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Stability and Ion Exchangeability of Clinoptilolite

By

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With 12 Tables and 25 Text figures

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ABSTRACT: The similar theme related to various kinds of zeolites and clay minerals has so far often been dealt with by many investigators from the standpoint of industry or of pure science. Nevertheless, a considerable part of the data given previously as those of the ion exchangeability or absorbability for the zeolites have been not so much reliable in the severer sense because of ignoring the instability of their inner structure easily convertible with a slight variation of condition, chemical and/or physical treatments and duration of the reaction even though held at a slightly varied states whereas the most part of their frameworks or the skeletons of so-called channel structure constructed of several-membered rings are seemingly remained to have not been changed. In view of this, some experiments as to clinoptilolite easily obtainable at pure state have been carefully carried out and certain conlcusion expected on the basis of presumption has been reached to more or less satisfactory extent.

CONTENTS

I. INTRODUCTION

Recently plenty of the investigators in several fields have given attention to the zeolites produced authigenically in the sedimentaries, pyroclastics and altered volcanics as a sort of indicator for diagenetic process, low-grade metamorphism and so forth. Prior to various assumption connected with their genesis, however, the relationships among their modes of occurrence, geochemical and structural stability, cation exchange property combined with variation of physical characteristics and the like are in more detail to be considered and scrutinized in order to find out necessity for the reasonable conclusion to certain extent. In the light of these circumstances, the present works have been concerned with stability and cation exchangeability of clinoptilolite immersed in some media. It has so far been known that the mineral in question becomes less stable with decrease of *Si* : *Al* ratio in the frameworks. The related theme as to natrolite, analcite and stilbite treated in acid solution has been dealt with by KAPPEN and FISCHER (1929) and that for stilbite, heulandite and chabazite by HEY (1930), while that for laumontite and its relation to presence of calcium carbonate have been discoursed by ÔKI (1967). There have also been many works concerning the ion exchangeability of zeolites. That of mordenite (ptilolite) has been studied and regarded as a sort of molecular sieve by BARRER (1948) and by AMES (1964), whereas presence of the stacking faults in the structure of the same mineral as well as its structural resemblance to heulandite with an axis of 7.5Å in length have been proposed by MEIER (1960) because of being constructed of the five-membered rings of tetrahedra in each case and probably of an intimate relation in natural occurrence. Numerically, the cation exchange capacity for heulandite has been estimated about 330 meq/100g (BARRER, 1958), that for *Si*-rich clinoptilolite 1.7 meq/g and that for *Al*-rich one 2.0 meq/g (AMES, 1964). As for clinoptilolite with several pairs of cations such as alkalies and alkali earths, the reactions of cation exchange and the sieve-like character have been thermodynamically studied by AMES (1961. 1963 and 1964). The thermal stability of the same mineral subjected artificially to the exchange reaction of *Na* and *K* ions with *Ca* ions has been researched by MUMPTON (1960) and that of the framework structure of natural chabazite has been attributed to the effects of exchangeable cations by BARRER. The reliable data for the structural analysis of clinoptilolite are still remained to have not been given since its crystal is commonly of platy one with less than 2∼5 μ in size and very hard to be taken out at the state of ideally pure single crystal. Accordingly, those for the mineral in question have been represented by those for heulandite considered as a variety of the former though merely on the basis of the of powder diffraction data. The parameters of the unit cell of heulandite have already been given by WYCKOFF (1951), STRUNZ and TENNYSON (1960), and SMITH (1960), whilst all of its spacings have been assigned by SCHONER (1960), REGNIER (1960) and SUDÔ (1963). The data for infrared absorption of clinoptilolite has been attained by means of nonpolarized irradiation on the pulverized specimens by the present author (1967).

II. EXPERIMENTS

(1) Specimen

The specimens have been taken out from the altered products of rhyolitic tuff occurring in Shizuma-chô, Ôta City, Shimane Prefecture, being grouped into Type A derived from the altered volcanic glass, Type B filling the druses and the microscopically observable veinlets and Type C derived from alteration of plagioclase on the basis of classification proposed previously by UMEGAKI et al (1965).

Their X-ray diffraction patterns obtained at the room temperature clearly indicate those for clinoptilolite but admixing of a slight amount of "heulandite B" when heated, the related data being listed in the table 1, wherein assignment of the indices has been based on the Q values obtained through the repeated refinement referring to the data for the lattice constants of heulandite given by STRUNZ and TENNYSON (1956).

TABLE 1. X-RAY DIFFRACTION DATE FOR CLINOPTILOLITE.

$d_{obs.}$	$d_{calc.}$*	$I/I_0 \times 100$	(hkl)**	$d_{obs.}$	$d_{calc.}$*	$I/I_0 \times 100$	(hkl)**
9.01	8.980	100	(020)	3.424	3.423	8	(043)
7.905	7.953	14	(002)		3.410		(114)
6.765	6.887	2	(110)		3.409		$(20\bar{2})$
	6.748		$(10\bar{1})$	3.183	3.187	3	$(22\bar{2})$
6.645	6.653	11	(101)	3.123	3.134	12	(222)
5.994	5.954	3	(022)		3.118		$(23\bar{1})$
5.615	5.603	5	(031)	2.985	2.993	43	(060)
5.245	5.268	14	$(11\bar{2})$		2.986		(152)
5.118	5.148	12	(112)	2.978	2.977	35	(044)
4.664	4.669	19	(130)	2.737	2.741	14	$(16\bar{1})$
4.502	4.490	5	(040)		2.732		(161)
4.347	4.375	5	$(10\bar{3})$	2.687	2.682	5	(242)
3.973	3.976	72	(004)	2.534	2.542	7	(026)
3.910	3.910	54	(042)		2.533		(071)
3.749	3.751	4	$(14\bar{1})$	2.485	2.486	5	(400)
3.742	3.728	4	(141)	2.452	2.451	4	(163)
3.544	3.542	5	(211)	2.425	2.426	2	(170)
3.496	3.504	4	(051)				

* calculated from $a_0 = 7.46\text{Å}$ $b_0 = 17.96\text{Å}$ $c_0 = 15.91\text{Å}$ and $\beta = 91°26'$.

** deduced from the repeated refinement of Q-values.

TABLE 2. CHEMICAL ANALYSES AND VALUES CALCULATED WITH REFERENCE TO 72 OXYGENS OF CLINOPTILOLITE.

Chemical analyses		Values calculated with respect to 72 Oxygens	
Comp.	% in weight	Cation	Atomic ratio
SiO_2	62.10	Si	27.77
Al_2O_3	16.80	Al	8.52
Fe_2O_3	1.63	Fe^{3+}	0.54
MgO	0.33	Mg	0.22
CaO	4.15	Ca	2.00
Na_2O	1.27	Na	1.07
K_2O	0.33	K	0.22
$H_2O(+)$	11.43	$H_2O(+)$	17.13
$H_2O(-)$	1.51	$H_2O(-)$	2.24
total	99.54	Z	36.83
		R	3.51

$Z = Si + Al + Fe^{3+}$

$R = Mg + Ca + Na + K$

Chemical compositions evidently correspond to those of clinoptilolite, as are ascertainable from inspection of the table 2 showing the numbers of cations in relation to

72 oxygen atoms.

(2) Procedure

As one of the sensitive but indirect means for pursuing variation of the specimens active in various ways in certain kinds of electrolyte solution, the pH values of the media concerned have been measured through the potentiometric method in combination of the standard calomel electrode with the hydrogen gas electrode so as to avoid incovenience caused with use of the other sorts of electrode in spite of somewhat longer duration necessary for saturating the gas in the solution or reaching the stable state of the media. The velocity of gas passing through the solution was regulated by counting the numbers of bubbles per second.

For tracing the stability of the specimen, each 0.5 g of the pulverized sample has been immersed for 48 hrs. in 100 ml of HCl with normality of 0.1, 0.05, 0.01, 0.001 and 0.0001 as well as with 6.23 in pH and for 144 hrs. in the same volume of $NaOH$ solution with 8.02, 9.01, 10.02, 11.13, 12.13 and 13.07 in pH respectively, when the temperature has been held constant at 25°C in each case. In the special case treated with 0.001 N and 0.0001 N HCl, variations of the reaction of 1.5 g in 500 ml of the acid have been chased respectively for 2, 4, 8, 12, 24, 36, 48, 72, 96, 120 and 144 hrs.

The cations dissolved into the acid have been gravimetrically analysed after filtering of the solution from the precipitate and estimated as a sort of solubility expressed in % of their ratio to those contained in the non-treated specimens.

Ion exchangeability and stability of the natural specimens have been examined in $NaCl$, KCl and $CaCl_2$ solutions prepared from the highest-class chemicals dissolved in the distilled water without any trace of carbon dioxide. As for the cations extracted from the specimens, the quantities of Ca and Al ions have been ordinarily determined in the cases of treatment with $NaCl$ and KCl and KCl and those of Na, K and Al ions in the case treated with $CaCl_2$ after filtration of the precipitate from the solution, in which the specimens were dispersed and suspended. At the same time, the pH values of $NaCl$ solution after dispersing the pulverised specimens were traced continuously for 24 hrs. while those of KCl and $CaCl_2$ solution were measured after suspension for 24 hrs.

The specimens subjected to the chemical treatments mentioned above and their variations in structure were futhermore inspected by means of the röntgenographic and infrared spectroscopy. The X-ray diffraction patterns were obtained with ordinary scanning speed of 1°/min. as well as 0.25°/min. in 2θ for discovering a slight variation particularly concerning the spacings of (020), $(11\bar{2})$, (112), (130), (040) and (042) because of their remarkable intensity and stability. The infrared absorption bands for water at 2.78, 2.94 and 6.3 μ were examined with nujol and those for Si-O-Al within the range of 7~25 μ with KBr tablet.

III. RESULTS

Each 0.5 g of the pulverized specimen of clinoptilolite immersed in 100 ml of the distilled water (pH=6.85) reveal the gradual increase in the value for abrasion pH to 7.93 after 168 hrs. and then the decrease to 7.52, as are marked in the figure 1 and the table 3.

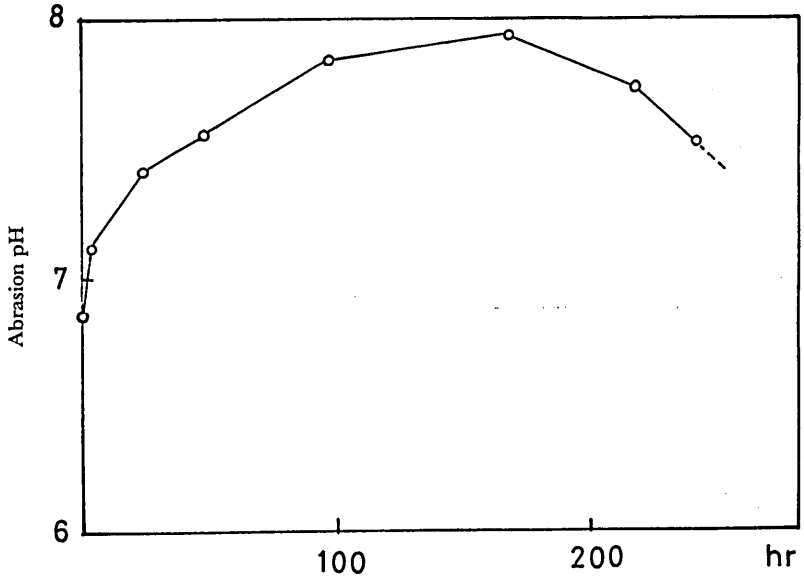


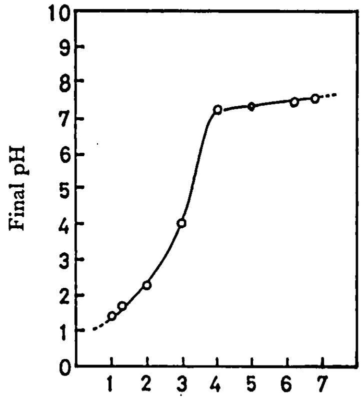
FIG. 1 Variation of abrasion pH of clinoptilolite with dulation.

TABLE 3. VARIATION OF ABRASION pH OF CLINOPTILOLITE IMMERSED IN DISTILLED WATER WITH pH 6.85 AT 25°C.

Hour	2	24	48	96	168	216	240
pH	7.11	7.40	7.54	7.83	7.93	7.73	7.52

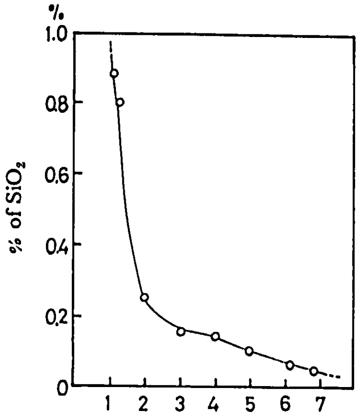
The relations of stability in the cases of treatment with various concentration of acid are shown in the figure 2 and the table 4. Difference of the pH value at the initial state from that after the reaction is conspicuous in the figure 2a, wherein 6.83 in the distilled water varies to 7.54 and variations to alkaline state, e. g. 6.23 to 7.44, 5.01 to 7.30, and 4.01 to 7.27 in pH value with use of acid are to be noted excepting the special case showing variation of 3.01 to 3.94. The insoluble residue, obtained through filtration of the precipitate from solution after the reaction and the repeated drying-up of the filtrate, is considered to be composed of SiO_2, though possible to comprise a slight amount of the colloidal part of the specimen, and its ratios to all amount of SiO_2 consisting the raw material are expressed by % in weight, the relation being illustrated in the figure 2b. It is distinct that the quantity of the residue, extracted through the above treatment and regarded as SiO_2, rapidly increases with acidity though really in a little amount such as 0.15 % for pH variation of 3.01 to 3.98 and 0.88 % for that of 1.07 to 1.47. As are clear in the figure 2C, the contents of *Al* in the residue amount to 0.50 % for pH variation of 3.01 to 3.98, to 5.06 % for that of 2.02 to 2.29 and to 29.04 % for that of 1.07 to 1.47. As are observable in the figures 2d, 2e and 2f, the quantities of *Ca*, *K* and *Na* ions dissolved in the distilled water are respectively estimated 1.64 %, 4.04 % and 15.01 %, those in the water with variation of 4.01 to 7.27 in pH value 8.19 %, 30.30 % and 39.37 % and those in the water with 1.07 in pH 45.54 %, 86.84 % and 87.82 %, while in the water with less than 3.01 in pH the rapid increase is recognized in the quantity of *Ca* ion but the gradual one in those of *K* and *Na* ions.

The relations of stability in the solution of various pH values regulated with *NaOH* are presented in the figure 3 and the table 5. Inspection of the figure 3a indicates that 6.84 in pH value shown in the distilled water containing the definite amount of



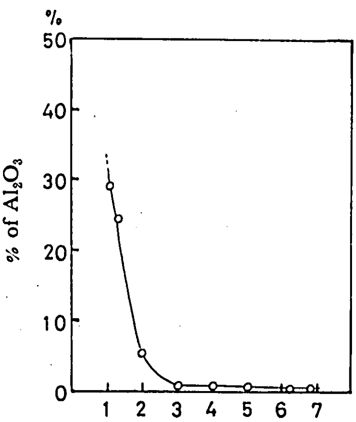
Initial pH of medium

FIG. 2a Variation of pH after reaction of clinoptilolite with HCl.



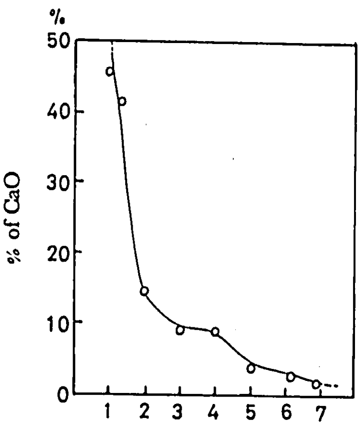
Initial pH of medium (HCl)

FIG. 2b Extracted amount of SiO_2 from clinoptilolite with variation of pH.



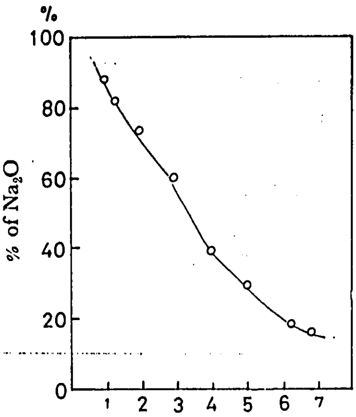
Initial pH of medium (HCl)

FIG. 2c Extracted amount of Al_2O_3 from clinoptilolite with variation of pH.



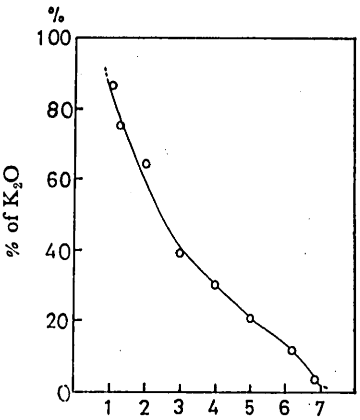
Initial pH of medium (HCl)

FIG. 2d Extracted amount of CaO from clinoptilolite with variation of pH.



Initial pH of medium (HCl)

FIG. 2e Extracted amount of Na_2O from clinoptilolite with variation of pH.



Initial pH of medium (HCl)

FIG. 2f Extracted amount of K_2O from clinoptilolite with variation of pH.

TABLE 4. STABILITY OF CLINOPTILOLITE IMMERSED IN ACID SOLUTION FOR 48 HRS. AT 25°C.

No.	Initial pH with HCl	Final pH	% of compositions dissolved.				
			SiO_2	Al_1O_3	CaO	Na_2O	K_2O
1	1.07	1.47	0.88	29.04	45.54	87.82	86.84
2	1.29	1.69	0.80	24.64	40.48	82.14	75.75
3	2.02	2.29	0.25	5.06	14.69	74.02	64.64
4	3.01	3.98	0.15	0.50	8.39	59.93	39.39
5	4.01	7.27	0.14	0.23	8.19	39.37	30.30
6	5.01	7.30	0.10	0.26	3.61	29.31	21.21
7	6.23	7.44	0.06	0.20	2.52	18.64	12.12
8	6.83	7.54	0.04	0.21	1.64	15.01	4.04

the specimen is convertible to 7.85 after immersion for 144 hrs., whereas the pH values given with addition of *NaOH* are generally decreased: e. g. 8.02 to 7.24, 9.01 to 7.26, 10.02 to 7.50, 11.13 to 8.25, 12.12 to 11.65 and 13.07 to 12.79. The figure 3b suggests the solubility of SiO_2 to be 0.02∼0.03 % with variation of 10.02 to 7.50 in pH value, 0.42 % with that of 11.13 to 8.25 and 4.04 % with that of 13.07 to 12.79. The figure 3c shows that of *Al* ion to be less than that in the case with acid treatment but, on the contrary, to increase with alkalinity, e. g. 1.79 % with variation of 12.12 to 11.65 in pH value. The figures 3d and 3e clarify either the gradual decrease of solubility of *Ca* ion with pH variation of 8.02 to 7.24 and of 9.01 to 7.26 together with its remarkable increase (2.89 % in maximum amount) with that of 11.13 to 8.25 or the similar tendency in the case of *K* ion (33.99 % in maximum amount)

Behaviors of the specimen dispersed in the water bearing pH value of 3∼4 for many hours have been scrutinized, the experimental data being given in the figures 4 and 5 and the tables 6 and 7. The figure 4a reveals that pH values of the solution, in which the specimens are dispersed, increase from 4.02 at the initial state to 5.32 for 2 hrs. and to 7.22 for 48 hrs. but then begin to diminish and become constant at 6.9 after reaction for 72 hrs. The figure 4b displays such behavior of *Al* ions that begins to dissolve after 36 hrs., reaches a maximum solubility (1.09 %) after 72 hrs. and then becomes constant in the range of somewhat lower amount. The figures 4c, 4d and 4e illustrate that *Ca*, *Na* and *K* ions begin to be soluble just after dispersion of the specimen in the water held at the same state, reach the maximum quantities such as

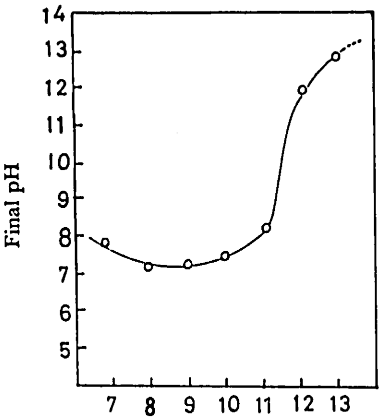


FIG. 3a Variation of pH after reaction of clinoptilolite with NaOH.

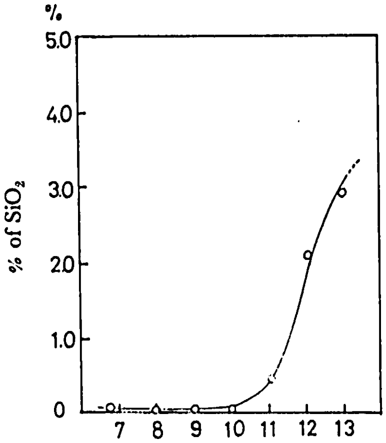


FIG. 3b Extracted amount of SiO_2 from clinoptilolite with variation of pH.

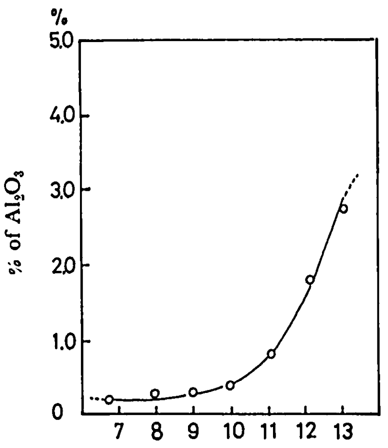


FIG. 3c Extracted amount of Al_2O_3 from clinoptilolite with variation of pH.

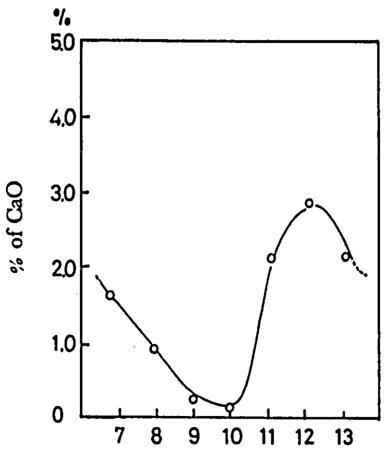


FIG. 3d Extracted amount of CaO from clinoptilolite with variation of pH.

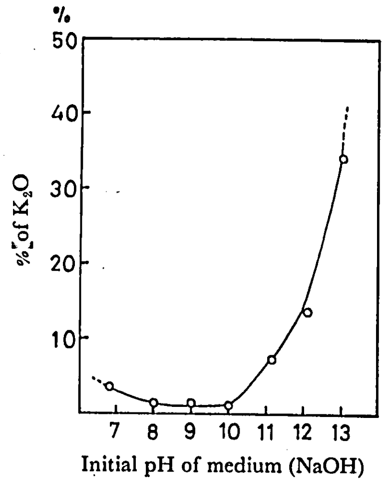


FIG. 3e Extracted amount of K_2O from clinoptilolite with variation of pH.

TABLE 5. STABILITY OF CLINOPTILOLITE IMMERSED IN ALKALINE SOLUTION FOR 144 HRS. AT 25°C

No.	Initial pH with NaOH	Final pH	% of compositions dissolved			
			SiO_2	Al_2O_3	CaO	K_2O
1	6.84	7.85	0.08	0.21	1.65	3.61
2	8.02	7.24	0.03	0.28	0.96	1.43
3	9.01	7.26	0.02	0.30	0.24	1.30
4	10.02	7.50	0.02	0.38	0.12	1.30
5	11.13	8.25	0.42	0.77	2.16	7.27
6	12.12	11.65	2.08	1.79	2.89	13.39
7	13.07	12.79	4.04	2.74	2.16	33.99

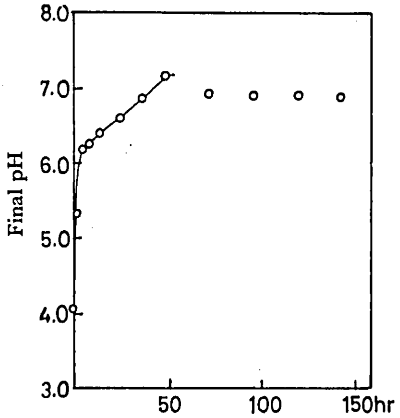


FIG. 4a Variation of pH with duration.

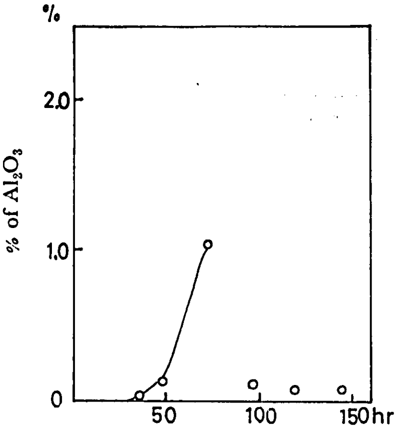


FIG. 4b Extracted amount of Al_2O_3 from clinoptilolite with duration.

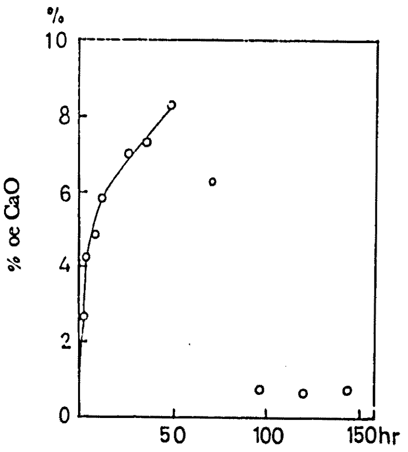


FIG. 4c Extracted amount of CaO from clinoptilolite with duration.

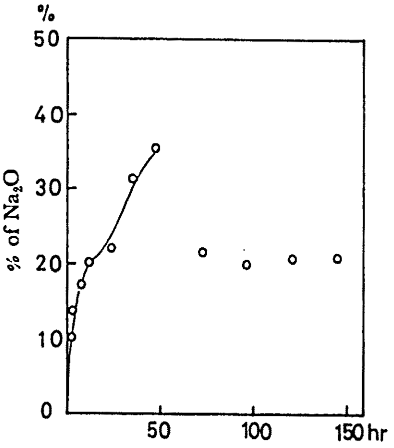


FIG. 4d Extracted amount of Na_2O from clinoptilolite with duration.

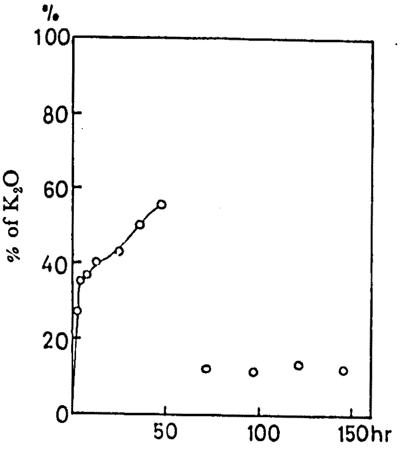


FIG. 4c Extracted amount of K_2O from clinoptilolite with duration.

TABLE 6. EFFECT OF DURATION OF WASHING WITH 0.0001N HCl AT 25°C.

No.	Hour	pH	% of compositions dissolved			
			Al_2O_3	CaO	Na_2O	K_2O
1	2	5.32	—	2.65	10.49	20.27
2	4	6.20	—	4.25	13.64	35.35
3	8	6.25	—	4.81	17.00	37.37
4	12	6.40	—	5.78	19.94	40.40
5	24	6.62	—	6.98	22.04	43.43
6	36	6.86	0.08	7.30	31.23	50.50
7	48	7.22	0.24	8.27	35.43	56.56
8	72	6.94	1.09	6.24	21.52	12.12
9	96	6.91	0.20	0.72	20.47	11.11
10	120	6.90	0.16	0.64	20.04	13.13
11	144	6.87	0.16	0.72	20.73	12.12

Initial pH: 4.01
Amount of sample in solution: 1.5g/500ml

8.27 %, 35.43 % and 56.56 % respectively and then the equilibrium with solubility of 0.7 %, 20 % and 13∼15 %. The figure 5a discloses variation from the pH value of 3.01 at the initial state of the water suspending the specimens to 3.38 after 2 hrs., to that of 3.98 after 48 hrs. and furthermore its gradual increment. The figure 5b reveals the quantity of *Al* ion with the maximum of 1.94 % at pH of 3.67 after 12 hrs. and its decrement to 0.3 % at the equilibrium state with variation of the pH value to 3.98. The figure 5c shows the behavior of *Ca* ion resembling that of the former. The figure 5d is related to those of *Na* and *K* ions similar to those of *Al* and *Ca* ions for 12 hrs. but different with regard to increase of the quantity from the latters revealing the reverse relationship. The figure 5e is concerned with the gradual solubility of *K* ion into the water in the course of time.

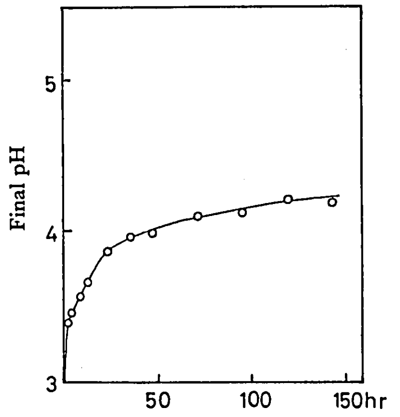


Fig. 5a Variation of pH with duration.

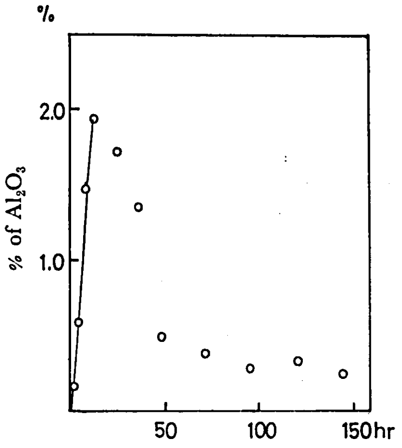


Fig. 5b Extracted amount of Al_2O_3 from clinoptilolite with duration.

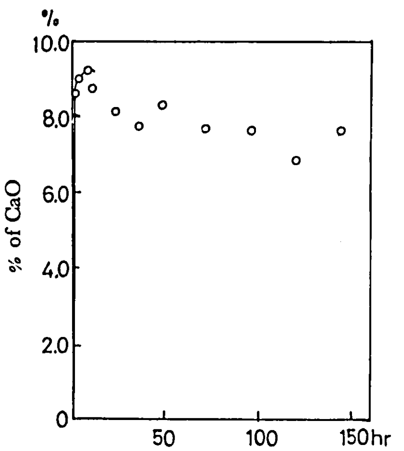


Fig. 5c Extracted amount of CaO from clinoptilolite with duration.

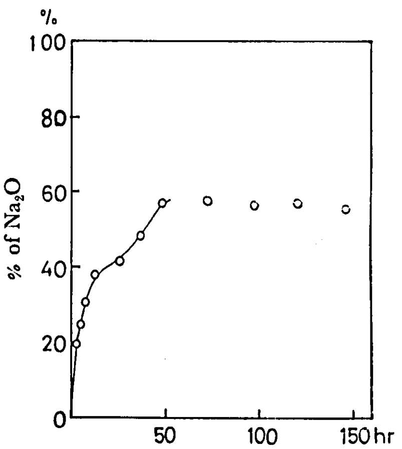


Fig. 5d Extracted amount of Na_2O from clinoptilolite with duration.

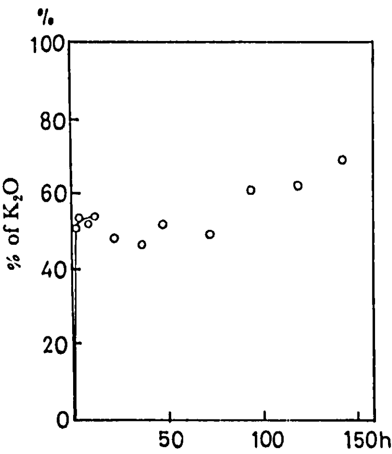


FIG. 5c Extracted amount of K_2O from clinoptilolite with duration.

TABLE 7. EFFECT OF WASHING WITH 0.001N HCl AT 25°C.

No.	Hour	pH	% of compositions dissolved			
			Al_2O_3	CaO	Na_2O	K_2O
1	2	3.38	0.16	8.67	19.68	51.51
2	4	3.45	0.59	9.08	25.19	54.54
3	8	3.57	1.47	9.24	30.97	52.52
4	12	3.67	1.94	8.83	38.06	53.53
5	24	3.86	1.71	8.11	41.47	48.48
6	36	3.95	1.35	7.71	48.55	46.46
7	48	3.98	0.49	8.27	57.22	51.51
8	72	4.10	0.39	7.71	57.74	48.48
9	96	4.11	0.28	7.63	56.95	60.60
10	120	4.20	0.33	6.83	57.48	61.61
11	144	4.18	0.22	7.68	56.69	68.68

Initial pH: 3.01
Amount of sample in solution: 1.5g/500m*l*

The experiments of tracing variation of the pH values in various concentration of *NaCl* solution immersing the specimens in the cases of no treatments and of being washed for 24 hrs. in *HCl* (pH=4) have been continuously put into operation for 24 hrs., the data obtained being plotted in the figures 6a and 6b. The pH values for the non-treated specimen show such variations as 6.63 to 5.74 in 0.001N salt solution, as 6.65 to 5.41 in 0.05N (0.046N),* and as 6.66 to 5.14 in 0.01N (0.009N) respectively after 2 hrs., and 6.63 to 5.27, 6.65 to 5.08 and 6.66 to 4.95 in each case of normality

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* The values of normality embraced in the parenthesis are those recalculated under consideration of the ionization ratio or the real activity and shown similarly in all of the following cases.

mentioned above after 24 hrs. The fact is that the increase of normality to 0.05N (0.041N) and to 0.1N (0.079N) far more easierly results in the equilibrium of the state for less time and that to 0.5N (0.34N) as well as to 1.0N (0.66N) are able to reach the pH values higher than those discerned in the former cases at the earlier stage of the reaction, then the values of the same order after 4 hrs. and at last the lower values. In the case of the specimens subjected to washing for removing the absorbed ions, the pH variation appearing in the solutions indicate the wider range though with the tendency resembling those in the non-treated case, as are recognizable in the figure 6b. Those shown in different kinds, and various concentration, of the electrolyte solutions dispersing the non-treated specimens are yielded in the figure 7. The figure makes it evident that the equilibrated states are temporarily attainable with 0.05N (0.032N) of $CaCl_2$ solution but take place in the lower pH values in the case of 1.0N (0.52N), and the similar states are discernible with 0.5N of (0.32N) *KCl* solution but not obtained with 1.0N (0.66N) of *NaCl* solution. The lowest limits of the pH values observed in the cases of the experiments with $CaCl_2$, *KCl* and *NaCl* solutions are estimated respectively 5.29, 4.77 and 4.50.

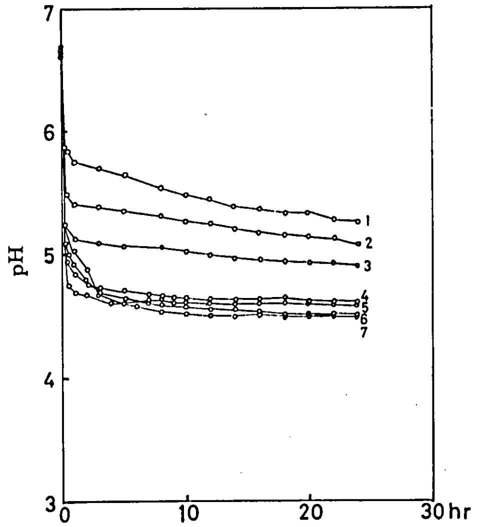

FIG. 6a Variation of pH during cation-exchange reaction of non-treated clinoptilolite in NaCl solution of different concentration.

1: 0.001N 5: 0.1N
2: 0.005N 6: 0.5N
3: 0.01N 7: 1.0N
4: 0.05N

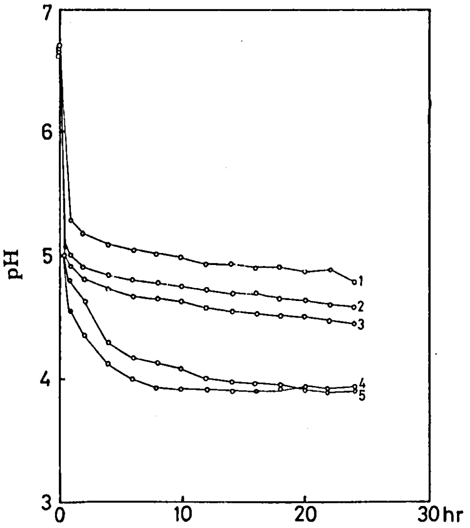

FIG. 6b Variation of pH during cation-exchange reaction of washed clinoptilolite in NaCl solution of different concentration.

1: 0.001N 4: 0.05N
2: 0.005N 5: 0.1N
3: 0.01N

Stability and ion exchangeability of the specimens in *NaCl*, *KCl* and $CaCl_2$ solutions with various concentration are scrutinized in the following. It seems general in all cases that the quantities of cations extracted through exchange increase in certain

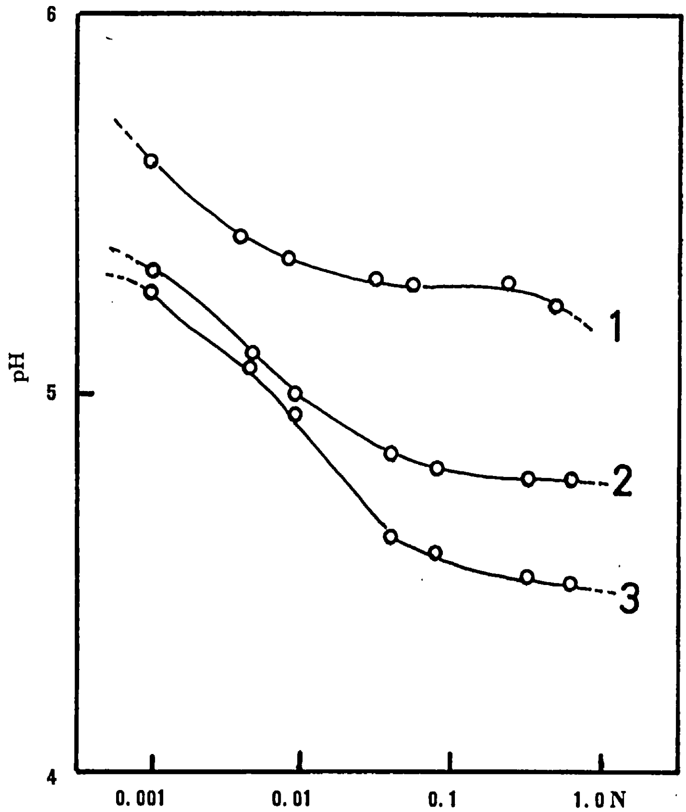

FIG. 7 Variation of pH in some electrolite dispersing clinoptilolite for 24 hrs.

1: $CaCl_2$ 2: KCl 3: NaCl

proportion to concentration of the electrolyte solution. The figure 8 and the table 8 indicate that the extracted amount of *Ca* ion is estimated 1.10 % in 0.001 N *NaCl* solution and increases almost linearly within the normality of 0.05 N (0.041 N) but above 0.1 N (0.079 N) rapidly to 7.42 % and in 1.0 N (0.66 N) to 12.30 % while the solubility of *Al* ion is recognized to increase above 0.1 N (0.079 N). The figure 9 and the table 9 are related to the extracted quantities of the same ions in *KCl* solution, revealing the relation similar to that appearing in the above case: that is, the quantities of *Ca* ions in the solution increase linearly from 1.80 % to 6.97 % with variation of normality from 0.001 N to 0.05 N but rapidly from 9.88 % to 16.14 % within the range of 0.1 N to 1.0 N, while those of *Al* ion are 1.85 % in 0.1 N and 3.95 % in 1.0 N, being a little less than those in the former case. The figure 10 and the table 10 are annexed to the similar relations of *Na*, *K* and *Al* ions dissolved in $CaCl_2$ solution. It is obvious that the amounts of *Na* ion increase from 16.01 % to 30.01 %, and those of *K* ion from 6.06 % to 26.45 % within the range of 0.001 N to 0.05 N, the quantity

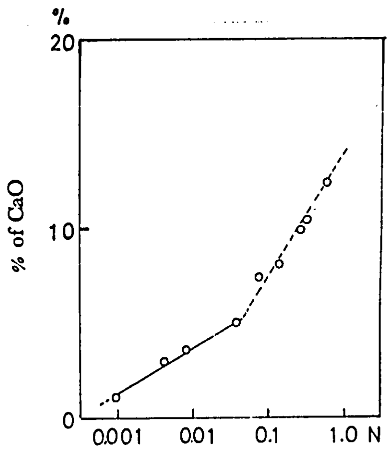

FIG. 8a Exchanged and dissolved amount of CaO from clinoptilolite with concentration of NaCl solution.

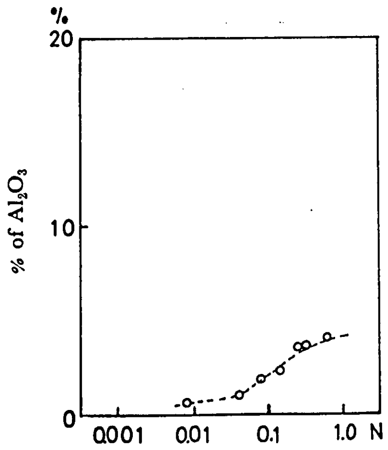

FIG. 8b Dissolved amount of Al_2O_3 from clinoptilolite with concentration of NaCl solution.

TABLE 8. EFFECT OF CONCENTRATION OF NaCl SOLUTION ON CATION EXCHANGEABILITY AND STABILITY OF CLINOPTILOLITE FOR 24 HRS. AT 25°C.

No.	Normality	Corrected normality	% of compoisitions dissolved	
			Al_2O_3	CaO
1	0.001	—	—	1.10
2	0.005	0.0047	—	3.02
3	0.01	0.0090	0.54	3.51
4	0.05	0.042	1.12	4.90
5	0.1	0.079	1.70	7.42
6	0.2	0.15	2.95	8.09
7	0.4	0.28	3.51	9.93
8	0.5	0.34	4.00	10.35
9	1.0	0.66	4.15	12.30

Amount of sample in solution: 1 g/200 m*l* (same as in the following cases)
Corrected normality (used similarly in the following): N(normality) × f(activity coefficient)

of the former reaches the equilibrated value (33 %) equal to that of the latter in 0.1 N but the latter furthermore increases to 35 % in 1.0 N, while the solubility of *Al* reveals the abrupt increase above 0.05 N (0.041 N) in the cases of *NaCl* and *KCl* as well as above 0.05 N (0.032 N) in the case of $CaCl_2$. It is inferable from the phenomena described in the preceding that *Ca* ions dissolved in *NaCl* and *KCl* solutions together with *Na* and *K* ions present in $CaCl_2$ solution are ascribable not only to their exchangeability but also to a part of decomposition of the specimens. It is here to be noted that the amounts of the ions extracted are in general likely to show increment with increase of concentration of the solution provided for the experiments but those per

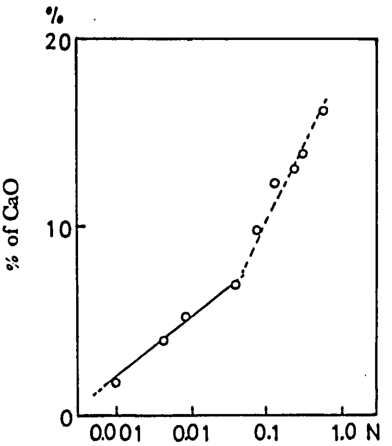

FIG. 9a Exhanged and dissolved amount of CaO from clinoptilolite with con. centration of KCl solution.

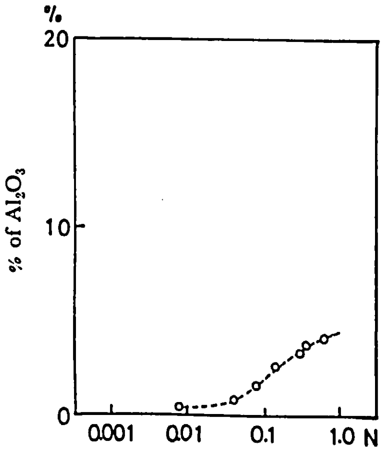

FIG. 9b Dissolved amount of Al_2O_3 from clinoptilolite with concentration of KCl solution.

TABLE 9. EFFECT OF CONCENTRATION OF KCl SOLUTION ON CATION EXCHANGEABILITY AND STABILITY OF CLINOPTILOLITE FOR 24 HRS. AT 25°C.

No.	Normality	Corrected normality	% of compositions dissolved	
			Al_2O_3	CaO
1	0.001	—	—	1.80
2	0.005	0.0047	—	4.09
3	0.10	0.0090	0.68	5.30
4	0.05	0.041	1.05	6.97
5	0.1	0.076	1.85	9.88
6	0.2	0.14	2.40	12.40
7	0.4	0.26	3.71	13.05
8	0.5	0.32	3.72	13.91
9	1.0	0.60	3.95	16.14

equivalent indicate rather less values because of decrease of the ionization ratio with increase of normality.

Variations in the inner structure of the specimens subjected to some chemical treatments have been röntgenographically examined. X-ray diffraction pattern for the spacing (020) of the specimen treated with acid for 48 hrs. is shown in the figure 11 obtained with the scanning speed of 0.25° per min., from which the value of the half width and the respective maxima appearing in a single peak have been read in order to clarify the grade of heterogeneity of the specimens in question statistically. The values of 2θ and of d for (020), $(11\bar{2})$, (112), (130), (004) and (042) concerning the specimens treated with various procedures are presented in the figures from 12 to 18. Variations in the intensity of (020) and (004) are given in the figures 19 (from a to g).

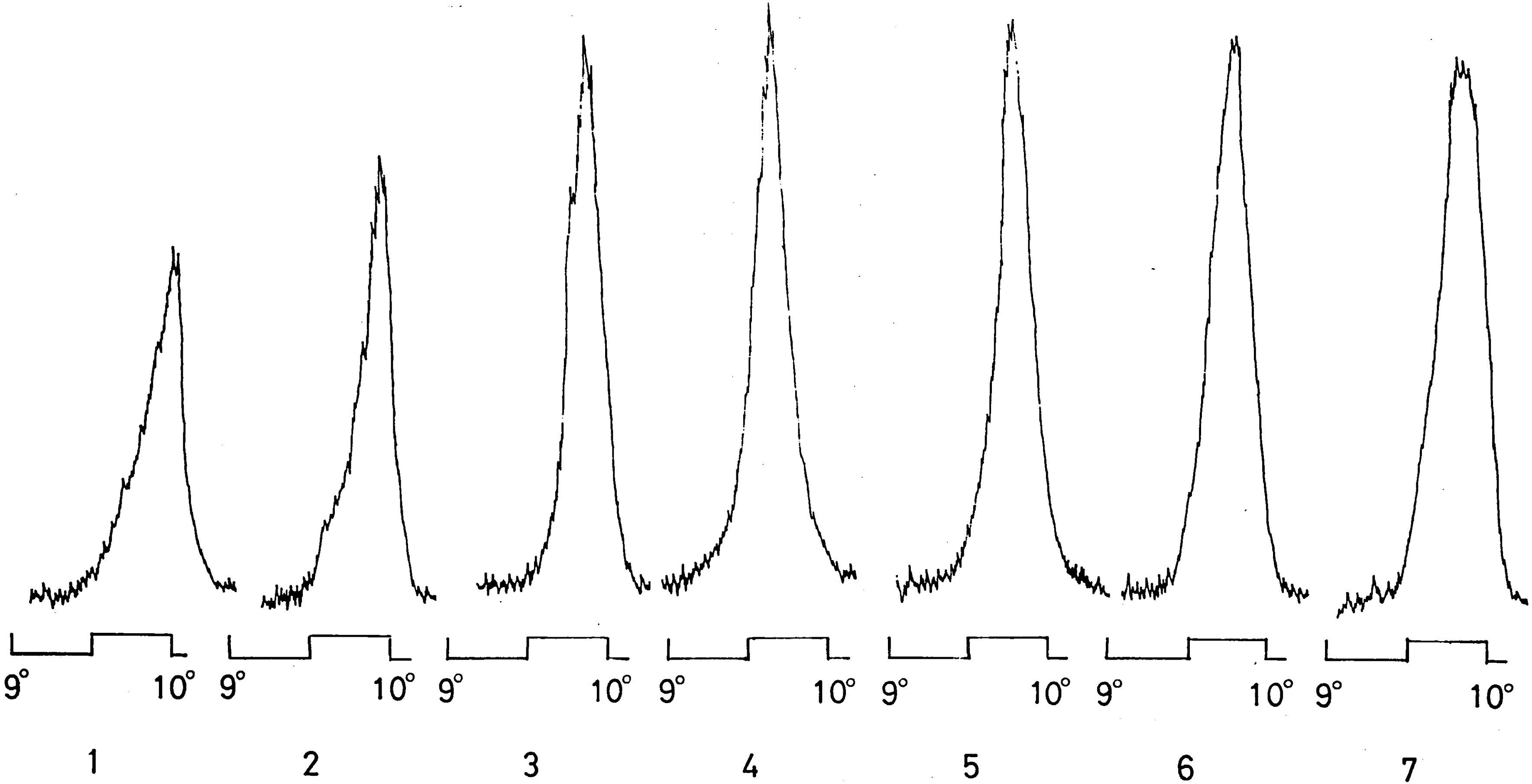

FIG. 11 Variation in X ray diffraction patterns of (020) spacing of clinoptilolite treated with various concentration of HCl solution and distilled water.

1: 0.1N 2: 0.01N 3: 0.001N 4: 0.0001N 5: HCl solution (pH 5)
6: HCl solution (pH 6.2) 7: distilled water (pH 6.85)

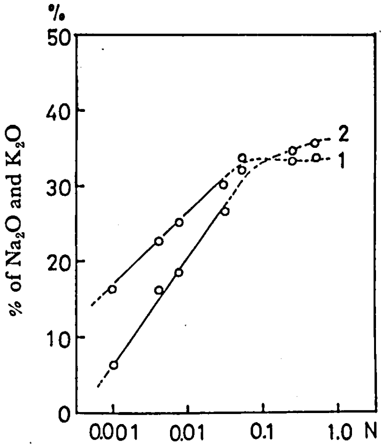

FIG. 10a Dissolved amount of Na_2O and K_2O from clinoptilolite with concentration of $CaCl_2$.
1: Na_2O 2: K_2O

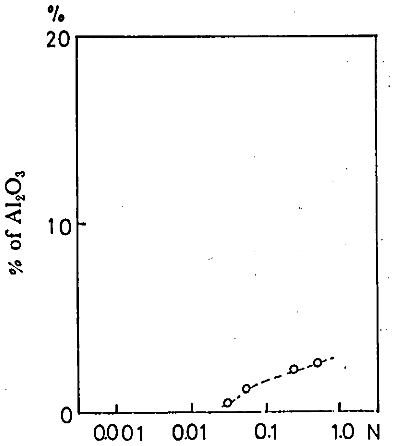

FIG. 10b Dissolved amount of Al_2O_3 from clinoptilolite with concentration of $CaCl_2$.

TABLE 10. EFFECT OF CONCENTRATION OF $CaCl_2$ SOLUTION ON CATION EXCHANGEABILITY AND STABILITY OF CLINOPTILOLITE FOR 24 HRS. AT 25°C.

No.	Normality	Corrected normality	% of compositions dissolved		
			Al_2O_3	Na_2O	K_2O
1	0.001	—	—	16.01	6.06
2	0.005	0.0042	—	22.59	16.36
3	0.01	0.0079	—	25.43	18.78
4	0.05	0.0032	0.62	30.01	26.45
5	0.1	0.057	1.17	33.78	32.42
6	0.5	0.25	2.40	32.95	34.06
7	1.0	0.52	2.59	33.98	35.08

Comparison of the data obtained for the specimens in pure water and in the acid solutions with various concentration with one another suggests contraction of the unit cell with increase of acidity in various ways. In the cases of treatment with the alkaline solutions somewhat complicated variations are observable, as are deduced from the figure 13, exhibiting that the spacings (020) and (130) indicate the shift to contraction in the solutions with pH less than 12 and then that to expansion in the solutions with higher pH values, and contraction of the spacing (004) and $(11\bar{2})$ in association with expansion of (112) are more noticeable with increase of the pH values, resulting in decrease of difference between $Q_{11\bar{2}}$ and Q_{112}, i. e. decrease of β in angle. Remarkable is that intensity of the spacing (020) is strengthened in the solutions with pH less than 12 but abruptly weakened in the solutions with higher pH values, as are clear in the figure 19b. The effects of duration are to be noted since the variations of the spacings

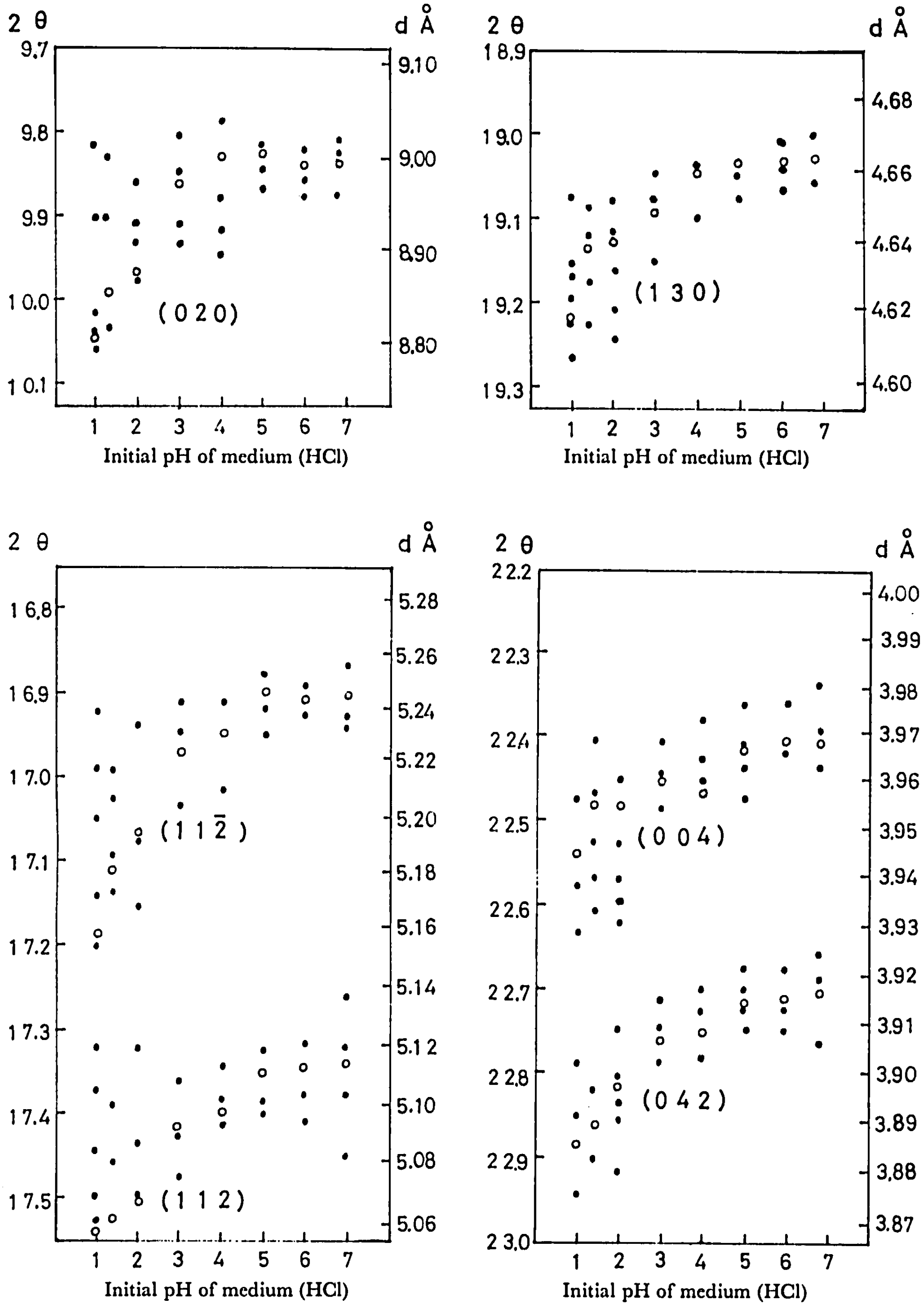

FIG. 12 Variation of 2θ and d of clinoptilolite treated with acid solution.

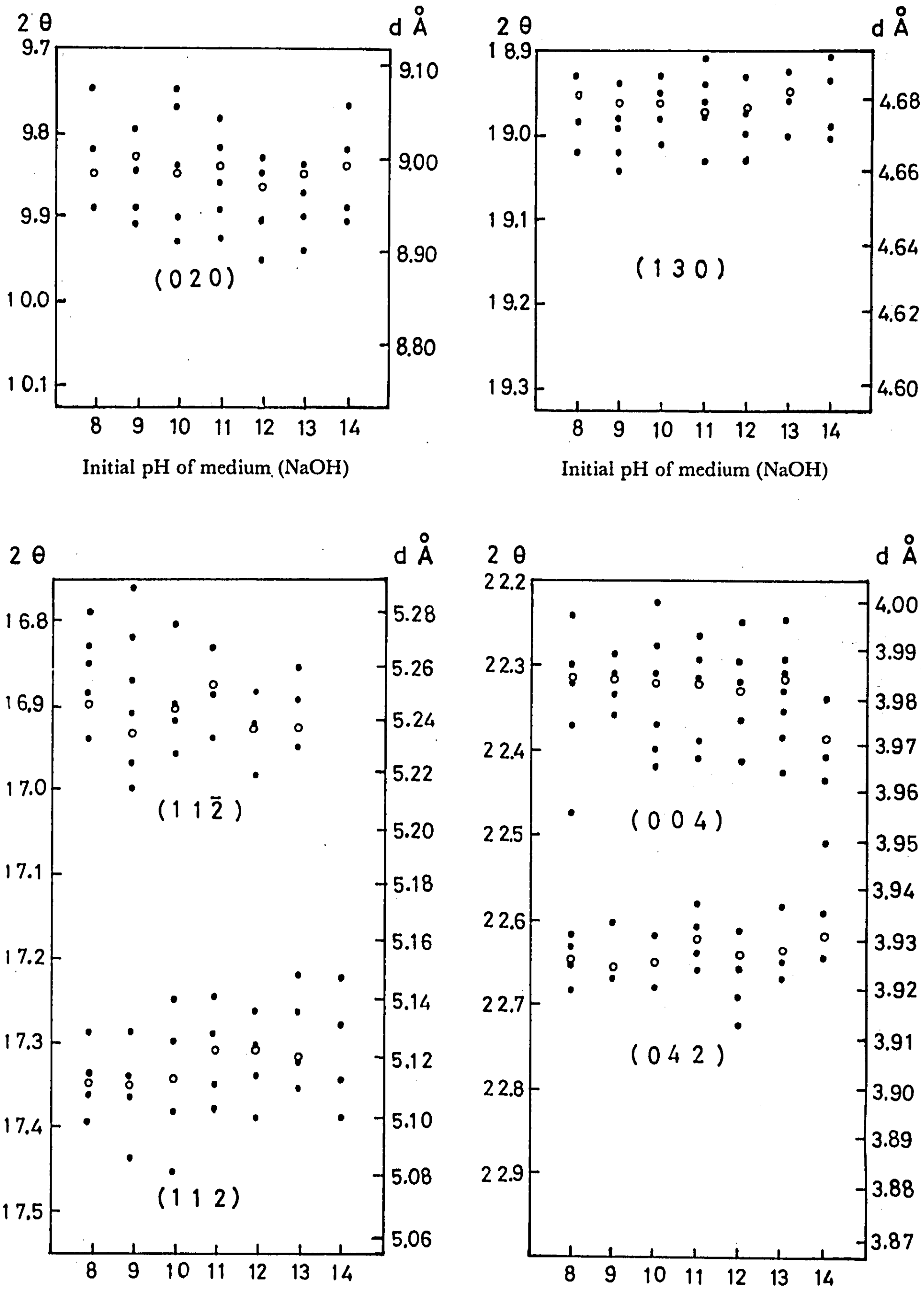

FIG. 13 Variation of 2θ and d of clinoptilolite treated with alkali solution.

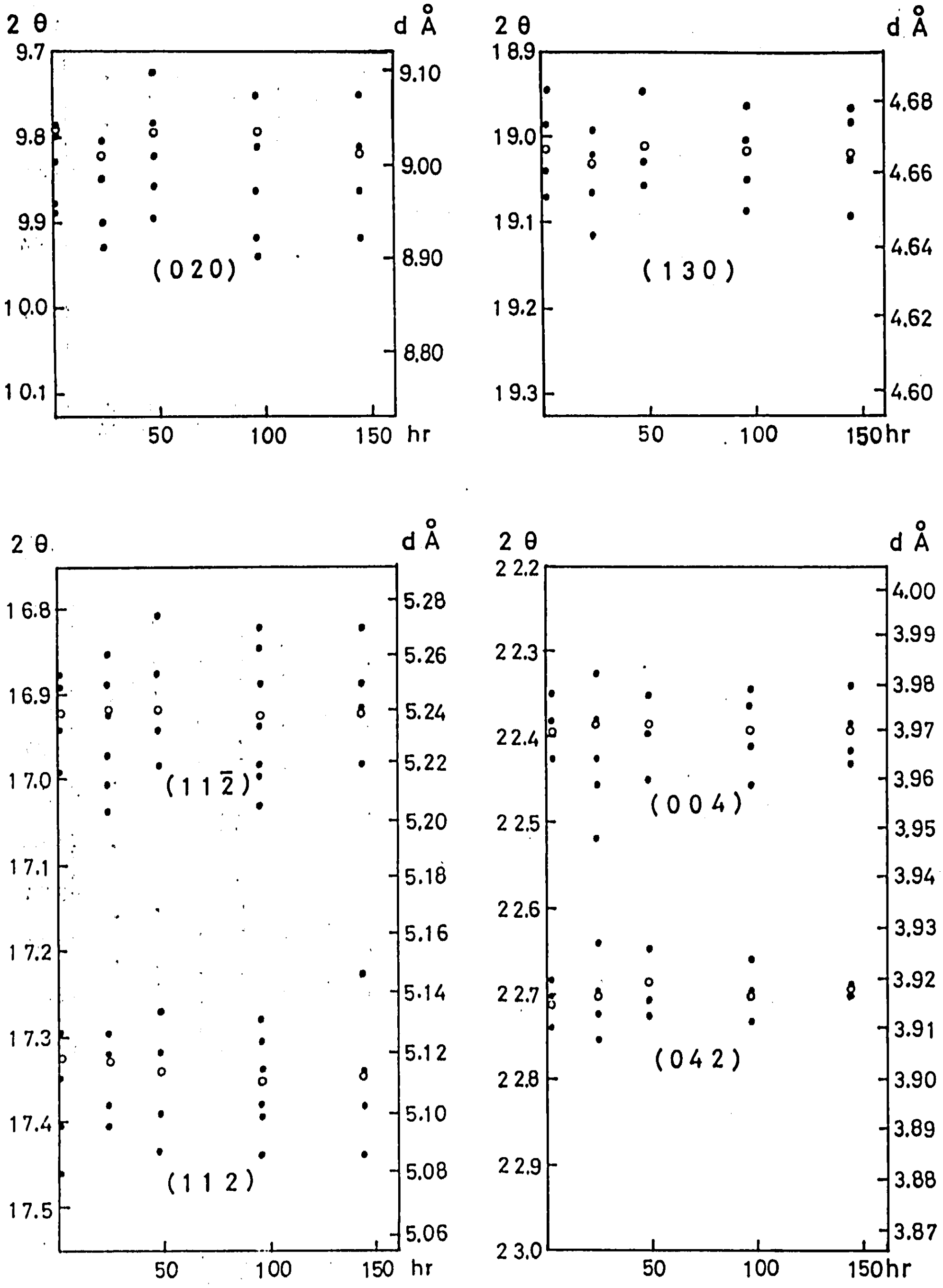

FIG. 14 Variation of 2θ and d of clinoptilolite treated with 0.0001 N HCl solution in relation to duration.

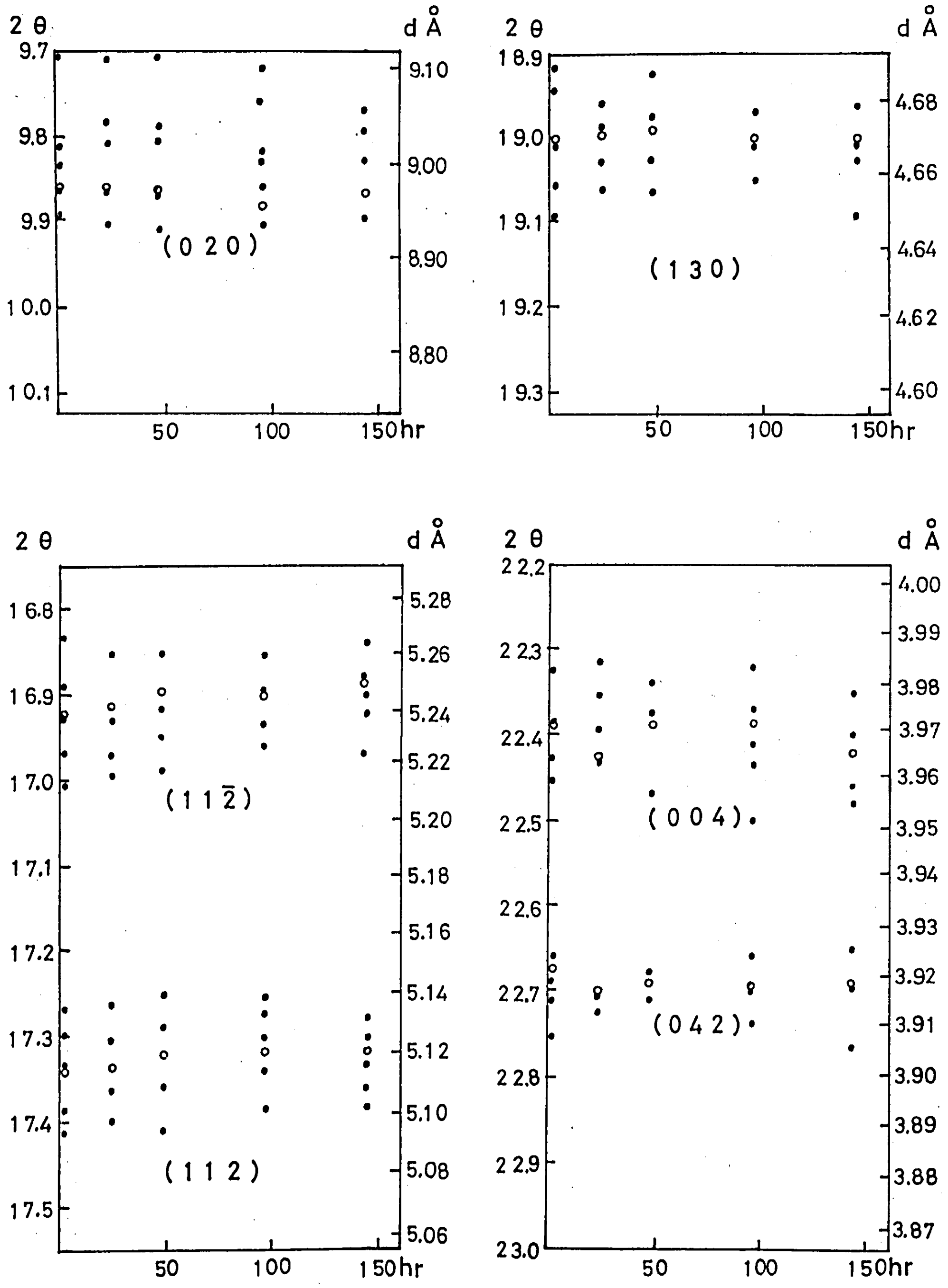

FIG. 15 Variation of 2θ and d of clinoptilolite treated with 0.001 N HCl solution in relation to duration.

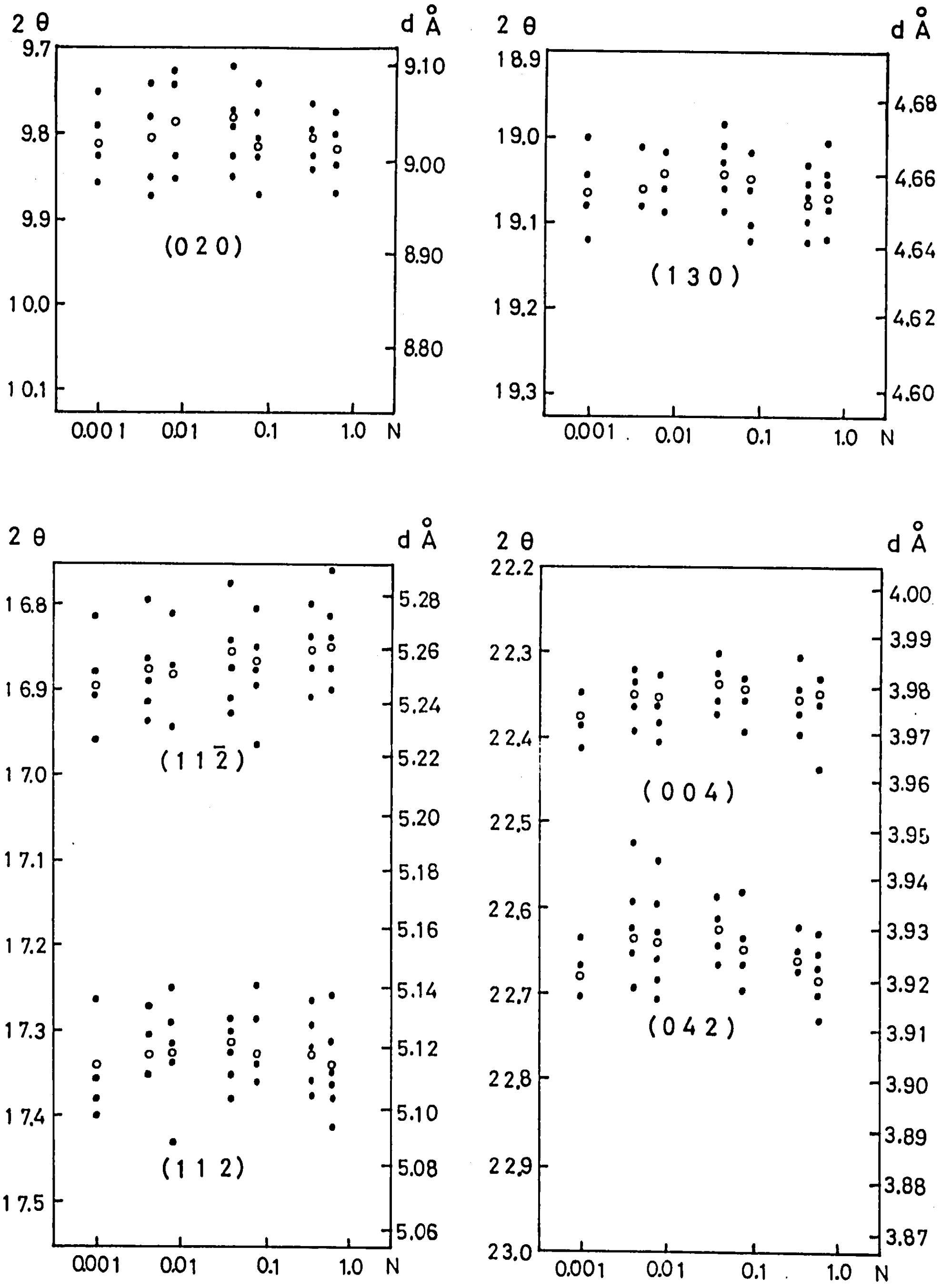

FIG. 16 Variation of 2θ and d of clinoptilolite in various concentration of NaCl solution.

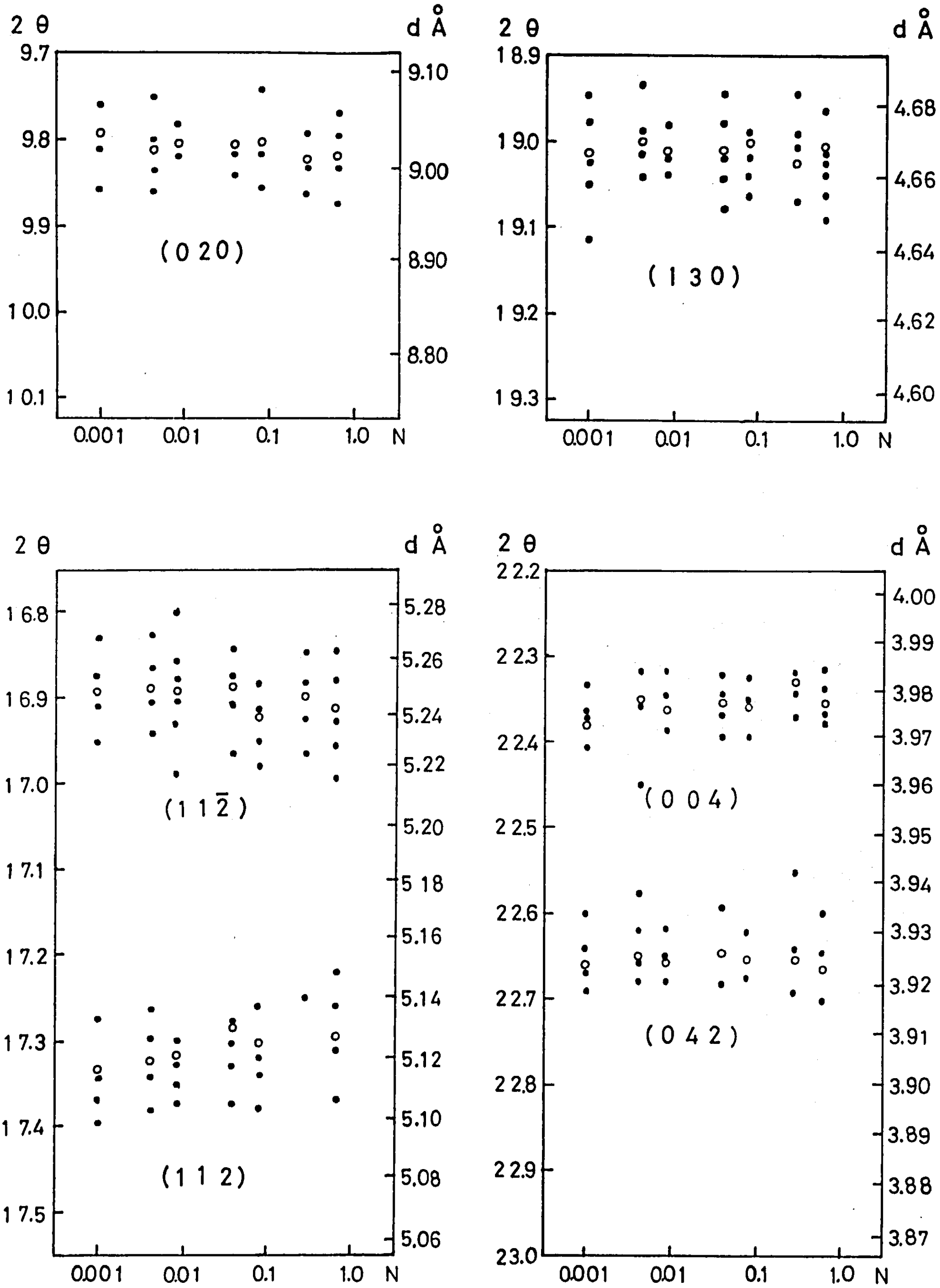

FIG. 17 Variation of 2*θ* and d of clinoptilolite in various concentration of KCl solution.

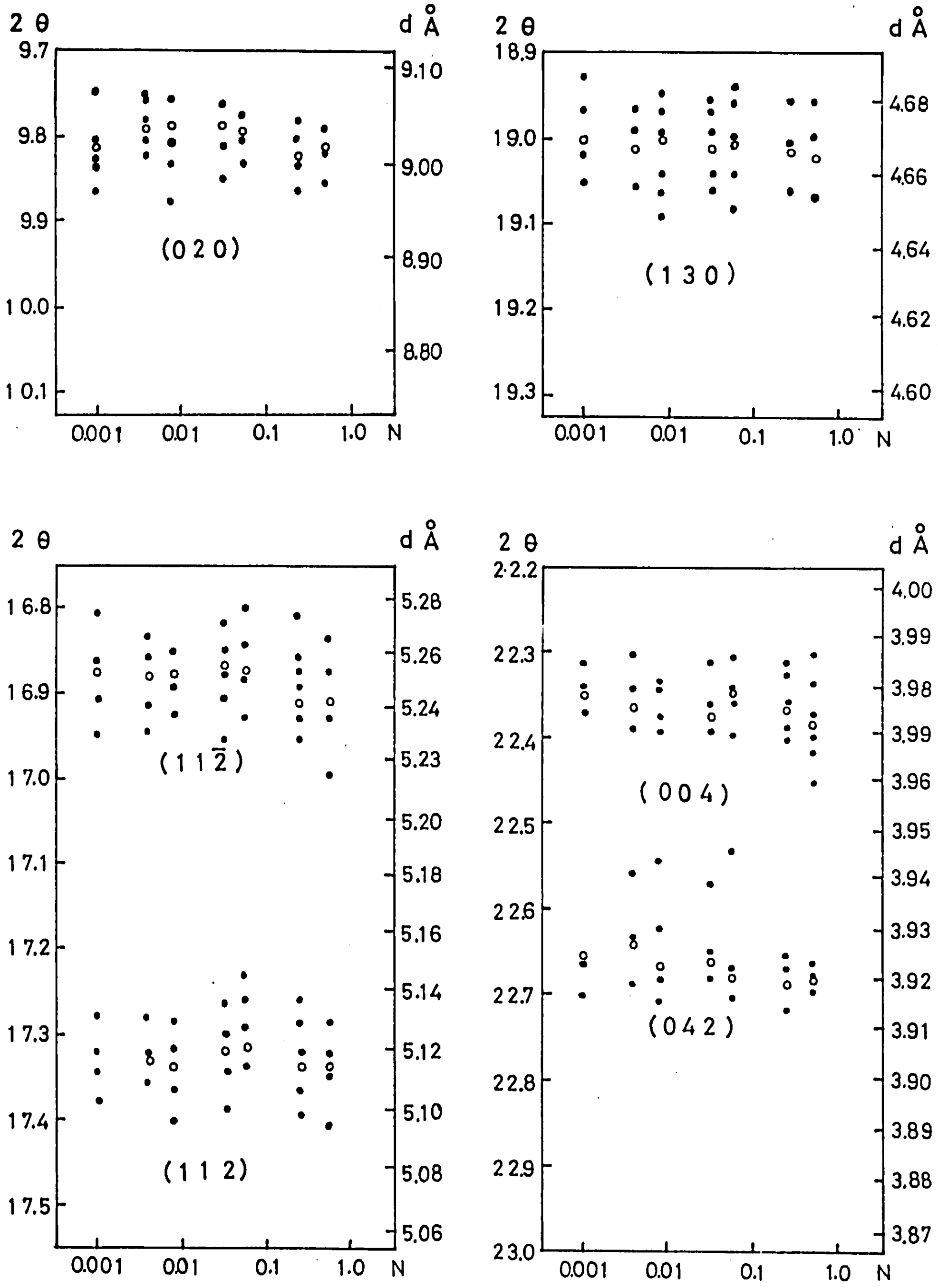

FIG. 18 Variation of 2θ and d of clinoptilolite in various concentration of CaCl$_2$ solution.

are evidently recognizable in the cases of treatment with *HCl* of 0.0001N and 0.001N while the intensity for the spacings (020) and (004) manifests decrease after immersion for 48 hrs. and then increase, as are ascertainable in the figure 19c. In the cases of being treated with *NaCl* solutions of various normality for 24 hrs., as are discernible in the figure 16, the spacings (020), (130), (042), (112) and $(11\bar{2})$ indicate expansion in less than 0.05N whereas the spacing $(11\bar{2})$ furthermore expands, (112) contracts and (004) is held constant in the case of higher normality, causing variation of β. Intensity of the spacing (020) increases in less than 0.05N and decreases in higher normality, as are observed in the figure 19e. In the cases of *KCl* treatments, as are confirmable

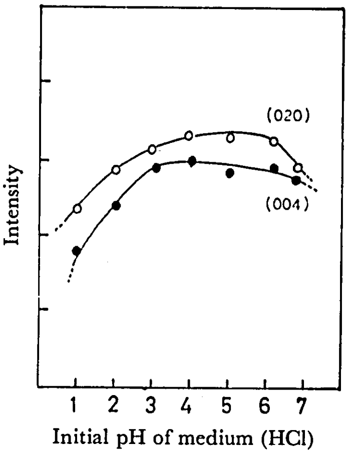

FIG. 19a Variation of intensity of clinoptilolite treated with acid solution.

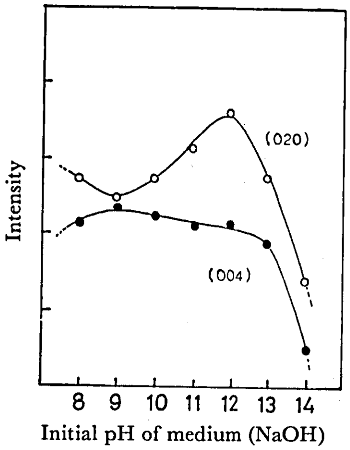

FIG. 19b Variation of intensity of clinoptilolited treated with alkaline solution.

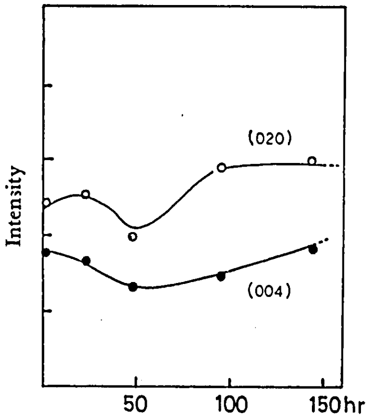

FIG. 19c Variation of intensity of clinoptilolite treated with 0.0001 N HCl solution inrelation to duration.

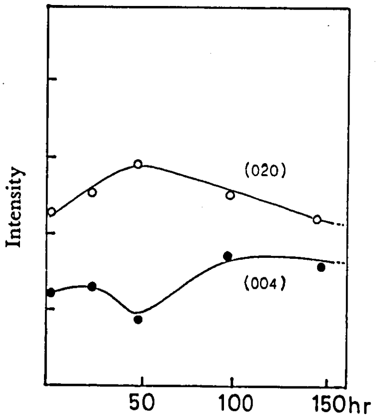

FIG. 19d Variation of intensity of clinoptilolite treated with 0.001 N HCl solution in relation to duration.

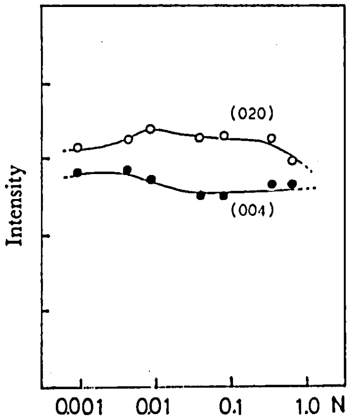

FIG. 19c Variation of intensity of clinoptilolite in various concentration of NaCl.

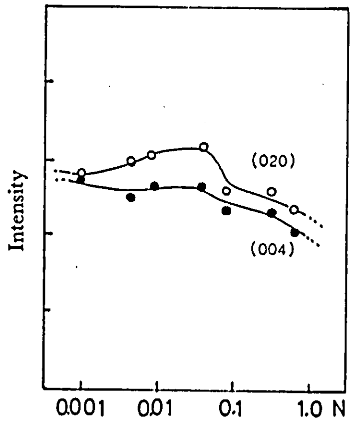

FIG. 19f Variation of intensity of clinoptilolite invarious concentration of KCl.

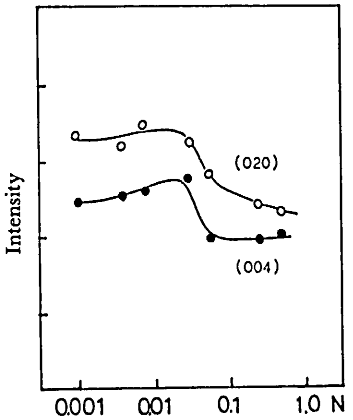

FIG. 19g Variation of intensity of clinoptilolite in various concentration of $CaCl_2$.

in the figure 17, the spacings (020), (130) and ($11\bar{2}$) indicate contraction, the spacing (112) expansion, and the spacing (042) is intermediate in grade with increase of concentration, resulting in increase of b as well as decrease of c, decrease of difference between $Q_{11\bar{2}}$ and Q_{112} and of β. The spacing (020) becomes more intense in less than 0.05N but weakens in higher normality while the spacing (004) diminishes its intensity with increase of concentration, as are notable in the figure 19f. In the cases of $CaCl_2$ treatments, all of the spacings mentioned above show the tendency of shrinkage specifically even in more than 0.1N solutions, as are observable in the figure 18, while the spacing (020) suddenly decreases its intensity in more than 0.05N solutions and the spacing (004) however indicates the similar tendency after increase of its intensity in less than 0.05N, as are distinct in the figure 19g.

Variations in the structure of the specimens with various kinds of treatment have also been inspected through scrutiny of their infrared absorption spectra. As for the absorption of water, no systematically defined shifts of the *OH* stretching bands on the lower side of wave-length together with the *HOH* bending bands are confirmable even after immersed in *HCl* solution with various concentration for 48 hrs., whereas the *OH* bands on the higher side of wave-length are found at $2.958\sim2.960\ \mu$ in the distilled water ($\mathrm{pH}=6.85$) as well as in 0.001 N *HCl* and indicate somewhat increase towards $2.968\sim2.970\ \mu$ in 0.01 N and 0.1 N acid, and intensity of the band near $2.785\ \mu$ reveals a trend decreased with increase of normality, as are obvious in the figure 20

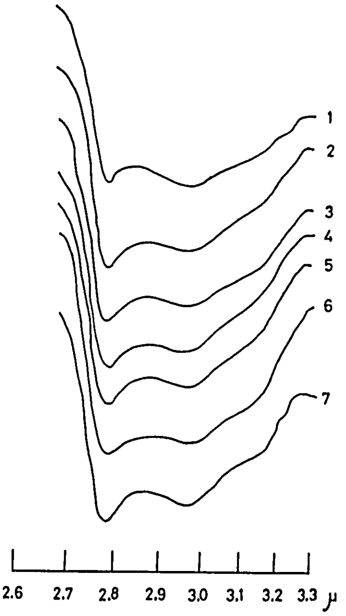

FIG. 20 Variation of infrared absoption spectra of OH stretching of clinoptilolite treated with acid solution.

1: treated with 0.1N HCl solution for 48 hours

2: treated with 0.01N HCl solution for 48 hours

3: treated with 0.001N HCl solution for 48 hours

4: treated with 0.001N HCl solution for 144 hours

5: treated with 0.0001N HCl solution for 48 hours

6: treated with 0.0001N HCl solution for 144 hours

7: treated with distilled water for 48 hours

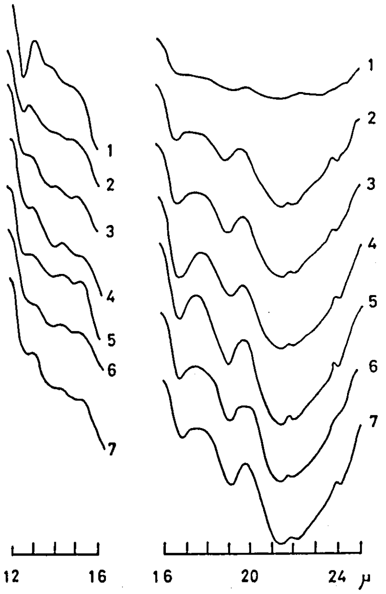

FIG. 21 Variation of infrared absorption bands of clinoptilolite treated with acid solution.

1: treated with 0.1N HCl solution for 48 hours

2: treated with 0.01N HCl solution for 48 hours

3: treated with 0.001N HCl solution for 48 hours

4: treated with 0.001N HCl solution for 144 hours

5: treated with 0.0001N HCl solution for 48 hours

6: treated with 0.0001N HCl solution for 144 hours

7: treated with distilled water for 48 hours

TABLE 11. INFRARED ABSORPTION DATA FOR H_2O IN THE STRUCTURE OF CLINOPTILOLITE.

No. of sample	OH stretching (μ)		HOH bending (μ)
1	2.784	2.965	6.201
2	2.782	2.976	6.195
3	2.784	2.968	6.201
4	2.783	2.958	6.204
5	2.787	2.960	6.210
6	2.783	2.959	6.201
7	2.788	2.961	6.201
8	2.786	2.960	6.204
9	2.785	2.965	6.201
10	2.791	2.958	6.195
11	2.787	2.964	6.191
12	2.786	2.963	6.191
13	2.787	2.936	6.198
14	2.787	2.935	6.195
15	—	2.966	6.162
16	2.785	2.952	6.201
17	2.787	2.947	6.201
18	2.789	2.950	6.208
19	2.785	2.946	6.201
20	2.786	2.951	6.188
21	2.787	2.958	6.195

1: non-treated.
2: treated with 0.1N HCl for 48 hours
3: 〃 0.01N HCl 〃
4: 〃 0.001N HCl 〃
5: 〃 0.001N HCl for 144 hours
6: 〃 0.0001N HCl for 48 hours
7: 〃 0.0001N HCl for 144 hours
8: 〃 distilled water for 48 hours
9: treated with NaOH solution of pH 8 for 144 hours
10: 〃 pH 9 〃
11: 〃 pH 10 〃
12: 〃 pH 11 〃
13: 〃 pH 12 〃
14: 〃 pH 13 〃
15: 〃 pH 14 〃
16: treated with 0.05N NaCl solution for 24 hours
17: 〃 1.0N NaCl solution 〃
18: 〃 0.05N KCl solution 〃
19: 〃 1.0N KCl solution 〃
20: 〃 0.05N $CaCl_2$ solution 〃
21: 〃 1.0N $CaCl_2$ solution

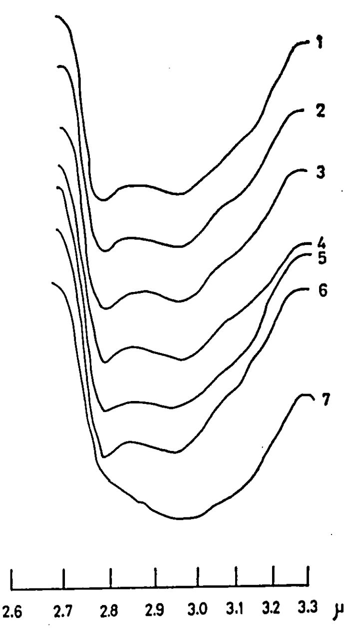

FIG. 22 Variation of infrared absorption spectra of OH stretching of clinoptilolite treated with alkaline solution.

1: treated with NaOH solution (pH 8) for 144 hours
2: treated with NaOH solution (pH 9) for 144 hours
3: treated with NaOH solution (pH 10) for 144 hours
4: treated with NaOH solution (pH 11) for 144 hours
5: treated with NaOH solution (pH 12) for 144 hours
6: treated with NaOH solution (pH 13) for 144 hours
7: treated with NaOH solution (pH 14) for 144 hours

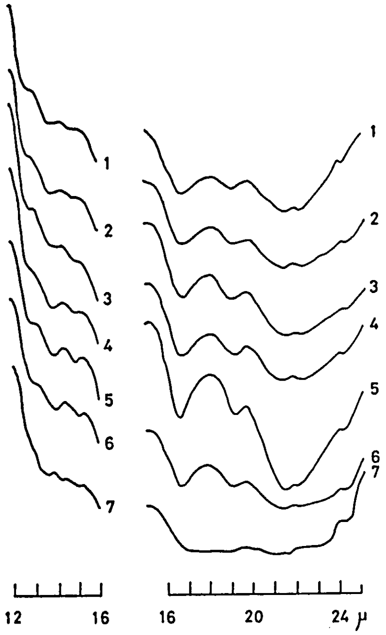

FIG. 23 Variation of infrared absorption bands of clinoptilolite treated with alkaline solution.

1: treated with NaOH solution (pH 8) for 144 hours
2: treated with NaOH solution (pH 9) for 144 hours
3: treated with NaOH solution (pH 10) for 144 hours
4: treated with NaOH solution (pH 11) for 144 hours
5: treated with NaOH solution (pH 12) for 144 hours
6: treated with NaOH solution (pH 13) for 144 hours
7: treated with NaOH solution (pH 14) for 144 hours

and the table 11. With *NaOH* treatment for 144 hrs., the *OH* bands situating at 2.785 μ are invariable within the range of 8 to 13 in pH value, extinguish above 14 and those at 2.958 μ indicate decrease to 2.938 μ within the former range of pH but again increase to 2.966 μ with more than 14 in pH while 6.19 μ representing the *HOH* band decreases to 6.16 μ only in the case of pH 14, as are known from the figure 22 and the tables 11 and 12. Moreover, it seems general that treatments with the alkaline solution weaken the intensity of the bands at 12.6∼12.8 μ and cause emergency of the new bands at 6.80∼6.83 μ, 7.11∼7.14, 11.33∼11.37 μ and 11.59∼11.65 μ

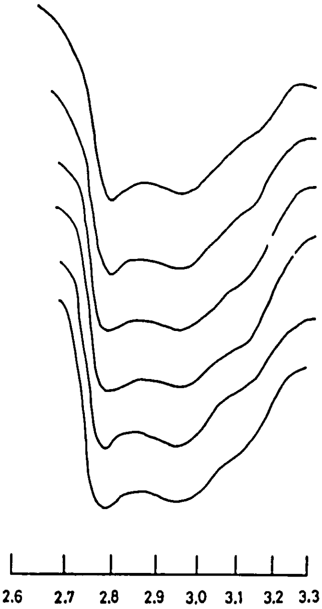

FIG. 24 Variation of infrared absorption spectra of OH stretching of clinoptilolite treated with some electrolite.

1: treated with 0.05N NaCl solution for 24 hours
2: treated with 1.0N NaCl solution for 24 hours
3: treated with 0.05N KCl solution for 24 hours
4: treated with 1.0N KCl solution for 24 hours
5: treated with 0.05N $CaCl_2$ solution for 24 hours
6: treated with 1.0N $CaCl_2$ solution for 24 hours

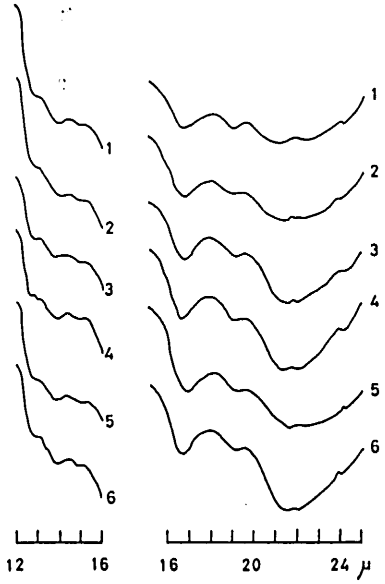

FIG. 25 Variation with infrared absorption bands of clinoptilolite treated with some electrolite.

1: treated with 0.05N NaCl solution for 24 hours
2: treated with 1.0N NaCl solution for 24 hours
3: treated with 0.05N KCl solution for 24 hours
4: treated with 1.0N KCl solution for 24 hours
5: treated with 0.05N $CaCl_2$ solution for 24 hours
6: treated with 1.0N $CaCl_2$ solution for 24 hours

though still not assigned, as are obvious in the figure 23 and the table 12. The conclusive results for the absorption bands have not yet been attainable in the experiments with 0.0001 N and 0.001 N solutions of *HCl* during long time-intervals because of the data present within deviation of the errors, as are illustrated in the figures 24 and 25 and the table 12.

IV. DISCOURSE

With respect to the structure of clinoptilolite under consideration, though still now remained not accurately to have been solved, various views have hitherto been made public by plenty of the authors. According to the excellent works given by SMITH (1960) and AMES (1961, 1963 and 1964), the general structure of zeolite is considered to be constructed mainly of the frameworks of the $(Si, Al)O_4$ tetrahedra and the water molecules absorbing the ions of the alkali and alkali-earth metals. Owing to the opened structure of zeolites, when immersed in certain kinds of the electrolyte solution, it is probable that the cations are movable through the passages in the structure. Prior to the experiments three cases have been expected to take place in the solutions dispersing the zeolites as follows:

(a) The frameworks are stable and the cations present in the structure are diffusible in the solution,

(b) The frameworks are decomposed and the cations, present in or consisting the structure, are dissolved in the solution, and

(c) The frameworks are stable and the cations in the structure with those ionized in the solution are exchanged with one another.

Variations of the abrasion pH in the distilled water and the behaviors of the specimens in the diluted solution of HCl with less than 0.0001 N are considered to represent the first case (a). It is at the same time inferable that such reactions as are given by:

$$NaOH + H_2CO_3 \rightarrow NaHCO_3 + H_2O$$

in the solutions of less than 8.35 in pH

and

$$2NaOH + H_2CO_3 \rightarrow Na_2CO_3 + 2H_2O$$

in those of more than the above value, when the simple exchange and the behaviors of the specimens in the diluted acid solutions seem similarly to be in correspondence to the first case (a) and the patterns for the X-ray diffraction as well as the infrared absorption become more sharp and intense, justifying formation of the more complete structure compared with that of the non-treated specimen. The reactions observed in the cases treated with the concentrated solutions of acid and alkali are considered to have a close relation to the second case (b) inasmuch as, owing to decomposition of the specimens in more than 0.001 N HCl, Al ions are dissolved and the cations absorbed are also diffused in the solution, terminating in formation of a sort of the skeletal structure rich in silica, due to that in more than 11 of the pH value, Si and Al ions become soluble and, in more than 0.1N (0.079N) of NaCl and KCl solutions as well as in more than 0.1 N (0.057 N) of $CaCl_2$ solutions, the breakdown of the frameworks is possible. The reality is that variations of the X-ray diffraction patterns generally point to contraction of the unit cell together with its distortion, while those of the infrared absorption spectra suggest a part of decomposition in such manner that formation of the amorphous figures shown by predominance of silica under the acid conditions and emergency of the new bands at the alkaline states are recognized. The phenomena appearing in the cases of dispersing the specimens in the electrolyte solutions are considered to represent the third case (c). The variations with less than

0.05 N (0.041 N) of *NaCl* and *KCl* solutions as well as less than 0.05 N (0.032 N) of $CaCl_2$ solutions are expressed by the relation: $Y = a \cdot \log X + b$, where Y is the dissolved amount of the absorbed cations in meq., X concetration of the solution, and a and b the constants. In more concentrated solutions the reactions become more complicated on account of decomposition of the structure representing the second case (b) as well as the ion exchange. On the other hand, it appears that absorbability of the specimens is greater for the alkali earths than for the alkaies and for *K* ion than for *Na* ion in relation to difference of the ionic radii: i. e. 5.60 Å for *Na* ion and 3.80 Å for *K* ion at the hydrated state, and that expansion, and contraction, of the unit cell are influenced by the ionic radii of the hydrated ions. As has been alluded to above, formation of the skeletal structure of silica has also been pointed out by KAPPEN and FISCHER (1929) and HEY (1936), although re-absorption of *Al* dissolved in the solution is to be attributed not to the ion exchange reaction manifested by KAPPEN but to formation of the complex body produced through combination of $Al\,(OH)_6^{3-}$ with the cations in the solution and captured on the specimen. The breakdown of the frameworks has, though necessary to be considered in the alkaline media with pH of more than 10 in not neglegible amount, been ignored in the case of study on the solubility of *Ca*-bearing zeolite by ÔKI (1967). The exchange reaction of the cations with those absorbed on the specimen has been taken as an example for Le Chātelier's principle by PAULING (1947) and such a view that dispersion of zeolite, active as a sort of acid named Brönsted in the electrolyte solutions, increases the acidity through its exchange with the cations contained in the solution has been given by VANDERWERF (1961). It is accountably expected that the exchange reactions continue until the equilibrated state taken place between the cations in the specimen and those comprised in the solution is performed. Be that as it may, these theories and the reactions are possible only within the stable range of the structure without any trace of decomposition and accordingly confined to be applied. Furthermore, to be noted is that the concentration dealt with in these cases is to be connected with that under consideration of the real normality of ions and their activity in the related solutions and the behaviors of anions such as HCO_3^- and CO_3^{2-} etc. as well as the effects of mixing of several kinds of electrolytes, with which the specimens may react selectively, are to be scrutinized at the following steps of the research.

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TABLE 12. INFRARED ABSORPTION DATA FOR CLINOPTILOLITE WITH VARIOUS TREATMENT.

No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
Wave length of absorption band in micron													6.83	6.81	6.80						
														7.04							
													7.11	7.14							
	8.30	8.3-9.5	8.34	8.32	8.34	8.31	8.30	8.34	8.30	8.32	8.34	8.33	8.32	8.32	8.21-9.52	8.34	8.32	8.34	8.35	8.30	8.32
	8.63																				
	9.65	(broad)	9.61	9.61	9.64	9.60	9.62	9.65	9.66	9.65	9.65	9.64	9.63	9.65	(broad)	9.65	9.64	9.65	9.65	9.64	9.65
													11.37		11.33						
													11.65	11.59	11.60						
								12.49		12.58			12.65			12.66			12.61		
	12.53	12.49	12.63	12.79	12.83		12.73	12.84	12.80	12.84	12.87	12.90	12.89	12.89		12.97	12.88	12.88	12.94	12.88	12.89
	13.65		13.75	13.94		13.95	13.94		13.84	13.92	13.87	13.91	13.94	13.96	13.54	13.87	13.89	13.88	13.85	13.83	13.83
					14.02																
	14.81		14.91	14.94	14.82			14.82	14.84	14.84		14.84	14.86	14.96	14.28	14.91	14.90	14.96			14.97
				15.14	15.05			15.00	15.02		15.03	15.06	15.05		15.02				15.01		
	16.44		16.56	16.84	16.56	16.70	16.62	16.58	16.50	16.58	16.63	16.54	16.51	16.56		16.60		16.57	16.62	16.86	16.63
		17.04															17.65				
	18.94		18.96																		
		19.08		19.14	19.01	19.00	19.02	19.01	19.01	19.00	19.07	19.08	19.10	19.03		19.07	19.08	19.11	19.31	19.23	19.18
								20.87							20.82						
	21.40	21.48	21.30	21.47	21.34	21.40	21.42	21.40	21.46	21.23	21.39	21.43	21.41	21.41		21.54	21.54	21.37	21.41	21.72	21.50
	22.00		22.01	22.34		22.12	22.11	22.14	22.11	22.04	22.20	22.16	22.03		22.75			22.08	22.19		22.24
		23.29																			
	24.02		24.09	24.07	24.03		24.04	24.02	24.04	24.01		24.07	24.03	24.06	24.07	24.09	24.11	24.01	24.10	24.11	24.08

Nos. of the samples are similar to those mentioned in the table 11.

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