activity of the solid phase as a function of time we got a curve which at the beginning formed an abrupt slope then became flat (Fig. 1). The trend of the curve was similar both in bentonite—sodium chloride solution and in soil—sodium chloride solution systems. According to the graphical evaluation of the isotope adsorption curve relating to bentonite—NaCl solution system, the isotope adsorption may be dissociated to three part processes and it seems to satisfy the formal kinetic equation applied by IMRE [3, 4] to describe the processes taking place on the surface of crystalline solid systems which are in equilibrium with their saturated solutions:

$$x_t = A_0 - (A_1 e^{-k_1 t} + A_2 e^{-k_2 t} + A_3 e^{-k_3 t})$$

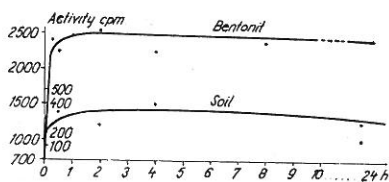


Figure 1

The activity of the adsorbent's surface in bentonite—NaCl solution system plotted against time

where  $x_t$  = the amount of isotope taken up by the adsorbent till  $t$  point of time

$A_0, A_1, A_2, A_3$  = constants

$k_1, k_2, k_3$  = velocity constants of the part processes.

The values of the velocity constants calculated on the basis of the above equations showed a difference in the order of magnitude. According to the data, the velocity constant of the third process is very small, therefore, it seems to be negligible in the course of further examinations. The first two processes take two hours which means that during that time a near state of phase-equilibrium may be reached for the distribution of isotopes. The explanation of the part processes would necessitate further investigations.

Table 1

The adsorption of  $\text{Na}^{24}$  isotope and that of  $\text{Na}^+$  ion as a function of time

Time (min.)	$\text{Na}^+$ adsorbed, as % of initial $\text{Na}^+$ conc.	Activity adsorbed, % of initial activity
2	16,55	8,05
15	17,05	18,85
30	18,10	22,30
60	19,50	24,60
120	19,40	25,35

It is quite probable, however, that the three part processes characterize cation exchange, isotope exchange as well as the rearrangement of the adsorbed ions on the surface. This is indicated by the fact that, in the course of our experiments, in the first two hours of the reaction, the amount of the active Na ions adsorbed on the surface was 5 per cent higher than the total amount of Na ions exchanged (Table 1). If we take into

consideration that in the second period marked by  $K_2$  velocity constant about 3 per cent of the total activity got to the surface, the second stage of the process seems to be identical with the isotope exchange.

When plotting the logarithm of the quantity of the soil's exchangeable Na ions as a function of the logarithm of the solution's initial Na ion concentration (Fig. 2) we get a linear logarithmic relation for the first two periods,

which seems to satisfy the isotherm by FREUNDLICH:

$$x = KC^p$$

where  $k$  and  $p$  are constants. Thus the amount of the absorbed  $\text{Na}^{23}$  is in proportion with the initial concentration.

The isotope exchange, characteristic of the second phase, seems to be supported by the fact that when plotting the converse of the isotope's distribution quotient against the Na ion concentration of the  $K_2$  process, we get a linear correlation (Fig. 3):

$$\frac{S_L}{S_0 - S_L} = \frac{C}{A}$$

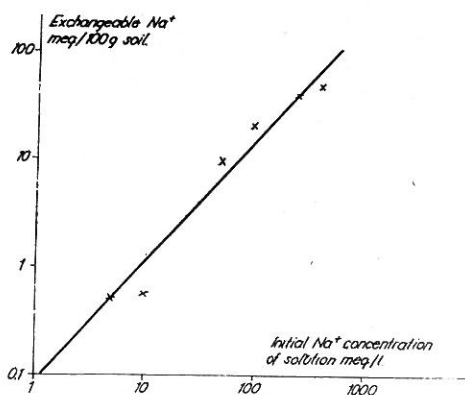


Figure 2

The amount of the exchangeable  $\text{Na}^+$  ions of bentonite plotted against the initial  $\text{Na}^+$  ion concentration of the solution



where  $S_L$  = the amount of  $\text{Na}^{24}$  in equilibrium in the solution  $S_0 - S_L$  = the amount of  $\text{Na}^{24}$  on the surface  $C = \text{Na}$  ion concentration of the solution.

The slope of the line gives the isotopically exchangeable surface size relating to  $\text{Na}^{24}$ . It is the first phase, however, that exercises influence on the precision of the determination.

The above facts seem to support that that the first two phases of the kinetic process may be characterized by cation exchange and isotope exchange processes. In order to clarify the character of the third phase, further examinations would be necessary. The aim of our experiments, however, was only to determine the minimum time of reaction necessary to reach the phase-equilibrium state of isotope exchange under our experimental conditions. On the basis of the conducted experiments it seems that, considering the very low velocity of the third reaction stage, this state sets in in about two hours and that the value of the isotope's distribution quotient gives the size of the surface exchangeable with the given isotope [7].

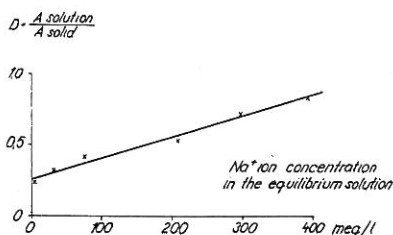


Figure 3

The distribution quotient of  $\text{Na}^{24}$  between the solid and liquid phases as a function of the  $\text{Na}^+$  ion concentration relating to the second part process

## 2. Examinations conducted with systems containing neutral sodium salts

a) Examinations carried out with bentonite— $\text{NaCl}$  solution and bentonite— $\text{Na}_2\text{SO}_4$  solution systems, where the solutions were of different concentration.

One part of the examinations was carried out in Ca-bentonite— $\text{NaCl}$  solution systems. The obtained data is presented in Table 2. The data indicate that the exchange took place in a nearly neutral medium. The pH value of the suspension varied between 7,43 and 7,26. The value of the isotope distribution quotient decreased all along with the increase of the solution's concentration. The values of the selectivity coefficients, calculated on the basis of Vanselow's equation and corrected with the activity coefficients of the ions present in the solution, were nearly the same. The selectivity coefficient reached its maximum value at  $5 \times 10^{-2}$  and  $1 \times 10^{-2}$  moles/l ionic strengths.

Similar data were obtained in bentonite— $\text{Na}_2\text{SO}_4$  solution systems. When expressing the activity of the solid phase in the percentage of the solution's initial activity and plotting it as a function of Na concentration, we obtained nearly identical values in bentonite— $\text{NaCl}$  solution and bentonite— $\text{Na}_2\text{SO}_4$  solution systems, except in the case of higher concentration values, where the distribution quotient of the bentonite— $\text{Na}_2\text{SO}_4$  solution system was larger than that of the bentonite— $\text{NaCl}$  solution system (Fig. 4).

b) Examinations carried out with phase-equilibrium systems of bentonite— $\text{NaCl}$  solution.

The experimental data obtained are presented in Table 3.

The adsorption of sodium ions could be measured only if the ratio of sodium to calcium ions was very high in the solution. By constant bentonite concentration and constant concentration ratio of calcium to sodium ions present in the solution, the degree of the sodium ions' adsorption changed

Table 2

The change in the  $\text{Na}^{24}$  isotope's distribution quotient and the value of the selectivity coefficient, calculated on the basis of Vanselow's equation in bentonite-NaCl solution systems

Concentration of NaCl solution (N)	pH of equil. solution	$\text{Na}^+ : \text{Ca}^{2+}$ in equil. sol. meq/l	Quotient of distribution $D_{\text{Na}^{24}}$	Mole fraction of Na in the Solid Phase N	Vanselow's Selectivity Coefficient $\frac{K_A}{K_B}$
0,005	7,43	0,147	4,40	0,0198	0,683
0,010	7,37	0,148	4,24	0,0258	1,037
0,050	7,37	2,040	3,09	0,3200	1,268
0,100	7,34	4,110	2,47	0,5390	1,109
0,250	7,34	6,348	1,93	0,7690	1,050
0,500	7,26	8,649	1,23	0,8470	1,000

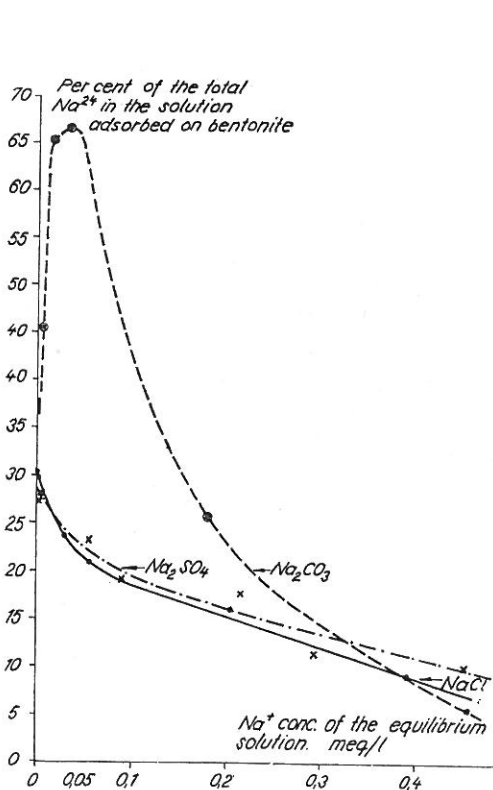


Figure 4

The activity taken up by bentonite in the percentage of the initial activity as a function of the equilibrium  $\text{Na}^+$  ion concentration in systems of bentonite-NaCl solution, bentonite- $\text{Na}_2\text{SO}_4$  solution and bentonite- $\text{Na}_2\text{CO}_3$  solution

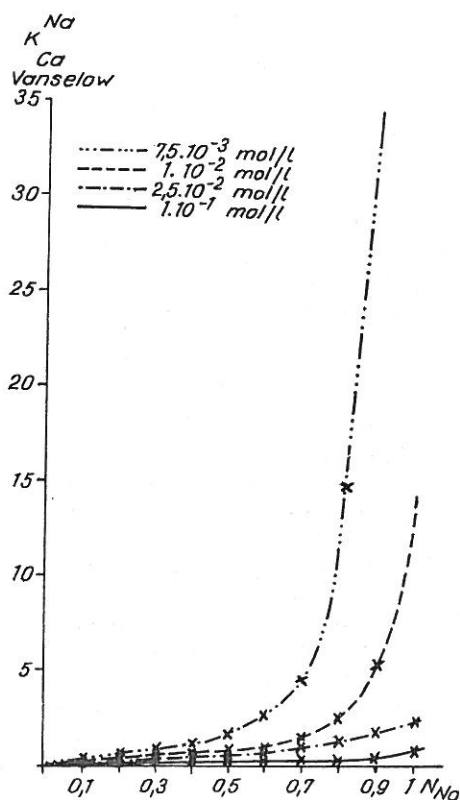


Figure 5

Vanselow's selectivity coefficient as a function of the exchangeable  $\text{Na}^+$  ion's mole fraction in bentonite suspensions prepared with NaCl solutions of various ionic strength

with the increasing ionic strength of the solution which was in equilibrium with the solid phase, so with increasing ionic strength the ratio of adsorption shifted for the favour of sodium ions.

Table 3

The amount of exchangeable sodium ions in bentonite-NaCl solution systems

Ionic strength of the solution mol/l	Na <sup>+</sup> : Ca <sup>2+</sup> in the equil. solution	Exchangeable Na <sup>+</sup> meq/100g	pH
I = 5 × 10 <sup>-3</sup>	15,4	16,03	7,29
	11,6	11,99	7,22
	9,1	7,70	7,05
I = 7,5 × 10 <sup>-3</sup>	15,4	23,00	7,26
	1,16	15,15	7,13
	9,1	9,78	7,10
I = 1 × 10 <sup>-2</sup>	15,4	(28,2)	7,27
	11,6	16,54	7,22
	9,1	11,82	6,84
I = 2,5 × 10 <sup>-2</sup>	15,4	38,07	7,28
	11,6	25,15	7,12

The selectivity factors were calculated on the basis of Vanselow's equation (Figure 5):

$$K_v = \frac{(N_{\text{RNa}})^2 \cdot (m_{\text{Ca}^{2+}}) (\gamma_{\text{Ca}^{2+}})}{(N_{\text{RCa}}) \cdot (m_{\text{Na}^+}) (\gamma_{\text{Na}^+})^2}$$

where:  $N_{\text{RCa}}$  = mole fraction of exchangeable Ca<sup>2+</sup> ion  
 $N_{\text{RNa}}$  = mole fraction of exchangeable Na<sup>+</sup> ion  
 $m_{\text{Ca}^{2+}}$  = concentration of Ca<sup>2+</sup> ions in equilibrium solution, mole/l  
 $m_{\text{Na}^+}$  = concentration of Na<sup>+</sup> ions in equilibrium solution, mole/l  
 $\gamma_{\text{Ca}^{2+}}$  = activity of Ca<sup>2+</sup> ions in the equilibrium solution  
 $\gamma_{\text{Na}^+}$  = activity of Na<sup>+</sup> ions the equilibrium solution

It appears from the data that the value of selectivity coefficients measured in bentonite-NaCl solution systems changed with the ionic strength of the solution. The value of Vanselow's selectivity coefficient increased with the solution's decreasing ionic strength — under the same conditions by the way — thus indicating that the system approached the ideal state if the ionic strength of the solution decreased.

In the case of the same ionic strengths the value of the selectivity coefficient was in close correlation with that of the exchangeable Na<sup>+</sup> ions' mole fraction and changed with it. The value of the selectivity factor, calculated on the basis of Vanselow's equation and corrected with the ion activity coefficients was nearly constant in the equilibrium solution — for example if the ionic strength of the liquid phase was 7,5 · 10<sup>-3</sup> mole/l — until the value of the exchangeable sodium ions' mole fraction did not surpass 0,5. When the value of the exchangeable Na ions' mole fraction rose over 0,5, then the value of Vanselow's selectivity factor increased significantly (Figure 5). The more

diluted the external electrolyte was, the lower was the sodium ion saturation at which the selectivity of the adsorbent for sodium ions increased. A change like this in the selectivity coefficient indicates that an increase in the sodium ion saturation is accompanied by certain alterations in the adsorbent's properties. It must be noted that in the course of the calculations — when the ionic strength of the external solution was constant — the value of the exchange capacity was considered constant in each case; thus the increase of the selectivity coefficient was at least partly apparent.

On the basis of the data obtained from the Vanselow's selectivity factors and the corresponding mole fraction values, we calculated the dependence of the selectivity factor on the values of the exchangeable cations, in mole fraction, according to the next equation:

$$\ln k_r = a_1 + a_2x + a_3x^2$$

From this dependence we calculated the value for the equilibrium constant:

$$\ln k = \int_0^1 \ln k_p dx$$

where

$$x = \frac{N_{\text{Na}}}{2N_{\text{Ca}} + N_{\text{Na}}}$$

$N_{\text{Na}}$  = mole fraction of the exchangeable sodium ion

$N_{\text{Ca}}$  = mole fraction of the exchangeable calcium ion

$k_p$  = Vanselow's selectivity factor corrected with the activity coefficients

$k$  = equilibrium constant.

The obtained value of the equilibrium constant is 2,57 in bentonite—NaCl solution system. The comparison of the data of examinations conducted in bentonite—sodium chloride solution and bentonite—sodium sulphate solution systems indicates that the degree of the sodium ion's adsorption was influenced but slightly by the kind of anions (in the case of chloride and sulphate ions). In general, the adsorption of sodium ions was higher in systems containing chloride ions if the ionic strength of the liquid phase was smaller, and in systems containing sulphate ions if the ionic strength was greater. In bentonite—sodium sulphate solution systems the value of the selectivity coefficient of the adsorbent was

nearly the same — in the case of low sodium saturation — as that of selectivity coefficients for bentonite—sodium chloride systems. With increasing sodium ion saturation, the selectivity coefficient considerably increased in bentonite—sodium sulphate solution systems and it surpassed the value of the

Table 4  
The amount of exchangeable  $\text{Na}^{2+}$  ions in bentonite- $\text{Na}_2\text{SO}_4$  solution systems

Ionic strength mol/l	$\text{Na}^+ : \text{Ca}^{2+}$ in the equil. solution	Exchangeable $\text{Na}^+$ meq/100 g
0,0500	15,12	51,9
0,0250		33,8
0,0100		21,7
0,0075		21,8
0,0250	11,60	25,4
0,0100		21,7
0,0075		13,9
0,0050		11,8

selectivity coefficient determined in bentonite–sodium chloride solution systems (Fig. 6).

### 3. Examinations carried out in bentonite–Na carbonate solution systems

a) Examinations were conducted with suspensions where the ratio of the solid and liquid phases was 1 : 10, 1 : 50 and 1 : 100. The distribution quotient of  $\text{Na}^{24}$  isotope between the solid and liquid phases was determined as a function of the sodium carbonate solution's concentration. The obtained data show (Table 5) that the value of the isotope distribution quotient was higher in each case than in systems containing  $\text{NaCl}$  or  $\text{Na}_2\text{SO}_4$  which were subjected to similar treatments. In the diluted solutions of the same systems at the 1 : 10 ratio of the solid and liquid phase, the isotope distribution showed maximum value if the  $\text{Na}$  ion concentration in the equilibrium solution was 50 meq./l.

The high values of the isotope distribution quotients and the maximum value observed in the 1 : 10 suspension indicate that the surface or rather the exchange capacity of the adsorbent changes in the examined systems.

The high distribution quotient might have also been caused by the fact that in alkaline medium the solubility of calcium carbonate decreases significantly and sodium ions dominate in the system.

b) Experiments were conducted in phase equilibrium system in order to clarify the question that to what

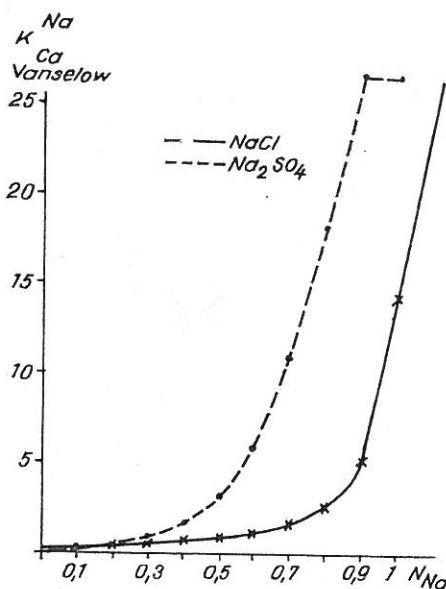


Figure 6

Vanselow's selectivity coefficient as a function of the exchangeable  $\text{Na}^+$  ions' mole fraction in bentonite– $\text{NaCl}$  solution and bentonite– $\text{Na}_2\text{CO}_3$  solution systems. The ionic strength of the solutions is 0,01 mol/l

Table 5

Distribution quotients of  $\text{Na}^{24}$  in bentonite– $\text{NaCl}$  solution, bentonite– $\text{Na}_2\text{SO}_4$  solution, and bentonite– $\text{Na}_2\text{CO}_3$  solution systems

Concentration of solution (N)	$D_{\text{Na}^{24}}^{\text{Na}}$ Bent.– $\text{NaCl}$ sol. 1 : 10	$D_{\text{Na}^{24}}^{\text{Na}}$ Bent.– $\text{Na}_2\text{SO}_4$ sol. 1 : 10	$D_{\text{Na}^{24}}^{\text{Na}}$ Bent.– $\text{Na}_2\text{CO}_3$ sol. 1 : 10	$D_{\text{Na}^{24}}^{\text{Na}}$ Bent.– $\text{Na}_2\text{CO}_3$ sol. 1 : 50	$D_{\text{Na}^{24}}^{\text{Na}}$ Bent.– $\text{Na}_2\text{CO}_3$ 1 : 100
0,005	4,40	3,64	5,97	29,30	39,80
0,010	4,24	3,66	8,35	23,45	38,00
0,050	3,09	2,94	18,90	21,25	28,40
0,100	2,47	2,41	19,80	17,50	20,20
0,250	1,93	2,19	5,16	7,09	7,95
0,500	1,23	1,10	0,47	2,37	2,65
0,750	0,61	0,46	0,10	—	—

extent, the increase of the isotope distribution quotient value, can be explained by the excess of sodium ions in the solution or rather by the change in the adsorption capacity, as compared with systems containing neutral sodium salts. In the course of the experiments the ionic strength of the solution changed between  $1,9 \times 10^{-3}$  and  $8 \times 10^{-3}$  mol/l. The obtained data are given in Table 6.

Table 6

The values of Vanselow's selectivity coefficients in bentonite- $\text{Na}_2\text{CO}_3$  solution equilibrium systems

Ionic strength	pH of the equil. solution	Exchangeable $\text{Na}^+$ meq/100 g	Mole Fraction of $\text{Na}^+$ Ion the Solid Phase ( $N_{\text{Na}}$ )	C E C meq/100 g Measured	Selectivity Coefficients	
					* $K_{V_1}$	** $K_{V_1}$
0,0019	9,62	16,50	0,310	90,21	31,87	18,00
0,0030	9,92	29,54	0,468	96,85	24,38	10,43
0,0050	10,09	61,62	0,642	130,57	88,00	17,68
0,0080	10,05	86,75	0,779	136,19	—	14,27

\* Calculated with constant adsorption capacity.

\*\* Taking the total of the measured exchangeable  $\text{Na}^+$  and  $\text{Ca}^{2+}$  ions for the adsorption capacity.

The selectivity factor was calculated from the measured data by the following two methods:

1. The exchange capacity was assumed stable just as in the case of systems containing neutral sodium salts.
2. The total amount of the measured exchangeable Na and Ca ions was considered as the bentonite's exchange capacity.

If the exchange capacity is supposed to be constant, then the value of the selectivity factor is extremely high. The value of the Vanselow's selectivity factor, calculated from the experimental data and corrected by the activity coefficients of ions present in the solution, was essentially lower but in comparison with the values obtained in bentonite—NaCl solution systems, it was still high and, at a low value of the exchangeable Na ions' mole fraction (0,31), it significantly differed from the values measured in systems containing neutral sodium salts.

It must be noted, that in our calculations we calculated the Ca ion concentration in the solution with the solubility product of calcium carbonate, taking into consideration the carbonate and hydrocarbonate concentration of the solution. It should also be noted that in the course of the examinations, the meq./g total amount of exchangeable Na and Ca ions expressed for bentonite changed essentially. At the  $1,9 \times 10^{-3}$  mol/l ionic strength it was 0,902 meq./g and along with the increase of the concentration it became 1,36 meq./g. Thus, the data show that in alkaline medium the value of Vanselow's selectivity coefficient, calculated with constant exchange capacity, significantly differs from those measured in systems containing the solution of neutral salts. The data obtained also show that with increasing pH and Na ion concentration of the solution, the exchange capacity of bentonite increased, too. The value of the selectivity coefficient calculated from the measured exchange capacities is still higher than those measured in systems containing solution

of neutral sodium salts, although they are near to each-other in the measured concentration range.

4. Colloid-chemical examinations

The conducted examinations show that in the case of 1 : 10 bentonite—Na carbonate solution system the swelling ability of the solid phase grew considerably in Na carbonate solution and it reached the maximum value at an initial Na carbonate concentration of 100 meq./l (Fig. 7). The time of thyo-

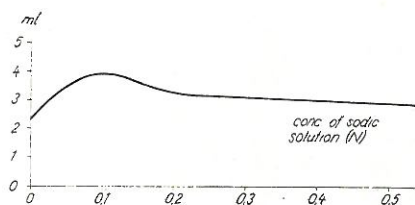


Figure 7

Swelling of bentonite suspension

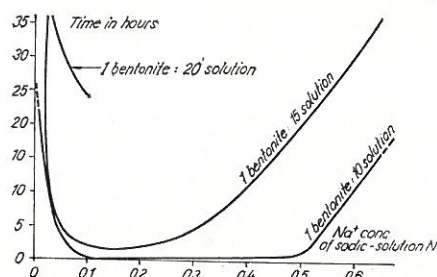


Figure 8

Time of thixotropic setting of bentonite— $\text{Na}_2\text{CO}_3$  solution systems as a function of the  $\text{Na}_2\text{CO}_3$  solution's concentration. The ratios of bentonite to solution were 1 : 10 and 1 : 15

tropic setting of these same systems considerably decreased due to the effect of Na carbonate solution, and it reached the minimum between 100—500 meq./l initial Na carbonate concentrations. Along with a further increase of the soda solution's concentration the time of thixotropic setting rapidly lengthened. In the 100—500 meq./l concentration range the system showed a characteristic reopexy (Fig. 8).

Similarly, the electro-kinetic potential determined on the basis of electroforetic migration velocity also showed the maximum value with the increasing concentrations of  $\text{Na}_2\text{CO}_3$  (Table 7).

The conducted experiments show that in the presence of Na salts capable of alkaline hydrolysis a significant change takes place in the colloid state of the particles, as well as in the size of the surface exchangeable with sodium ions.

5. Mineralogical examinations

The evaluation of TG curves showed that the value of hygroscopic water in bentonite did not change essentially, regardless whether the bentonite was or was not treated

Table 7

The change of the electrokinetic potential in 1 : 100 bentonite— $\text{Na}_2\text{CO}_3$  solution suspension as a function of the  $\text{Na}_2\text{CO}_3$  solution's concentration

Concentration of $\text{Na}_2\text{CO}_3$ solution (N)	Electrokinetic ( $\xi$ ) potential (mV)
0	25,6
0,005	44,2
0,010	60,8
0,050	63,0
0,100	66,4
0,250	55,6
0,500	51,9
0,750	48,1

The electrokinetic potentials were determined by measuring the electroforetic migration velocity in suspensions of bentonite and  $\text{Na}_2\text{CO}_3$  solutions of different concentrations.

Table 8

Water forms calculated from the DT graph of bentonite samples not-treated or treated with  $\text{Na}_2\text{CO}_3$  solutions of different concentration

Treatment	Hygroscopic water %	Total loss of weight % 100°—1000° C	Loss of weight %			Endotherm peaks °C	
			100—300	300—760	760—1000		
			°C				
—	15,17	19,20	17,00	1,70	0,50	700	880
0,01 N $\text{Na}_2\text{CO}_3$	13,54	20,30	14,50	2,70	3,10	700	800
0,1 N $\text{Na}_2\text{CO}_3$	11,05	23,95	14,50	4,70	4,70	700	800
0,5 N $\text{Na}_2\text{CO}_3$	17,62	21,55	11,25	3,80	6,50	700	800

with sodium carbonate solutions of different concentration. The relation, however, between the different forms of water altered. Special attention should be paid to the amount of the heated bentonite's weight-loss between 300—1000°C because that gives the amount of the so-called textural water (Table 8). It is apparent from the data presented in Table 8 that while the amount of the easily losable water decreased by increasing concentration of the soda solution, that of the textural water increased. To a certain degree this fact indicates the deformation of the montmorillonite's lattice layer. This deformation is not considerable, in certain cases, however, it can be detected with an X-ray examination of the texture. According to our examinations, the lattice layer distance of not treated bentonite, calculated on the basis of its 0,01 base-reflection, was 13,7 Å. This value was 16,2 Å, measured after treating the bentonite with 0,01 N sodium carbonate solution.

### Evaluation of the experimental data and conclusions

The data of the conducted kinetic examinations show that in bentonite — solution systems containing neutral sodium salts the curve of isotope adsorption may be described as the function of three, kinetically first rate reactions and it satisfies the formal kinetic equation to describe the processes taking place on the surface of crystalline solid systems which are in equilibrium with their saturated solutions. By analysing the part processes it can be seen that their velocity constants show a difference in the order of magnitude. It is apparent from the conducted examinations that the first two part processes correspond to cation exchange and isotope exchange while, in all probability, the third one characterizes the rearrangement taking place on the surface of the adsorbent. Under the conditions of the employed experimental arrangements it took about two hours till the first two part processes reached the state of equilibrium. This means that in the given systems the quasi phase-equilibrium state of isotope exchange may be reached in about two hours.

In the followings, phase equilibrium systems set in on the basis of the kinetic examinations, were subjected to thorough analyses.

In equilibrium systems of bentonite—sodium chloride solution the value of the selectivity coefficient, calculated on the basis of Vanselow's equation and corrected with the ion activity coefficients depended on the ionic strength of the external electrolyte, and decreased with increasing ionic strength. In the



case of diluted solutions the selectivity coefficient was nearly constant till the value of the exchangeable sodium ions' mole fraction did not surpass 0,5. If the value of the exchangeable sodium ions, expressed in mole fraction, surpassed the value of the calcium ions' mole fraction on the surface of the adsorbent, the selectivity coefficient increased significantly.

Both in bentonite—sodium sulphate solution and in bentonite—NaCl solution systems the values of selectivity coefficients were approximately the same and their changes also displayed similar characteristics. From the minor differences measured it cannot be concluded that there is a significant difference between the selectivities of the adsorbents in systems containing sodium sulphate and sodium chloride, respectively.

The value of the selectivity coefficient changed significantly in bentonite—sodium carbonate solution systems.

It is obvious that the low solubility of calcium carbonate in alkaline medium allows the sodium ions to play a dominating role in the solution and that under the same conditions otherwise, (the same ionic strength, identical ratio of the solid and liquid phases, etc.) the degree of the sodium ion adsorption is larger and it depends mainly on the Na ion concentration in the solution.

The examinations carried out with phase-equilibrium systems show, however, that in addition to the differences caused by the solubility, further changes must be also taken into consideration. In systems containing soda solutions, assuming constant exchange capacity, the value of the selectivity coefficients increased significantly. If the value of the mole fraction of the exchangeable Na ion was below 0,5, the value of the selectivity coefficient calculated with constant exchange capacity value was as high as 24—31.

The selectivity coefficients were considerably lower if the sum of the exchangeable Na and Ca ions determined isotopically was taken as the value of the exchange capacity but still they were higher than those measured in systems containing neutral sodium salts. For example, at 0,3 mole fraction value the selectivity coefficient was 18. With a further increase in the relative amount of the exchangeable sodium ions, the value of the selectivity coefficient calculated on the latter basis did not change significantly.

The measured values indicated that, correlated with sodium ions, the selectivity of the exchanger increased in systems containing sodium salts capable of alkaline hydrolysis.

This increase may be traced back to the change in the activity coefficients of the exchangeable ions. It is obvious, that the activity coefficients of ions adsorbed on the surface in systems swelling to a large extent in alkaline medium differ from those of ions in systems containing neutral sodium salts.

Both the measured distribution quotients and, in phase equilibrium systems, the total amount of exchangeable sodium and calcium ions measured by Na<sup>24</sup> and Ca<sup>45</sup> labelling indicate that in these systems the changes in the colloid-chemical and mineralogical properties of the adsorbent must also be taken into consideration. When calculating the value of the selectivity coefficient, we assumed previously that the value of the exchange capacity was constant. The increase in the value of the selectivity coefficient as well as the high value of the isotope distribution quotient measured in systems containing sodium salts capable of alkaline hydrolysis and its maximum measured in the 1 : 10 suspension indicate that that presumption was not justified. If we

state the material balance of the system and relate it to the isotope distribution quotient, we get the following equation:

$$\frac{S_0 - S_L}{S_L} C V = M N_{\text{Na}}$$

where  $S_0$  = initial activity of the solution imp.min/ml  
 $S_L$  = activity of the equilibrium solution, imp.min/ml  
 $C$  = Na ion concentration in the equilibrium solution  
 $V$  = volume of solution corresponding to 1 g of the adsorbent  
 $M$  = cation exchange capacity of the adsorbent  
 $N_{\text{Na}}$  = mole fraction of the exchangeable Na ion.

Rearranging the equation, we get the following correlation for the distribution quotient:

$$\frac{S_0 - S_L}{S_L} = \frac{M}{C V} N_{\text{Na}}$$

It can be seen from this equation that if the ratio of the solid to the liquid phase is constant in the suspension and we presume that the cation exchange capacity of the adsorbent is constant, too, then the isotope distribution quotient should decrease when the Na ion concentration increases.

Table 9

Value of CEC calculated on the basis of the selectivity coefficient in bentonite- $\text{Na}_2\text{CO}_3$  solution (of  $7 \cdot 10^{-3}$  mol/l ionic strength) system

pH of equil. solution	Equil. $\text{Na}^+$ concentration meq/l	Exchangeable $\text{Na}^+$ meq/100 g	Mole Fraction of Na in the Solid Phase ( $N_{\text{Na}}$ )	CEC meq/100 g		Selectivity coefficient det. in graphic way
				calculated	det. in graphic way	
9,84	4,48	53,98	0,471	127,8	} 137	} 0,801
9,62	5,13	74,82	0,306	166,1		
9,62	5,78	80,60	0,698	150,8		
9,64	5,95	89,78	0,709	163,8		
10,12	5,81	95,76	0,857	128,2		

This is valid in the case of solutions containing neutral sodium salts. If the distribution quotient increases in spite of the increase in the solution's Na ion concentration then it means that the cation exchange capacity of the adsorbent increases. This is indicated by the values of distribution quotients measured in soda-containing systems. This capacity increase may be either apparent or actual. If we determine the  $\text{Na}^+$  concentration of the equilibrium solution, calculate the  $\text{Ca}^{2+}$  ion concentration from the solubility product of  $\text{CaCO}_3$  and measure the value of the exchangeable sodium, then the value of the solid phase's adsorption capacity and the selectivity coefficient may be calculated from the transformed Vanselow's equation with the graphic method (in a graphic way).

$$\frac{1}{RN a^2} = \frac{1}{T^2} + \frac{1}{K_r T^2} \frac{4 a_{\text{Ca}}}{a_{\text{Na}}^2}$$

where:  $RNa$  = exchangeable  $Na^+$  ion, meq./100 g  
 $T$  = CEC of adsorbent, meq./100 g  
 $a_{Ca}$  =  $Ca^{2+}$  ion activity of equilibrium solution, mol/l  
 $a_{Na}$  =  $Na^+$  ion activity of equilibrium solution, mol/l  
 $K_v$  = selectivity coefficient.

The obtained values of cation exchange capacity and selectivity coefficient indicate the behaviour of the adsorbent at constant ionic strength of the solution.

For the given system — taking granted that the value of the selectivity coefficient is constant — the cation adsorption capacity of the adsorbent is given by the following equation:

$$T = \sqrt{\frac{4(RNa^2)}{K_v} \cdot \frac{a_{Ca}}{a_{Na}^2} + RNa^2}$$

The calculated value of cation exchange capacity gives both the actual change of the adsorbent's cation exchange capacity originating in the structural state and the apparent increase caused by the change of the exchangeable cations' activity coefficients in swelling systems (Table 9).

If we take for granted that the selectivity coefficient — measured in neutral systems at low concentration of the liquid phase, when the proportion

Table 10

Measured values of exchangeable  $Na^+$  and the calculated CEC values in bentonite- $Na_2CO_3$  solution systems

Ionic strength of the $Na_2CO_3$ solution mol/l	pH of the equil. solution	$Na^+$ conc. of the equil. solution meq/l	Isotopically exch. Na meq/100 g	CEC meq/100 g calculated
0,0083	10,19	4,08	17,21	65,1
0,0158	10,21	7,39	25,46	98,8
0,0869	11,22	45,20	113,17	115,3
0,1684	11,45	106,00	168,40	169,3
0,4221	11,58	256,00	181,36	181,7
0,8737	11,65	513,00	121,40	121,1

of solid phase to liquid phase is large — is constant as related to the 0,5 mole fraction of the exchangeable Na ion and if we calculate the value of cation exchange capacity, then we get that to what extent the behaviour of systems containing sodium salts capable of alkaline hydrolysis differs from the ideal one.

Calculations of this kind were performed in connection with bentonite- $Na_2CO_3$  solution systems, where the ratio of the solid phase to the liquid phase was 1 : 100. The difference between the approximately constant exchange capacities measured in neutral systems and the exchange capacities calculated in the case of systems containing sodium salts capable of alkaline hydrolysis gives the apparent and actual changes of cation exchange capacity arising from the exchangeable cations' activity coefficients and from the changes occurring in the colloid-chemical and structural state of the adsorbent (Table 10).

### Summary

1. The low solubility of calcium carbonate, forming in the course of exchange, increases significantly the relative amount of sodium ions in the liquid phase and, consequently, the degree of the sodium ions' exchange in systems containing sodium salts capable of alkaline hydrolysis.

2. In systems containing sodium salts capable of alkaline hydrolysis (including the bounding between the adsorbing complex of the soil and the exchangeable Na ions) the selectivity of the exchanger correlated with Na ions increases to a large extent. This manifests itself in the increase of the values of selectivity coefficients.

3. The increase in selectivity may be explained partly by the change in the exchangeable cations' activity coefficients in swelling systems and partly by the capacity change resulting from the changes taking place in the state of the adsorbent.

4. The change in selectivity may be expressed in the value of Vanselow's selectivity coefficient.

5. Taking for granted that the selectivity coefficient, measured at 0,5 mole fraction value of the exchangeable sodium ion, is constant in systems containing neutral sodium salts, the value of the exchange capacity belonging to bentonite—sodium carbonate solution system can be calculated.

The difference between the exchange capacity values calculated this way and measured in systems containing neutral salts gives the total of the apparent and actual values of capacity change and, consequently, the change in the selectivity of the adsorbent.

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