

SOME SORPTION PROPERTIES OF CLINOPTILOLITIZED PYROCLASTICS OF TOKAJ MOUNTAINS, HUNGARY

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INTRODUCTION

Clinoptilolite is one of the most wide-spread zeolites originating from pyroclastics. Numerous occurrences of the Soviet Union, Japan, New-Zealand etc. are introduced in the literature, geological, genetic, geochemical, etc. characterization is available regarding these beds. These occurrences have special importance since then specific features of clinoptilolite are known which result in its industrial significance and make possible its ever growing utilization [MERCER *et al.*, 1970].

The clinoptilolite occurrence of the Tokaj Mountains, Hungary is interesting not only from the point of view of geology, metallogeny and mineralogy-petrology and is worthy of research also in the future, but the recognition of its exploitability and manifold applicability proved to be also important. The ever growing utilization both in Hungary and in abroad favours the further research of the area, of the rock and of the clinoptilolite itself.

On the afore-mentioned bases investigations were performed partly to determine the mineralogical, structural features of the clinoptilolitized pyroclastics, partly to discover the sorption features of the original rock and separates made from it. These investigations have both theoretical and practical significance.

It is well-known that clinoptilolite is used for different industrial purposes (catalysator, adsorbent, ion-exchanger, molecule-sieve). Consequently, the knowledge of the mineral composition, of the ratio of composition, of the features of structural changes following due to heat treatment, further the recognition of the adsorption features being connected to these peculiarities gives the possibility to discover the structural (theoretical) features and promotes the wider utilization.

NEMECZ and VARJÚ [1962] demonstrated in the elaboration of the mineralogy-petrology that investigating several occurrences of zeolitized volcanic tuff known as "clinoptilolite", this is a rock consisting of several minerals: clinoptilolite, adularia, cristobalite, quartz and occasionally montmorillonite.

In the course of our investigations the Hungarian "clinoptilolite" was investigated by X-ray diffractometer, derivatograph and infrared spectroscope, its total chemical analysis was performed and its trace element content was determined by Q-24 spectrograph (12).

The material of two not totally similar clinoptilolite occurrence of the Tokaj Mountains was investigated by X-ray diffractometer, and in all cases not only the unheated but the heated samples (up to 200, 300, 500, 600, 800 and 1000 °C, sample No. 1) as well as the sample heated up to 600 °C (on which the ion exchange and adsorption investigations were done, sample No. 2) were controlled.

As regarding the mineral composition of the two unheated clinoptilolites, they showed smaller differences. In the sample No. 1 in addition to the amorphous phase adularia, quartz, cristobalite and less montmorillonite were identified, in the other sample (No. 2) no amorphous phase was found, and in addition to clinoptilolite adularia, quartz and cristobalite were identified.

EXPERIMENTAL PART

The composition of clinoptilolite

On the basis of the X-ray diffractometric records of the heated material of sample No. 1 it was obvious that in every material of clinoptilolite heated under 600 °C it could be identified by the original intensity, while in the material heated up to 600 °C it showed smaller decrease of intensity.

Though 1—2 $d(\text{Å})$ values could be identified in the material heated up to 1000 °C, this sample became essentially X-ray amorphous.

When heating at 300 °C the mineral assemblage quartz, cristobalite, adularia, clinoptilolite of the sample No. 1, in the unheated material these minerals could be identified by smaller decrease in intensity, except quartz (*Fig. 1*).

In addition to the chemical analysis, quantitative determination was done from the unheated X-ray diffractometric record of the sample No. 1 with the aid of the chemical analysis.

Data of the chemical analysis:

SiO ₂	69.12
Al ₂ O ₃	11.60
TiO ₂	0.39
Fe ₂ O ₃	1.39
MnO	0.01
MgO	0.18
CaO	1.27
Na ₂ O	0.17
K ₂ O	5.50

98.51 per cent

From this composition theoretically

35 per cent clinoptilolite

34 per cent adularia

30 per cent cristobalite, quartz and amorphous material could be calculated.

TABLE 1

Mineral	Unheated	Heated to				
		200	300	400	500	600 °C
		percentual distribution				
clinoptilolite	35	34.6	32.2	28.1	30.3	29.8
adularia	34	20.8	25.4	17.4	19.2	19.2
amorphous and SiO ₂ varieties	30	50	39	12.5	1.3	32.8

CLINOPTYLOLITE, Tokaj Mts. Hungary

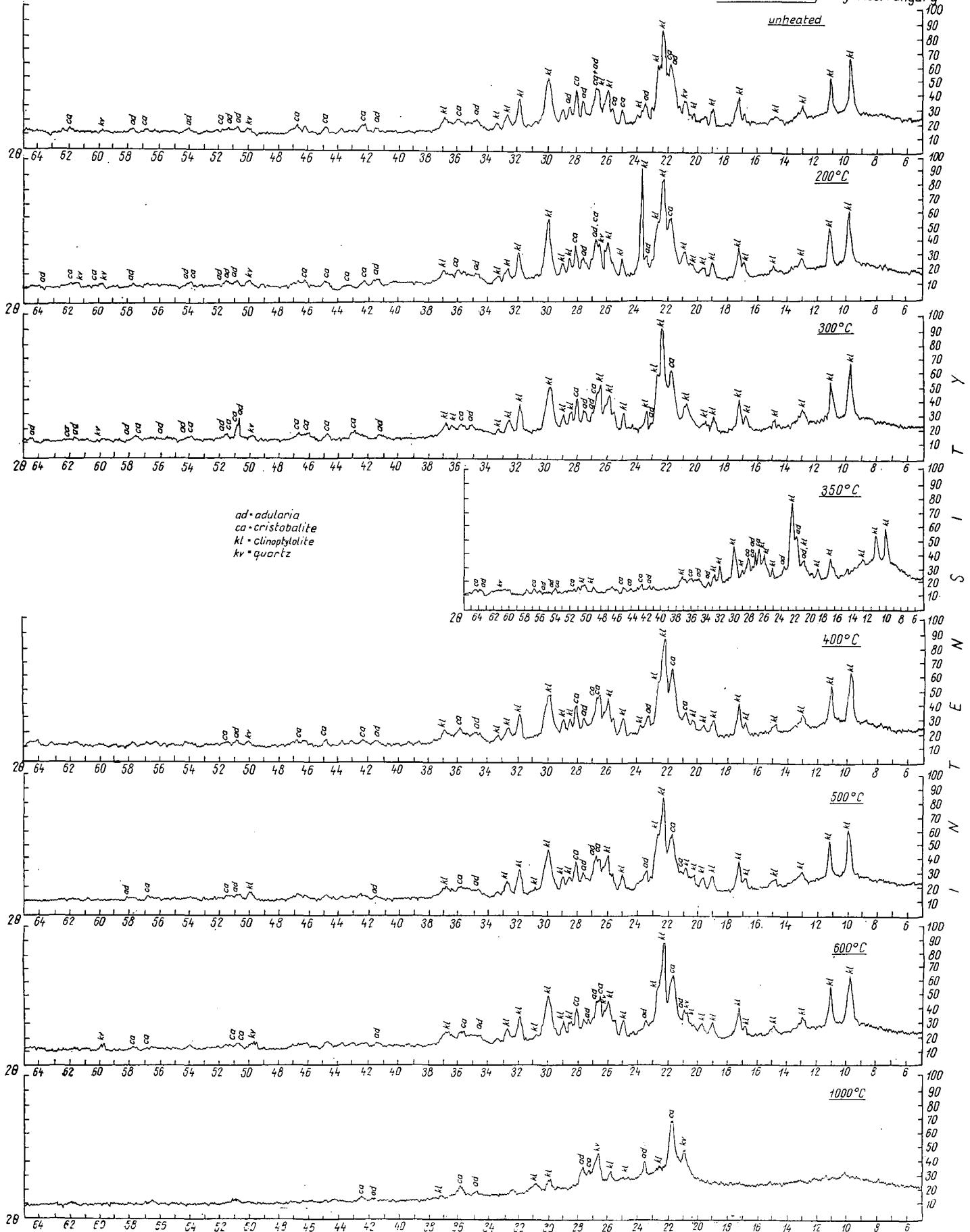


Fig. 1. Diffractometric records of unheated and heated clinoptilolite, Tokaj Mts., Hungary

TABLE 2

Siderophile elements			Chalcophile elements						
Fe	Co	Ni	Ag	Cu	Zn	Ge	Sn	Pb	As
+	0	tr	0	tr	tr	0	tr	tr	0

Litophile			Pegmatophile elements							Sedimentophile					
Li	Na	K	Cs	Ca	Mg	Sr	Ba	Ti	V	Ga	Cr	Mo	Mn	Be	B
0	+	+	0	+	tr	tr	tr	tr	tr	tr	tr	0	tr	tr	tr
		+													
		+													

note: tr = traces

On this basis using the measured areas calculated composition was determined graphically.

The graphically recalculated composition shown in the data of Table 1. indicates the quantitative changes of the single minerals compared with one another.

The trace element content is given in the Table 2.

Investigation of the water content of clinoptilolite

The thermal decomposition of clinoptilolite was followed by derivatograph. On the basis of Fig. 2 its water-release is continuous up to 500 °C, with slight endothermal deepening at 120 and 656 °C.

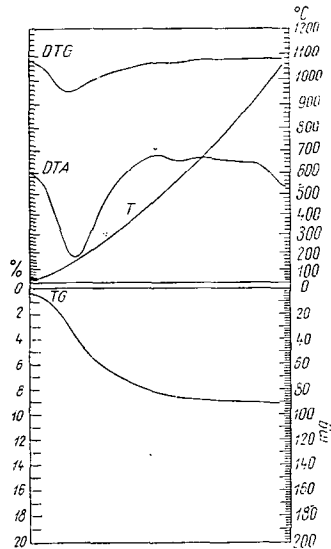


Fig. 2. Derivatogram of "clinoptilolite", Tokaj Mts., Hungary

On the basis of infrared spectroscopic investigations the adsorption bands of the unheated material as well as of the material heated up to 350 and 700 °C of the clinoptilolite are nearly the same. In addition to the adsorption bands characteristic of the water content of OH—Al, the cation-OH band around 670 cm^{-1} also appeared. In the adsorption band range between 3600 and 3400 cm^{-1} two adsorptions (at 3530 and 3240 cm^{-1}) relate to the fact that the water of clinoptilolite is bound in several forms. As regarding the character of its water content it was stated that the arrangement of the water molecules is partly around the Al-ion, partly around the cations as a hydrate sphere. On the basis of the absorption bands between 400 to 1000 cm^{-1} being characteristic of the silicate bond its structure is similar to that of the inosilicates. The absorption range of 670 cm^{-1} being characteristic of the cations indicates considerable sodium and potassium built-in into the lattice. The intense band of 8000 cm^{-1} characteristic of the feldspars is due to the adularia content of the clinoptilolite (Fig. 3).

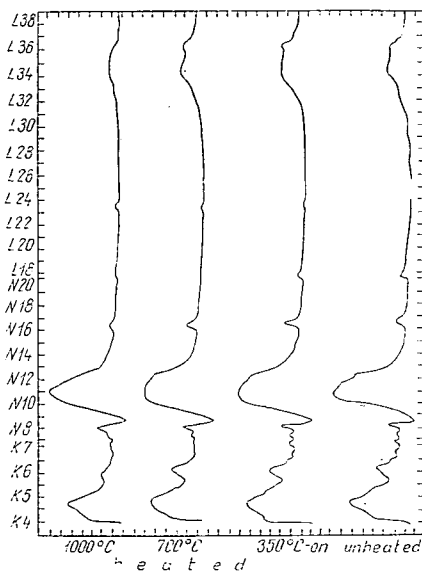


Fig. 3. Infrared spectra of "clinoptilolite", Tokaj Mts., Hungary

The infrared spectrum showed both structure modification and change in water content of the clinoptilolite only in cases heated up to 1000 °C.

Investigation of the sorption capacity of clinoptilolite

These investigations were performed on the clinoptilolite-bearing rock of the Tokaj Mountains, Hungary (in the following clinoptilolite) and on the so-called "clinosorb" material produced from it by the Reanal Fine Chemicals Factory, Budapest.

These materials were previously treated by ammonium-chloride solution for several hours, then they were heated at 400 °C. The products obtained in this way were brought into contact with different electrolyte solutions. During the investigations the equipment demonstrated in Fig. 4 was used.

TABLE 3

Investigation of the ion exchange of clinoptilolite in diluted solution of ammonium chloride

Adsorbent	Concentration NH ₄ Cl mmol/l		Specific conductivity of the solution, μ S		Specific conductivity of the solution calculated from ion mobility, μ S		Duration of measurement	Cell potential between silver-glass electrode, mV		Apparent pH		Adsorbent NH ₄ ⁺ capacity mmol/100 g
	initial	final	initial	final	initial	final		initial	final	initial	final	
1	2	3	4	5	6	7	8	9	10	11	12	13
clinosorb, original	1.35		197	204	184		7.5	-7	+62	5.94	7.52	
clinosorb, original	1.353		205	227	184		7.15	-55	+57	6.75	7.05	
flushed, heated clinoptilolite	1.454		198	201	200		7.0	-38	+60	5.38	7.13	
activated clinosorb	ion-free boiled water		3,1	7,0	184		6.0	+33	+9	6.70	6.18	
clinosorb, activated	1.35	0.25	192	361		466	6.0	-3	-147	6.02	3.58	8.10
activated clinoptilolite	1.39	0.29	197	392	189	472	5.5	-37	-151	5.40	3.50	8.00

RESULTS OF THE MEASUREMENTS AND CONCLUSIONS

The first measurements should have provide data on the fact that the ion exchange feature of the natural resp. activated clinoptilolite is the same or not. Thus the phenomenon was investigated that how the natural and activated clinoptilolites taken into a given ammonium-chloride solution of given concentration change the electrochemical features of the solutions being in interaction with them, resp. how they change the concentration of the NH_4Cl solution. *Figs. 5 and 6* contain the results of these measurements. In the solution interacting with the inactivated clinoptilolite the electrode potential increases at the beginning (during about 2 to 3 hours), then it becomes constant. In case of the activated zeolites, however, the electrode potential considerably decreases at the beginning (during about 30 to 40 minutes) and becomes constant only leaving this time (*Fig. 5*).

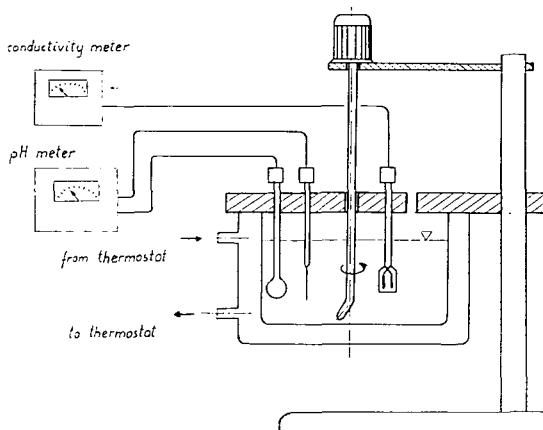


Fig. 4. Equipment for electrochemical investigation

The starting resp. equilibrium values of the electrode potential are involved in the columns 9—12 of Table 3, in case of sorbents of different features. It is obvious from the figure that the conductivity of the ammonium-chloride solution did not change in case of natural zeolites, in presence of activated sorbents, however, it considerably increased during about two hours, then it became constant (*Fig. 6*). The columns 4 and 5 of Table 3 contains the starting and equilibrium specific conductivities of the solutions interacting with the sorbents.

On the basis of the obtained results conclusion may be drawn that at the active places of the natural sorbents such ions were originally present the electrochemical features of which are nearly the same than those of the ammonium ion. The sorbents, however, activated by us contained such contra-ions which had opposite electrochemical features. The considerable increase in specific conductivity and strong decrease in electrode potential (and pH) show that after activation in the active places of the sorbents there should be hydrogen ions. The sorbents treated previously with ammonium ions lost ammonium at 400°C , and transformed into hydrogen-zeolites.

The specific conductivity of different rate of the activated sorbents shown in the *Fig. 6* (curve a, b) is due to the different grain size.

The other aim of the investigations was to obtain data that how the ammonium is bound on the clinoptilolite. It was plausible that depending on the different

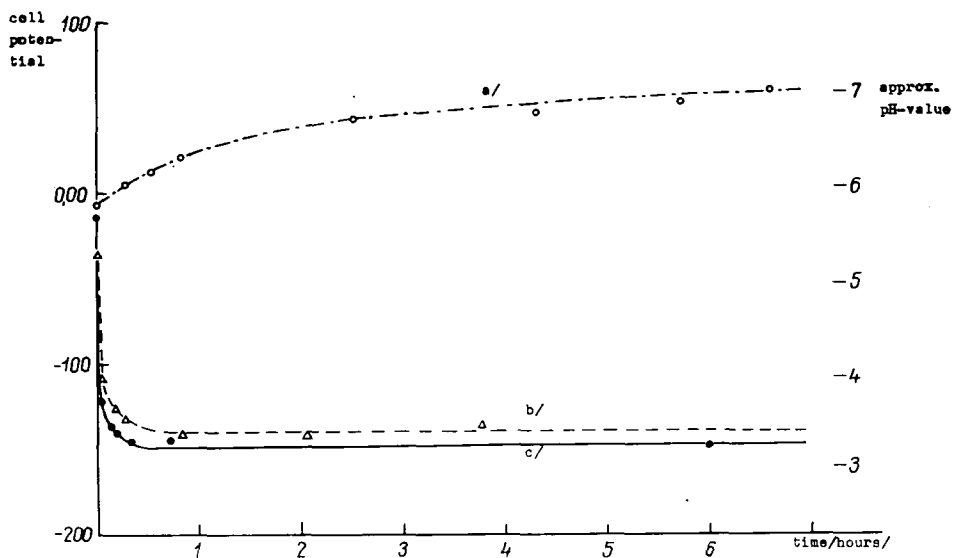


Fig. 5. Following of adsorption, resp. ion exchange on clinoptilolite by electrode potential measurement. a) 1 g clinisorb in 80 ml ammonium chloride solution of 1,35 mmol/litre; b) 1 g activated clinoptilolite in 73 ml ammonium chloride solution of 1.39 mmol/litre; c) 1 g activated clinisorb in 73 ml ammonium chloride solution of 1.35 mmol/litre

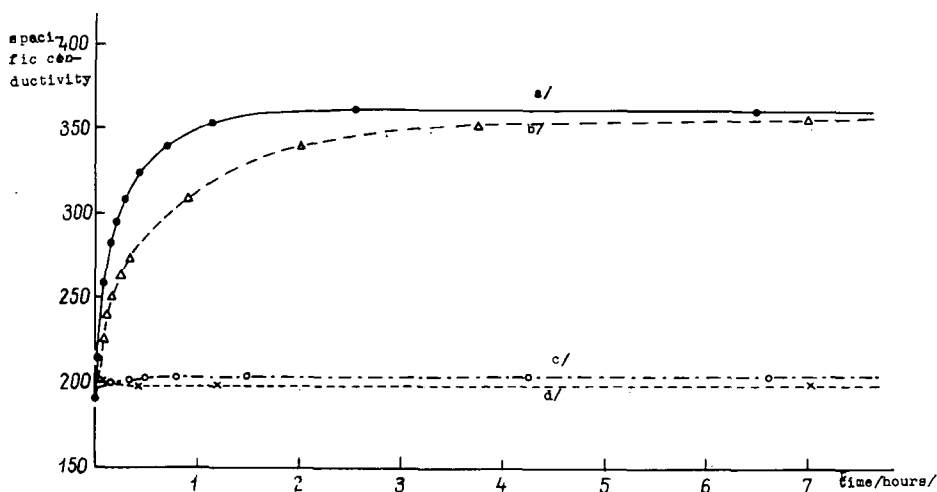


Fig. 6. Following of adsorption, resp. ion exchange on clinoptilolite by conductivity measurement. a) 1 g activated clinisorb in 73 ml ammonium chloride solution of 1.35 mmol/litre; b) 1 g activated clinoptilolite in 73 ml ammonium chloride solution of 1.39 mmol/litre; c) 1 g clinisorb in 80 ml ammonium chloride solution of 1.35 mmol/litre; d) 1 g clinoptilolite in 80 ml ammonium chloride solution of 1.39 mmol/litre

conditions in addition to ion exchange adsorption may also follow. Thus, in favour of the observation of the change of concentration of the starting ammonium solution, in case of every electrochemical measurement the concentration of ammonium ion of the solutions of equilibrium state was also determined (7). These data are shown in the columns 2 and 3 of Table 3.

On the basis of these data calculations were performed to determine that the conductivity of the solutions in questions obtained by calculation shows any deviations from the measured values or not. The following relation served as a basis of calculations (WEAST, 1967—68).:

$$\kappa = \sum_i \frac{c_i u_i}{1000},$$

where κ = specific conductivity, Sm^{-1} .

c_i = ion-concentration. gequ/l .

u_i = relative ion mobility.

The column 6, 7 of Table 3 contains the results obtained in this way.

Data show that the measured and calculated specific conductivities of the starting ammonium chloride solutions are nearly the same. The specific conductivity values, resp. both the measured and the calculated ones of the equilibrium solutions being in interaction with the activated zeolites show considerable differences (5,7 column, Table 3). Supposing that all the ammonium ions being absent in the solutions were replaced hydrogen ions as contra-ions, the value of calculated specific conductivity proved to be the values given in the column 7 of Table 3. These values are higher than the measured ones in case of both sorbents. It may be concluded that in the equilibrium solution more ions were taken into account in the calculations than their number determined by measurement.

TABLE 4

HCl adsorption of clinoptilolite from HCl-solution

Activated sorbent	Initial solution concentration, HCl mmol/l	Concentration from initial conductivity on the basis of calibration, mmol/l	Specific conductivity of the solution, μS		Concentration of the equilibrium solution mmol/l	Adsorbed HCl, mmol	Adsorbed HCl, specific mmol/100 g sorbent	Duration of measurement (hour)
			initial solution	equilibrium solution				
1	2	3	4	5	6	7	8	9
clinosorb	2.0	2.09	838	735	1.86	$1.84 \cdot 10^{-2}$		1.1
clinosorb	2.0	2.09	838	539	1.41	$5.44 \cdot 10^{-2}$		7.7
clinosorb	2.0	2.09	838	669	1.70	$3.12 \cdot 10^{-2}$	3.28	8.3
clinoptilolite	2.0	2.09	838	713	1.82	$2.16 \cdot 10^{-2}$	2.20	26.8

On this basis it could not be decided that from the solution the ammonium, hydrogen resp. chloride ions were adsorbed on the surface of the sorbent in such an extent which surpassed the ion exchange capacity. To study this problem two kinds of investigations were performed. On the one hand, activated clinosorb and clinoptilolite were taken into a solution of hydrochloric acid the concentration of which was nearly the same than that of the ammonium chloride used in the experiments

and then the conductivity of the hydrochloric acid solution was measured till the equilibrium reached. It can be seen from the data of Table 4 that the conductivity of the hydrochloric acid solutions taken in interaction with the sorbents has decreased. Consequently, ions originating from the solution were bound in the surface of the sorbents which relates to adsorption, since the sorbents contained the same number of cations as contra-ions and ion exchange could not be taken into account.

In the other type of investigations activated clinoptilolite was put into ammo-

TABLE 5
Ion exchange and adsorption of ammonium hydroxide on clinoptilolite in diluted solution

Activated sorbent	Solution concentration NH ₄ OH mmol/l		Specific sorbed NH ₄ ⁺ mmol/100 g	Concentration of the solution after flushing mmol/l	Flushed NH ₄ OH mmol	NH ₄ ⁺ remained on the sorbent after flushing, mmol/100 g sorbent	Flushed NH ₄ OH, mmol/100 g sorbent
	initial	equilibrium					
1	2	3	4	5	6	7	8
clinosorb	1.98	0.025	16.07				
clinoptilolite	1.98	0.02	15.84				
clinosorb	4.49	0.22	33.44	0.0858	6.8 · 10 ⁻³	32.76	0.68
clinosorb	6.07	1.54	36.43	0.3428	27.4 · 10 ⁻³	33.68	2.75

nium hydroxide solution of different concentration and the specific conductivity values of the equilibrium solutions were measured, further the change of ammonium ion concentration of these solutions was determined. The concentration of the most diluted ammonium hydroxide solution agreed with that of the ammonium chloride used in the experiments.

Data of Table 5 summing up the results of these experiments show that the greater was the concentration of the starting ammonium hydroxide the greater was the adsorbed ammonium quantity.

Separating the sorbents from the equilibrium solutions by decanting and flushing them twice in 5—5 ml distilled water, the sorbents were put into 80—80 ml ion-free distilled water and the conductivity of the solutions of equilibrium as well as the quantity of the ammonium ions getting the solution were measured. Regarding the fact that the water being in interaction with the sorbents did not contain contra-ion, only adsorbed ammonium could get the solution (in addition to the exchange capacity).

It is obvious from the data of the Table that independently of the concentration of the ammonium hydroxide solution, after flushing always the ammonium ion quantity corresponding to the ion exchange capacity remained and the ammonium quantity over the ion exchange capacity got the solution. The quantity of this, however, increased with the increasing starting concentration of the ammonium hydroxide solutions contacting the clinoptilolite.

On this basis it is expected that in the sorbents taken in interaction with solutions containing ammonium ions the ion exchange and adsorption may form simultaneously. The ratio of ion exchange and adsorption, however, is the function of the concentrations of the starting solutions. When these solutions contain contra-ions corresponding to only the ion exchange capacity, only the ion exchange should be taken into

account, since the energy of valence of this process is greater than the adsorption of the ion in question.

It is exactly demonstrated in Tables 4 and 5 that from the hydrochloric acid and ammonium hydroxide solutions of same concentration the measure of specific adsorption is also the same.

The mineralogical data of the clinoptilolite-bearing rock showed that in addition to clinoptilolite other accessory minerals are also present which do not possess ion exchange character but they are able to adsorb different ions. On this basis it is plausible that the measure of ion exchange is the function of clinoptilolite content, while adsorption depends on the quantitative ratio of the other accessories having sorption capacity. Thus, the applied electrochemical method may be suitable to characterize the surficial features, resp. zeolite content of the zeolite-bearing rocks having ion exchange possibilities.

SUMMARY

The mineralogical and sorption features of the clinoptilolite-bearing rocks of the Tokaj Mountains were investigated. On the basis of X-ray diffractometric, infrared spectroscopic and chemical analyses the qualitative and quantitative composition of the rock was determined, further the water content of the clinoptilolite was characterized. On the basis of electrochemical investigations (joint measurement of conductivity and potential) it was stated that the rock possesses ion exchange and adsorption features. The ion exchange capacity proved to be 0.33 mval/g. The adsorption capacity is a function of the concentration of the solution being in interaction with the rock.

The applied electrochemical method seems to be suitable to characterize the surficial features, resp. zeolite content of the zeolitized pyroclastics of ion exchange capacity.

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