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## ACID AND THERMAL TREATMENT OF NATURAL HEULANDITE

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Acid treatment of natural zeolites is considered to be an effective method of “improving” their structure and properties, among which thermal stability occupies a special place, especially for catalytic applications of zeolites. The influence of hydrochloric acid solutions with concentrations up to 2 mol/L and calcination at temperatures up to 1100 °C on the structure and properties of heulandite-containing tuff from the Georgian Dzegvi-Tedzami deposit, selected for the creation of new bactericidal zeolite filter materials for purification and disinfection of water from various sources, was studied by the X-ray energy dispersion spectra, diffraction patterns and thermal analysis, as well as by adsorption of water, benzene and nitrogen methods. It has been found that an acidic environment leads to significant dealumination (Si/Al molar ratio increases from 3.6 to 9.5) and decationization (total charge of metal ions per Al atom decreases from 1 to 0.68) of the sample; solutions of hydrochloric acid do not lead to amorphization of the zeolite microporous crystal structure, but gradually dissolve it. As a result of acid treatment, there is also a sharp increase in the volume of micropores available for large molecules (from  $\approx 7$  to 80–90 mm<sup>3</sup>/g) and surface area (from  $\approx 13$  to 120–175 m<sup>2</sup>/g), as well as changes in the mesoporous system, leading to the prevalence of pores with a diameter of up to 4 nm. Heulandite heating leads to stepwise dehydration proceeding up to  $\approx 800$  °C, amorphization starting at  $\approx 250$  °C, and structural changes: the transition to metastable heulandite B phase at  $\approx 340$  °C is not fixed, but at  $\approx 500$  °C wairakite (Ca(Al<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>)·2H<sub>2</sub>O) is formed, at temperatures above  $\approx 1000$  °C, amorphous aluminosilicate contains crystalline inclusions of cristobalite (polymorph of SiO<sub>2</sub>),  $\alpha$ -quartz, albite (Na(AlSi<sub>3</sub>O<sub>8</sub>), hematite (Fe<sub>2</sub>O<sub>3</sub>) and magnetite (FeO·Fe<sub>2</sub>O<sub>3</sub>); heating-induced changes in micro- and mesopore systems are insignificant. It is also shown that heat treatment increases the acid resistance of heulandite, which is expressed in a decrease in the degree of dealumination after acid treatment of calcined samples. Thus, acid and heat treatment of heulandite make it possible to obtain materials with different sorption and ion-exchange properties.

**Keywords:** heulandite, dealumination, decationization, dehydration, amorphization

### INTRODUCTION

Natural and synthetic zeolites, hydrated microporous crystalline aluminosilicates of the general formula M<sub>x</sub>[Al<sub>x</sub>Si<sub>y</sub>O<sub>2(x+y)</sub>]mH<sub>2</sub>O (M<sup>+</sup> = Na<sup>+</sup>, K<sup>+</sup>, ... ½Ca<sup>2+</sup>, ½Mg<sup>2+</sup>, ...), have a wide application due to unique set of molecular-sieve, sorption, ion exchange and catalytic properties [1]. In general, synthetic zeolites are more suitable for use as adsorbents (in particular, for the sequestration of heavy metals in wastewater treatment) due to the high uniformity of pore size distribution and the presence of a single compensation cation, while natural varieties, although very attractive from an economic and environmental points of view, demonstrate a lower sorption capacity (including that with respect to most heavy metals [2]). The problem is related to the porous crystalline structure of zeolites, built

from alternating SiO<sub>4</sub> and AlO<sub>4</sub><sup>-</sup> tetrahedra, forming open framework uniform structures with cages and channels, and to improve the performance of the zeolite, its structure can be changed by neat or chemical treatment. For example, acid treatment makes it possible to increase the surface area of the adsorbent and the effective porosity of the original natural zeolites [2–4], since exchangeable cations M<sup>+</sup> located in channels and cavities throughout the zeolite structure sometimes block the channel system [5]. However, concentrated acid solutions at high processing temperatures can cause significant aluminum leaching (dealumination with formation of a hydroxyl nest according to the reaction Al(Si–O<sup>-</sup>) + H<sub>3</sub>O<sup>+</sup> + 3HCl → 4(OH–Si–O) + Al<sup>3+</sup> + 3Cl<sup>-</sup> + H<sub>2</sub>O) and even destruction of the zeolite crystal structure.

Thus, the advantage of acid treatment is the removal of cations, which occupy a significant space in the micropores of zeolites, as well as other impurities, resulting in the development of new pores and active sites; the disadvantage of acid treatment, which occurs at a high concentration of acid, is dealumination, which can cause partial or complete destruction of the zeolite framework. As has been shown [6], hydrochloric and nitric acids are more efficient dealuminating agents than sulfuric and phosphoric acids, not to mention weak organic acids. The most widely used is hydrochloric acid, its effect on the structure and properties of zeolites is well studied for clinoptilolite rich natural zeolites [7, 8].

On the other hand, heat treatment is also used to improve the properties of natural zeolites [4]. The crystal structure of zeolites  $M[AlSi_xO_2(1+x)]_nH_2O$  includes three components: an aluminosilicate framework  $[AlSi_xO_2(1+x)]$ , cations  $M^+$  that compensate for its negative charge, and water molecules. When the zeolite is heated, water molecules gradually leave the crystal lattice, cations change their positions, which can lead to changes in the structure of the aluminosilicate framework. The stability of the zeolite framework plays an important role, and it can be assumed that preliminary heat treatment can affect the acid resistance of the sample.

The purpose of this paper is to consider changes in the structure and properties of heulandite-containing tuff from the Tedzami-Dzegvi deposit (Eastern Georgia) under influence of acid and thermal treatment based on new and previously published data on characterization [9], dehydration and structural transformations [10], acid [11, 12] and thermal [13] treatment, as well as on acid resistance and ion-exchange capacity [14] of this natural zeolite selected as a raw material to create new bactericidal zeolite filter materials for purification and disinfection of water from various sources.

## EXPERIMENTAL

**Materials.** Samples of heulandite-containing tuff were collected in the southern section of the Tedzami-Dzegvi deposit, Eastern Georgia. According to the results of recent study [9], the sample contains up to  $\approx 90$  % of zeolite phase consisting of high-silica heulandite mixed with chabazite in a ratio of 8:1. Zeolitic tuff was crushed on a standard crusher, fractionated to a

particle size of 1–1.4 mm (14–16 mesh), washed with distilled water to remove clay impurities, and dried at a temperature of 95–100 °C.

**Treatment.** Acid treatment of samples was carried out by mixing 10 g of sieved, washed and dried original zeolitic tuff with 100 ml of 0.5, 1.0, and 2.0 mol/L HCl solutions in a shaking water bath (OLS26 Aqua Pro, Grant Instruments, US) operating in linear mode at 75 °C. To achieve maximum effect, acid treatment was carried out in three steps: the first lasted 1 hour, the second – 2 hours, and the third – 3 hours, each step was followed by washing with distilled water until no  $Cl^-$  ions were detected in the washing water by using  $AgNO_3$  solution. The washed and dried samples were weighed to determine the weight loss (see Table 1).

**Table 1.** Weight loss (%) from acid treatment steps

Step	Concentration of HCl solution (mol/L)		
	0.5	1.0	2.0
1 <sup>st</sup>	9.75	12.8	15.4
2 <sup>nd</sup>	7.05	7.8	7.95
3 <sup>rd</sup>	4.5	6.1	5.25

Calcination of prepared samples in the temperature range of 200–1100 °C was carried out in a muffle furnace B400/410 (Nabertherm, Carl Stuart Group). Zeolite samples were placed in a muffle furnace in heat-resistant round-bottom cups, subjected to heat treatment under static conditions for 1 hour, and then, after a while, these cups were placed in desiccators with calcined  $CaCl_2$  until complete cooling.

**Characterization.** Chemical composition of samples was calculated from the X-ray energy dispersive (XR-ED) spectra obtained from a scanning electron microscope JSM-6490LV (Jeol, Japan) equipped with an INCA Energy 350 XRED analyzer (Oxford, UK). Powder X-ray diffraction (XRD) patterns were obtained from a D8 Endeavor diffractometer (Bruker, Germany) and a modernized Dron-4 (USSR) diffractometer both employing the  $CuK_\alpha$  line ( $\lambda = 0.154056$  nm); the samples were scanned in the  $2\theta$  range of  $5^\circ$  to  $68^\circ$  with a  $0.02^\circ$  step at a scanning speed of  $1^\circ/\text{min}$ . Thermogravimetric analysis was based on weight loss (TG), difference thermal analysis (DTA) and difference thermogravimetric (DTG) curves recorded on an STA 2500 Regulus thermal analyzer (NETZSCH group) at the heating rate of

10°C/min. The adsorption capacity for water and benzene vapors was measured under static conditions at room temperature; samples calcined at 260–280 °C and then weighed on an electronic analytical balance (FA 2204N, JOAN LAB, China) were placed in a desiccator and kept for 96 hours at a constant pressure of water vapor (relative pressure  $p/p_0 = 0.4$  and saturated vapor pressure  $p/p_0 = 1.0$ ) and benzene ( $p/p_0 = 1.0$ ) and then the samples that absorbed the vapors were weighed again. Nitrogen adsorption/desorption isotherms were measured at 77 K using an ASAP 2020 Plus analyzer (Micromeritics, USA) on samples vacuum degassed at 350 °C, data analysis was carried out using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) models.

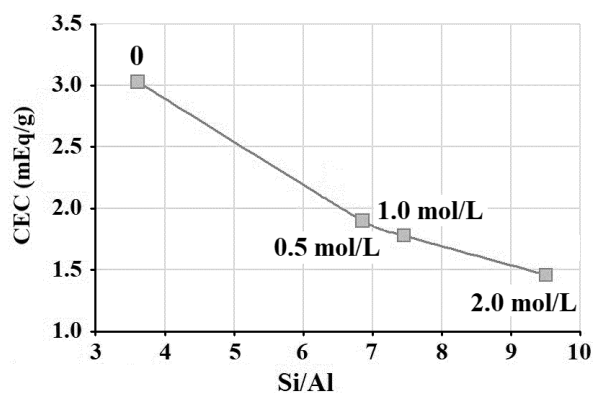
## RESULTS AND DISCUSSION

**Chemical composition.** The results for chemical composition of the acid-treated samples calculated for 72 oxygen atoms in the unit cell are given in Table 2 in terms of averaged empirical formulas of dehydrated zeolites; the Si/Al molar ratio shows the degree of dealumination.

An increase in the Si/Al molar ratio by more than two and half times indicates a rather high degree of acid-mediated dealumination. Dealumination of acid-treated samples limits their use as ion exchangers due to a significant reduction in cation-exchange capacity (CEC), calculated from XR-EDS data as the number of milliequivalents of ionogenic groups per gram of the ion exchanger fully converted to the  $H^+$  form (see Fig. 1).

The degree of decationization is shown in Fig. 2 by a decrease in the total charge of the compensating ions  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$ , as well as the share of each of these cations in compensating the negative charge of the zeolite framework as they are leached and replaced in the framework by  $H^+$ .

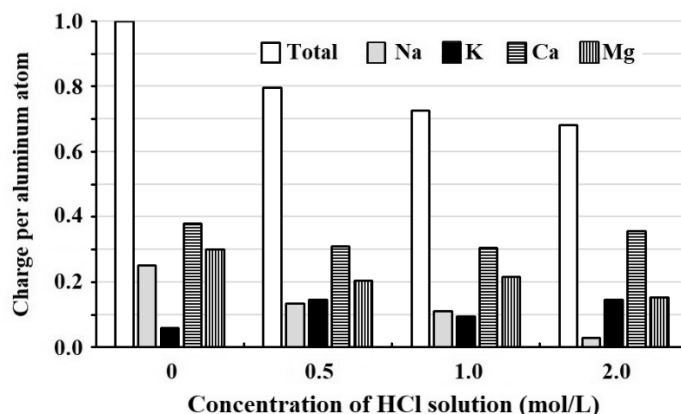
The total charge of metal cations per one aluminum atom monotonically decreases from  $\approx 1$  to  $\approx 0.68$  with increasing acid concentration. The contribution of  $Na^+$  ions to compensate for the negative charge on aluminum atoms decreases, so that sodium is leached to the greatest extent (its content decreased  $\approx 9$  times after treatment with 2.0 mol/L solution);  $Mg^{2+}$  ions are washed out to a lesser extent, the content of  $Ca^{2+}$  ions decreased slightly ( $-7\%$ ), and  $K^+$  ions do not take part in the decationization process. This conclusion is consistent with the results of the study of decationization and dealumination of clinoptilolite tuff [7] where was also found that natural clinoptilolite samples treated with HCl solutions exchanged mainly  $Na^+$  ions, followed by  $Mg^{2+}$  and  $Ca^{2+}$  ions, whereas  $K^+$  ions from the clinoptilolite practically did not participate in an exchange process. However, our results do not correspond to the data of work [8] that the removal of monovalent cations, such as  $Na^+$  and  $K^+$  ions, is insignificant for the temperatures of 25–100 °C and changed little with acid concentration, but the results are difficult to compare, since high-silica clinoptilolite ( $Si/Al = 6.22$ ) was used in the study of Turkish scientists.



**Fig. 1.** Dependence of CEC on the Si/Al molar ratio of original (0) and acid-treated samples

**Table 2.** Chemical composition of original and acid-treated samples

Concentration of HCl solution (mol/L)	Empirical formula	Si/Al
0	(Na <sub>1.96</sub> K <sub>0.47</sub> Ca <sub>1.49</sub> Mg <sub>1.17</sub> )[Al <sub>7.8</sub> Si <sub>28.2</sub> O <sub>72</sub> ]	3.6
0.5	(Na <sub>0.62</sub> K <sub>0.67</sub> Ca <sub>0.71</sub> Mg <sub>0.47</sub> )[Al <sub>4.59</sub> Si <sub>31.4</sub> O <sub>72</sub> ]	6.85
1.0	(Na <sub>0.47</sub> K <sub>0.40</sub> Ca <sub>0.65</sub> Mg <sub>0.46</sub> )[Al <sub>4.26</sub> Si <sub>31.7</sub> O <sub>72</sub> ]	7.45
2.0	(Na <sub>0.096</sub> K <sub>0.50</sub> Ca <sub>0.61</sub> Mg <sub>0.26</sub> )[Al <sub>3.43</sub> Si <sub>32.6</sub> O <sub>72</sub> ]	9.5

**Fig. 2.** Cationic charge per Al atom of native (0) and acid-treated samples**Table 3.** Chemical composition of original and heat-treated samples

Calcination temperature (°C)	100	200	400	500	600	700	800
Si/Al	3.60	3.68	3.72	4.26	3.77	3.67	3.72
Na/Al	0.25	0.26	0.26	0.26	0.27	0.26	0.25
K/Al	0.06	0.07	0.06	0.07	0.07	0.06	0.07
Ca/Al	0.19	0.195	0.19	0.195	0.20	0.19	0.19
Mg/Al	0.15	0.145	0.15	0.155	0.15	0.14	0.15
[Na+K+2(Ca+Mg)]/Al	0.99	1.01	1.00	1.04	1.06	0.98	1.00

According to the XR-ED spectra, chemical composition of the surface of the calcined samples undergoes slight changes, which are most reflected in the Si/Al molar ratio (see Table 3) – after annealing at the temperature of 500 °C, dealumination is observed; at higher temperatures, the modulus Si/Al returns to its previous values.

The data presented in Table 3 indicate that, as a result of heating, decationization of heulandite does not occur, the negative charge of the framework is completely compensated by sodium, potassium, calcium and magnesium cations.

**Structure.** Powder XRD patterns show no changes after treatment with a dilute HCl solution (0.5 mol/L), but treatment with concentrated solutions leads to a change in the intensity of some peaks (see Fig. 3, left).

Thus, the intensity of the low angle peak at  $2\Theta = 9.85^\circ$  (Miller indices  $hkl$  020;  $d$ -spacing 8.98 Å) decreases with increasing acid concentration, the peak intensities at  $\approx 22^\circ$  ( $hkl$  131, 400, 330;  $\approx 4$  Å) first increase (at acid concentration 1.0 mol/L), and then decrease (2.0 mol/L), while the intensity of the weak peak at  $\approx 28^\circ$  ( $hkl$  -422 and/or -441;  $\approx 3.15$  Å) initially decreased and then sharply increases with increasing acid concentration to 2 mol/L. In addition, some peaks decrease and disappear from X-ray diffraction patterns with increasing acid concentration, this applies to peaks at  $2\Theta = 13^\circ$  ( $hkl$  -201; 6.8 Å),  $15^\circ$  ( $hkl$  220;  $\approx 6$  Å) and  $\approx 33^\circ$  ( $hkl$  -261 and/or 061;  $\approx 2.8$  Å).

No line broadening is observed, so that the acid treatment does not cause amorphization of the sample. The overall intensity of the XRD pattern decreases slightly with increasing acid



concentration, not correlating with the much greater weight loss resulting from the treatment shown in Table 1. Although the chemical composition of the zeolites does not change in the

third step of the acid treatment, there is still a slight weight loss, which indicates the gradual dissolution of the samples by the acid.

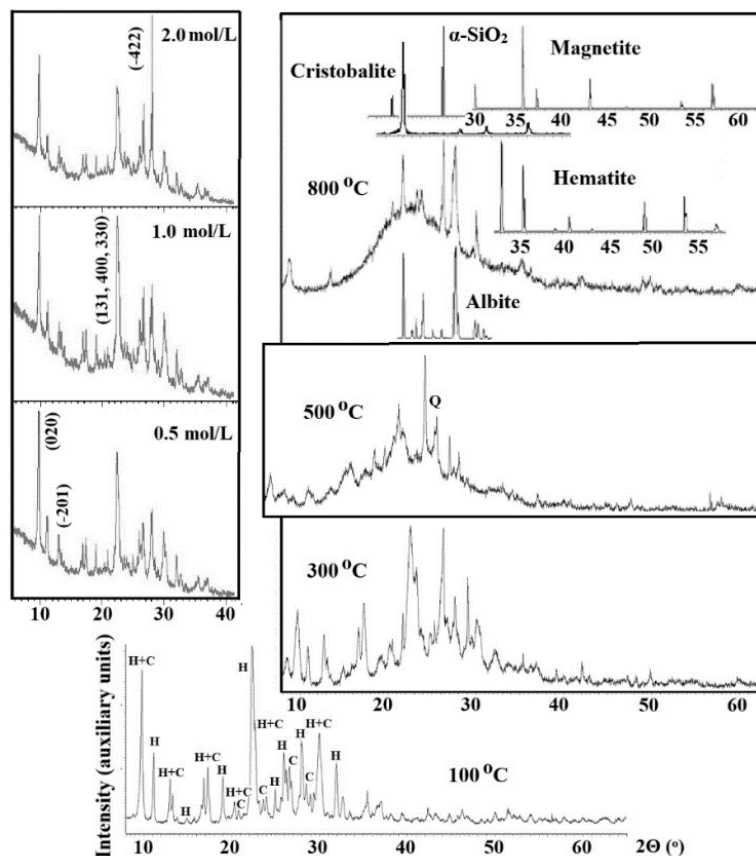


Fig. 3. Powder XRD patterns of dried at 100 °C sample (bottom, H – peaks of main heulandite phase, C – peaks of impurity chabazite phase), acid treated samples (left, numbers in parenthesis are Miller indices *hkl* of peaks changing intensity) and samples calcined at 300, 500 and 800 °C (right)

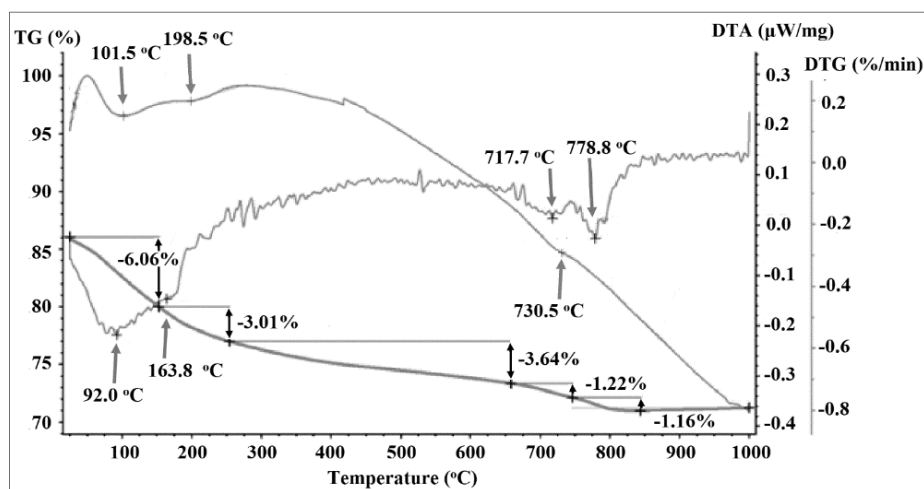


Fig. 4. Thermogravimetric curves of heulandite (red and blue arrows show endothermic peaks on DTA and DTG curve, respectively)

The result obtained does not contradict the known ones, since in a recent work [6], the amorphization of clinoptilolite recorded using XRD patterns was noted only after treatment of the zeolite with solutions with a high concentration of hydrochloric acid (5 and 10 mol/L).

XRD patterns do not change in the temperature range up to 200 °C, at higher temperatures the peaks begin to broaden, than the intensity of the heulandite peaks decreases, and at  $\approx 500$  °C a broad band and a sharp peak of quartz ( $2\Theta = 26.6^\circ$ ) appear (Fig. 3, right).

Thermogravimetric curves (Fig. 4) show slow endothermic peaks at relatively low temperatures (DTA at 101.5 and 198.5 °C, DTG at 92.0 and 163.7 °C), but no sharp endothermic peak at  $\approx 340$  °C, which is associated with the transition to the structure of “sluggish” [15] heulandite B, first described by Koizumi [16]. Probably, the absence of a transition to heulandite B is explained by the lower aluminum content in Georgian heulandite (Si/Al = 3.6) than that in the low-silica samples studied in works [15–17].

It is believed that when heulandite is heated, the metastable phase of heulandite B exists in the temperature range of 340–470 °C, and at temperatures exceeding 500 °C a mixture of quartz (SiO<sub>2</sub>) and minerals of the 9.GB.05 group such as wairakite (Ca(Al<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>)·2H<sub>2</sub>O) and/or anorthite (Ca(Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>)) starts to appear. The XRD patterns cannot unequivocally confirm the formation of these minerals, since the most intense peaks for wairakite and anorthite ( $2\Theta \approx 16$  and  $28^\circ$ , respectively) overlap with the peaks of chabazite (reflection with  $hkl = 113$  giving an intense peak at  $2\Theta = 16^\circ$  [18]) and heulandite ( $(hkl = -422$  at  $2\Theta = 28.1^\circ$ , and  $hkl = -441$  at  $2\Theta = 28.5^\circ$ ). However, the formation of wairakite containing “zeolite water” is confirmed by thermal analysis data: the measured total weight loss (15.09 %) is in good agreement with the calculated one (15.5 %) for 3 water molecules per aluminum atom, most of the water ( $\approx 6$  % of the total weight loss or  $\approx 60$  % of the total water content) is continuously lost at temperatures below  $\approx 250$  °C, and then part of the remainder ( $\approx 24$  % of the total water content) is slowly dehydrated up to 650 °C, complete dehydration of the sample is achieved at  $\approx 800$  °C; high-temperature endothermic peaks are registered on the DTA curve at 730.5 °C, on the DTG curve at 717.7 and 778.8 °C.

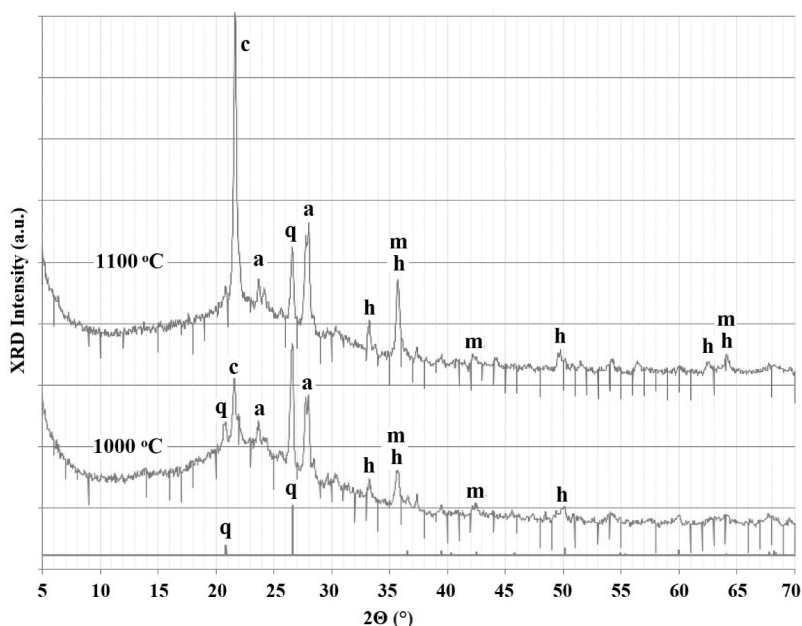
Apparently, these endothermic effects are associated with the formation of new crystalline phases – the silica polymorph cristobalite, which gives an intense peak at  $2\Theta = 26.6^\circ$  in the XRD pattern, and sodium feldspar albite (NaAlSi<sub>3</sub>O<sub>8</sub>), which gives intense peaks in a range of  $2\Theta = 22$ – $32^\circ$ . In the powder XRD pattern of the Dzegvi-Tedzami heulandite sample calcined at 800 °C (Fig. 3, right, top), low-angle broadened peak of chabazite is visible at  $2\Theta = 9.4^\circ$  (Miller indices  $hkl$  100;  $d$ -spacing 9.4 Å), but the main part of the amorphized zeolite phase is represented by a wide band at  $2\Theta$  from 12 to  $40^\circ$  superimposed by narrow lines of silica, cristobalite and albite peaks. It should be noted that the XRD pattern of calcium feldspar anorthite Ca(Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>) is characterized by an intense peak at  $2\Theta \approx 28^\circ$ , the XRD pattern of potassium feldspar orthoclase K(AlSi<sub>3</sub>O<sub>8</sub>) shows peaks in a range  $2\Theta = 20$ – $35^\circ$ , and these peaks may be overlapped by albite peaks, although the formation of orthoclase is unlikely due to the relatively low content of potassium in the sample. In addition, peaks of impurity oxides of iron, hematite (Fe<sub>2</sub>O<sub>3</sub>, peaks in a range of  $2\Theta = 33$ – $60^\circ$ ), and magnetite (FeO·Fe<sub>2</sub>O<sub>3</sub>, peaks in a range of  $2\Theta = 30$ – $65^\circ$ ) appear in the pattern after calcination at high temperatures.

Complete amorphization of all zeolite phases (heulandite, wairakite, and chabazite) is achieved after calcination at 1000 °C; at higher temperatures, the amorphous aluminosilicate contains crystalline inclusions of cristobalite,  $\alpha$ -quartz, albite (and possibly also anorthite), hematite and magnetite (see Fig. 5).

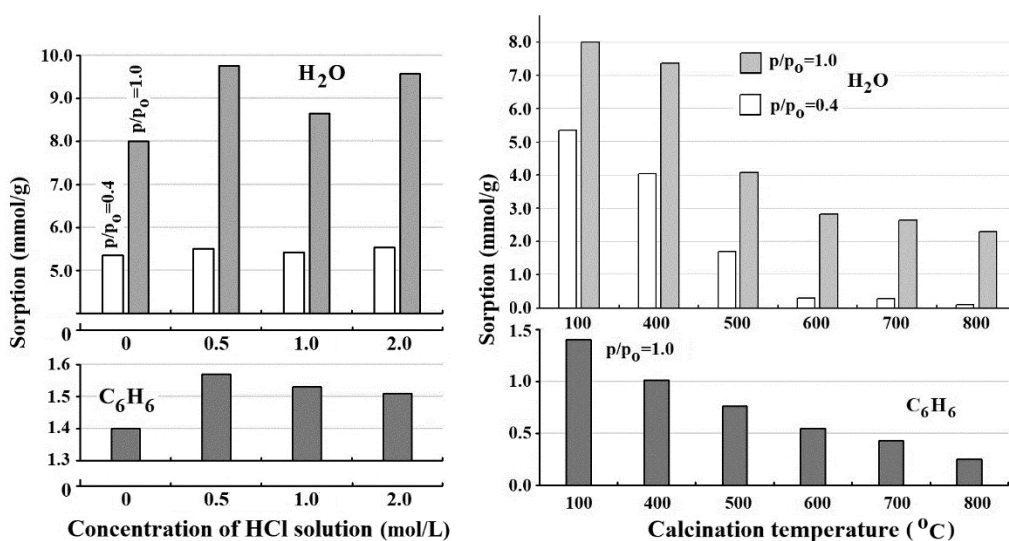
With an increase in the calcination temperature, the intensity of the quartz peak decreases, and the intensity of the cristobalite peak sharply increases, the feldspar (albite and possibly anorthite) peaks are preserved up to 1100 °C, and the peaks of iron oxides become more distinct. Hematite melts at 1565 °C, magnetite begins to decompose at 1950 °C [19], and in the XRD patterns of sample calcined at high temperature (1200–1300 °C), the ratio of the intensity of the peak at  $2\Theta = 35.8^\circ$ , consisting of the peaks of magnetite (75 %) and hematite (x), to the intensity of the magnetite peak at  $2\Theta = 33.2^\circ$  (100 %) is approximately 2:1, which allows us to estimate the relative content of hematite (x) as 125 % of the content of magnetite.

**Adsorption of water and benzene.** Water molecules have a small kinetic diameter of 0.266 nm and can freely pass through entrance windows into heulandite channels, and the adsorption of water vapor at a relative pressure  $p/p_0 = 0.4$ , corresponding to almost complete filling of micropores, is a measure of their volume available for small polar molecules [20], while adsorption at saturated water vapor pressure ( $p/p_0 \approx 1$ ) is a measure of the total pore volume.

The kinetic diameter of the benzene molecule (0.585 nm) significantly exceeds the sizes of micropores and channels, so that this non-polar molecule can be adsorbed only on the zeolite surface developed due to the presence of meso- and macropores; benzene adsorption capacity is a relative measure of surface area and its hydrophobicity. Results of measurements are shown in Fig. 6.



**Fig. 5.** Assignment of peaks in powder XRD patterns of the Dzegvi-Tedzami heulandite sample calcined at 1000 and 1100 °C: q –  $\alpha$ -SiO<sub>2</sub>, c – cristobalite, a – albite and anorthite, h – hematite, m – magnetite



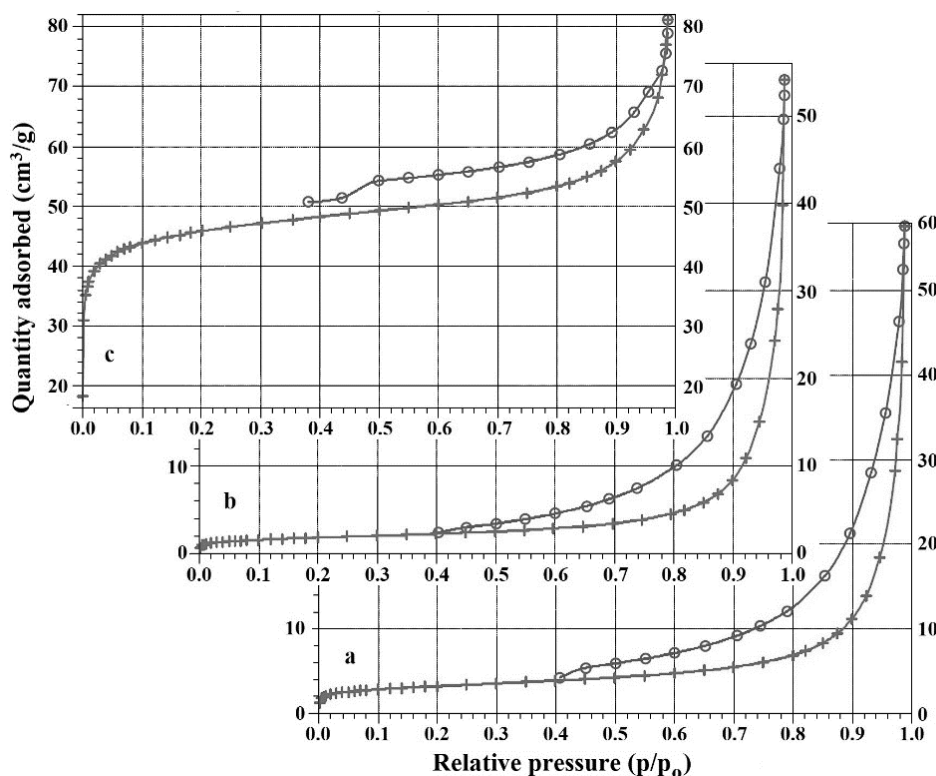
**Fig. 6.** Water vapor (H<sub>2</sub>O) and benzene (C<sub>6</sub>H<sub>6</sub>) adsorption capacity of acid-treated (left) and calcined (right) samples

The volume of micropores accessible for water molecules in native heulandite is about 60 % of the total pore volume. Adsorption in micropores practically does not change as a result of acid treatment and decreases with an increase in the calcination temperature, reaching very low values ( $< 0.3$  mmol/g) at temperatures above 500 °C; it is in no way related to the aluminum content, as was noted in studies of water vapor adsorption on high-silica synthetic zeolites reviewed in [20]. The adsorption capacity of all pores with respect to water vapor in acid treated samples changes nonmonotonically and decreases with an increase in the calcination temperature.

The adsorption of benzene vapor after treatment with a solution of hydrochloric acid with a concentration of 0.5 mol/L increases, which clearly indicates an increase in the

hydrophobicity of the surface, but with an increase in acid concentration, this effect is leveled; the heat treatment leads to decrease of hydrophobicity.

**Adsorption of nitrogen.** In heulandite crystal structure, a 10-membered ring ( $0.75 \times 0.31$  nm) and one of the 8-membered rings ( $0.47 \times 0.28$  nm) cannot accommodate a nitrogen molecule (kinetic diameter 0.364 nm), which can pass only into one 8-membered ring ( $0.46 \times 0.36$  nm). The low-temperature adsorption-desorption isotherms of nitrogen on studied native, acid-treated and calcined samples correspond to the filling of micropores (Langmuir plot) at low relative pressures ( $p/p_0 < 0.3$ ) and demonstrate a hysteresis loop with a jump at  $p/p_0 = 0.4-0.5$  indicating the presence of developed system of mesopores (see Fig. 7).



**Fig. 7.** N<sub>2</sub> adsorption-desorption isotherms on native Georgian heulandite (a) and its thermal treated (800 °C, b) and acid-treated (2.0 mol/L, c) samples

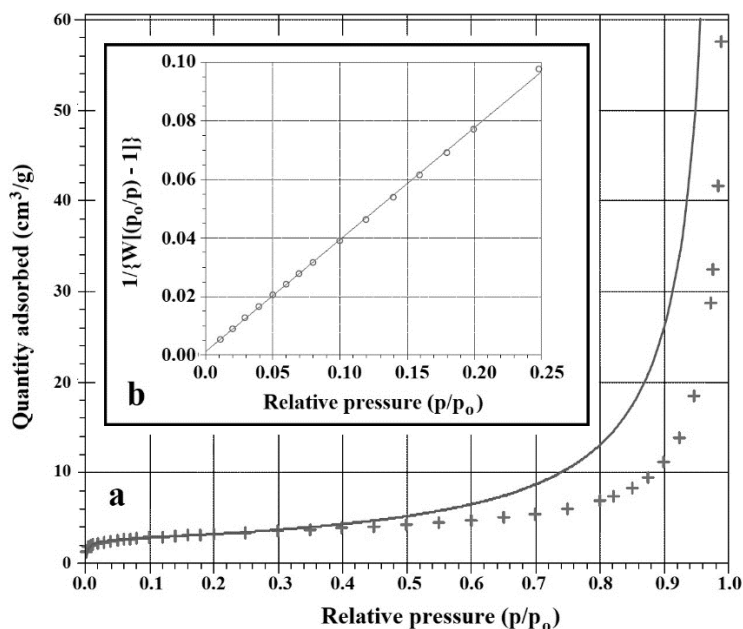
According to the so-called BDDT classification of isotherms [21] adopted by IUPAC, as well as the classification of hysteresis loops [22], the obtained isotherms belong to type IV (complete filling of pores) with a combined hysteresis loop: H<sub>1</sub> (cylindrical pore channels) in

the region of high relative pressures and H<sub>3</sub> (slit-shaped pores) in the region medium pressures  $0.4 < p/p_0 < 0.9$ .

The Brunauer-Emmett-Teller (BET [23]) model ideally describes the experimental data in the range of relative pressures  $0.01 < p/p_0 < 0.25$ ,

significant discrepancies between the BET equation ( $\{W[(p/p_0) - 1]\}^{-1} = (W_m C)^{-1} + \{(C - 1)/W_m C\} (p/p_0)$ ), where  $W$  is adsorption at pressure  $p$ ,  $W_m$  is the monolayer volume on the

adsorbent surface,  $C$  is the ratio of the adsorption equilibrium constant in the first layer and the condensation constant) occur at relative pressures  $p/p_0 > 0.5$  (see Fig. 8).



**Fig. 8.** BET isotherm plot (a, solid line – calculation according to the BET equation, crosses – measured values of adsorption) and BET surface area plot (b)

**Table 4.** Porosity parameters of initial, acid treated and calcined samples

Parameter	Initial	Concentration of HCl (mol/L)			Calcination temperature (°C)				
		0.5	1.0	2.0	400	500	600	700	800
$S_{BET}$ (m <sup>2</sup> /g)	12.8	127	155	175	11.4	10.5	9.45	9.16	6.52
$Q_{1.0}$ (cm <sup>3</sup> /g)	57.89	48.8	55.8	68.1	57.64	60.0	53.14	50.40	54.16
$Q_{0.4}$ (cm <sup>3</sup> /g)	4.184	35.0	42.3	48.2	3.879	3.668	3.286	3.207	2.258
$V_p$ (mm <sup>3</sup> /g)	89.5	109	113	126	89.2	92.8	82.2	78.0	83.8
$V_m$ (mm <sup>3</sup> /g)	6.47	78.2	85.6	88.9	6.0	5.7	5.1	5.0	3.5
$D_{BJH}$ (nm)	17.2	13.1	11.6	11.1	17.6	17.6	17.2	16.1	20.1

The constant  $C$  for a native sample is  $369 \pm 64$ , for calcined samples  $C$  decreases to  $170 \pm 10$ , for acid-treated samples it varies within  $(1200-1400) \pm 350$ , so that in any case  $C \gg 1$  and the BET equation can be simplified to  $\{W[(p/p_0) - 1]\}^{-1} = [(p/p_0)/W_m]$ . In this case, the constant  $C$  is no longer a parameter of the BET equation, the calculation of  $C$  from the slope  $s$  and the intercept  $i$  of the BET surface area plot (Fig. 6 b,  $C = s/i$ ) is purely formal ( $i \rightarrow 0$ ) and has no physical meaning.

Turkish researchers [6] processed data in the region of low relative pressures ( $p/p_0 < 0.1$ ) using the Dubinin-Astakhov equation ( $W = W_0 \exp\{-$

$[RT \ln(p_0/p)/E]^n\}$ , where  $W_0$  is total weight adsorbed,  $E$  is the characteristic energy,  $R$  – gas constant,  $T$  – temperature) and obtained fractal values of the heterogeneity parameter  $n$  for acid-treated samples. In our case, there is no need to use the Dubinin-Astakhov or simplified Dubinin-Radushkevich ( $n = 2$ ) equations, since the monolayer volume  $W_m$  can be determined with high accuracy ( $\pm 0.3-0.4\%$ ) from the slope of the BET surface area plot, from which the surface area  $S_{BET}$  can be calculated using the formula  $S_{BET} = W_m N_A A_x / M$ , where  $N_A$  is Avogadro constant ( $6.023 \cdot 10^{23} \text{ mol}^{-1}$ ),  $A_x$  – effective cross-

sectional area of N<sub>2</sub> molecule (0.162 nm<sup>2</sup>),  $M$  – adsorptive (nitrogen gas) molar volume (22.414 mL/mol). The  $S_{\text{BET}}$  values and other porosity parameters calculated on the basis of experimental adsorption-desorption isotherms on initial, acid-treated and calcined samples are given in Table 4.

The total volume of pores  $V_p$  is calculated from the maximum quantity adsorbed  $Q_{1.0}$ , measured at saturated pressure of nitrogen gas; micropore volume  $V_m$  is calculated from  $Q_{0.4}$ , quantity adsorbed at relative pressure  $p/p_0 = 0.4$ . Estimation of the mesopore size and calculation of the pore size distribution was carried out by the Barrett-Joyner-Halenda (BJH) method [24] using the Kelvin equation, which provides a correlation between the pore diameter and condensation pressure, so that the BJH desorption average pore diameter  $D_{\text{BJH}}$  is calculated as  $D_{\text{BJH}} = 2(r_k + t)$ , where the critical radius  $r_k(\text{Å}) = 4.15/[\log(p_0/p)]$  for nitrogen desorption at 77 K, and the statistical thickness  $t(\text{Å}) = 3.54[5/\log(p_0/p)]^{0.333}$ , according to the Halsey equation [25] and Faass correction [26].

The initial sample has a low surface area (12.8 m<sup>2</sup>/g), and the fraction of micropores accessible to nitrogen molecules is only 7 % of the total porosity. Under the influence of acid, the surface area and the volume of micropores accessible to nitrogen molecules increase sharply and continue to increase with increasing acid concentration in the treatment solution. A similar effect was noted in [6] for acid-treated clinoptilolite: (i) the volume of micropores accessible to nitrogen in the studied original clinoptilolite was only 0.005 cm<sup>3</sup>/g, which the authors attributed to the blocking of most of the pores by cations considered as impurities; (ii) with an increase in the concentration of HCl in the solution, the volume of micropores increased by more than 12 times, up to 0.064 cm<sup>3</sup>/g for 3 mol/L HCl solution but with further increase in the concentration, it decreased; (iii) the outer surface area of the HCl treated samples gradually increased with increasing the Si/Al ratio from 3 m<sup>2</sup>/g and reached a maximum of 33 m<sup>2</sup>/g after soaking in a 10 mol/L solution. Akimkhan [27] observed no increase in the total pore volume when clinoptilolite was treated at room temperature with 3 mol/L HCl solution for 24 hours, the increase was about 2 times when the concentration of acid was 12 mol/L, and over

3 times when the acid treatment was carried out at 96–98 °C.

According to the results obtained, the total pore volume  $V_p$  increases monotonically with increasing acid concentration, while the diameter of nanosized pores  $D_{\text{BJH}}$  sharply decreases. Silva and coworkers [28] found that HCl treatment decreased the zeolite pore diameter about 2.5 times and increased the surface area approximately 16 times.

Wide hysteresis loop of adsorption-desorption isotherms indicates broad pore size distribution, and the curve  $V(D)$  (pore volume  $V$  vs. pore diameter  $D$ , see Fig. 9, left) calculated using BJH model from desorption isotherm measured on original heulandite sample shows the presence of mesopores up to 100 nm in diameter.

As the pore size distribution curves  $V(D)$  of acid-treated samples show, the shape of the curve changes and the volume of mesopores decreases as a result of acid treatment. Thus, the observed slight increase in the total pore volume is mainly due to the “opening” of micropores for nitrogen molecules. According to the parameters given in Table 4, after processing the sample in solutions with a concentration of 0.5, 1.0 and 2.0 mol/L, the specific volume of micropores increases to 72, 716 and 71 % of the total pore volume, respectively.

Pore size distribution differential  $dV/dD$  vs. pore diameter curves (Fig. 9, right) show that the original heulandite is characterized by a wide size distribution of mesopores from 2 to 50 nm in diameter with a maximum at  $\approx 12$  nm; as a result of acid treatment, this maximum disappears, but a sharp maximum at  $\approx 4$  nm, which increases with increasing acid concentration, appears. Taking into account, albeit small, but still an increase in the total pore volume with increasing acid concentration, it can be concluded that after acid treatment, small in size, up to 4 nm, pores become predominant in the mesopore system of the acid-treated heulandite. These effects of acid treatment are most pronounced when using dilute solutions of hydrochloric acid (with a concentration of less than 0.5 mol/L), the pore size distribution curves for samples treated with 1 and 2 normal solutions practically do not differ.

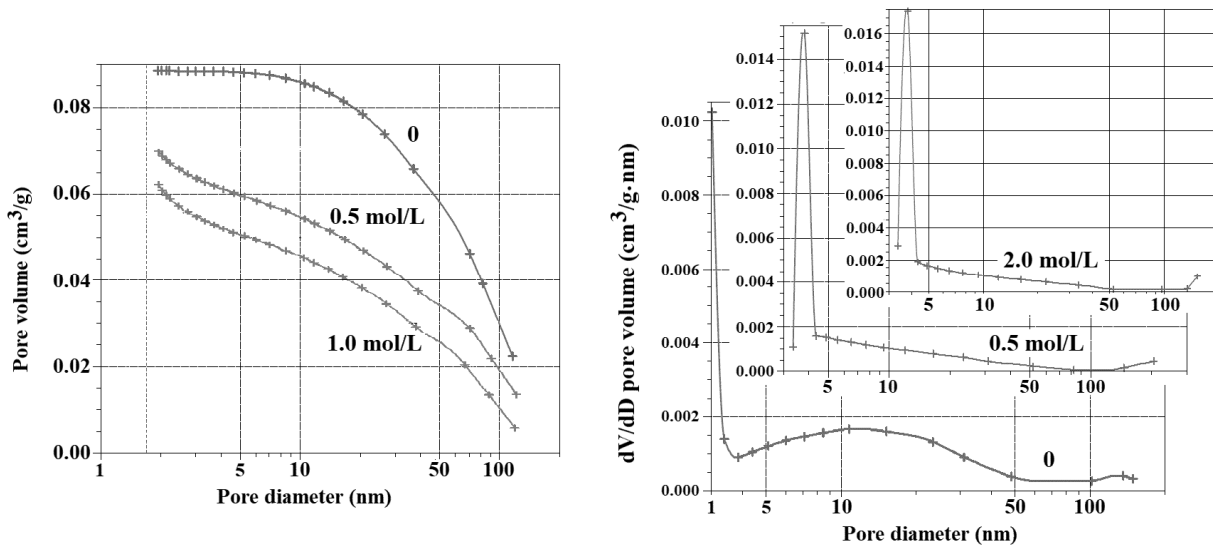
Apparently, the described changes in the distribution of mesopore sizes also lead to the fact that the hysteresis loop for acid-treated samples does not “close” (see Fig. 7) at a relative pressure

$p/p_0 = 0.4$ , which is considered as a conditional boundary between adsorption in micropores and mesopores.

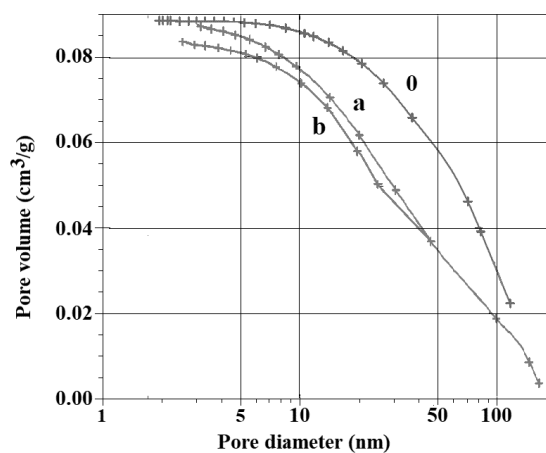
With regard to heat treatment, surface area  $S_{BET}$  decreases monotonically from 12.8 to 6.5  $m^2/g$  (see Table 4) with an increase in the calcination temperature, the total volume of pores varies insignificantly, reaching a maximum value after calcination at 500 °C and a minimum after annealing at 700 °C, while the volume of micropores accessible to nitrogen molecules decreases insignificantly up to 700 °C (from 6 to 5  $mm^3/g$ ), and after annealing at 700 °C it drops sharply to 3.5  $mm^3/g$ . Probably, the retention of such a low adsorption capacity up to high

temperatures is due to the existence of a heat-resistant impurity phase of chabazite and the formation of microporous wairakite.

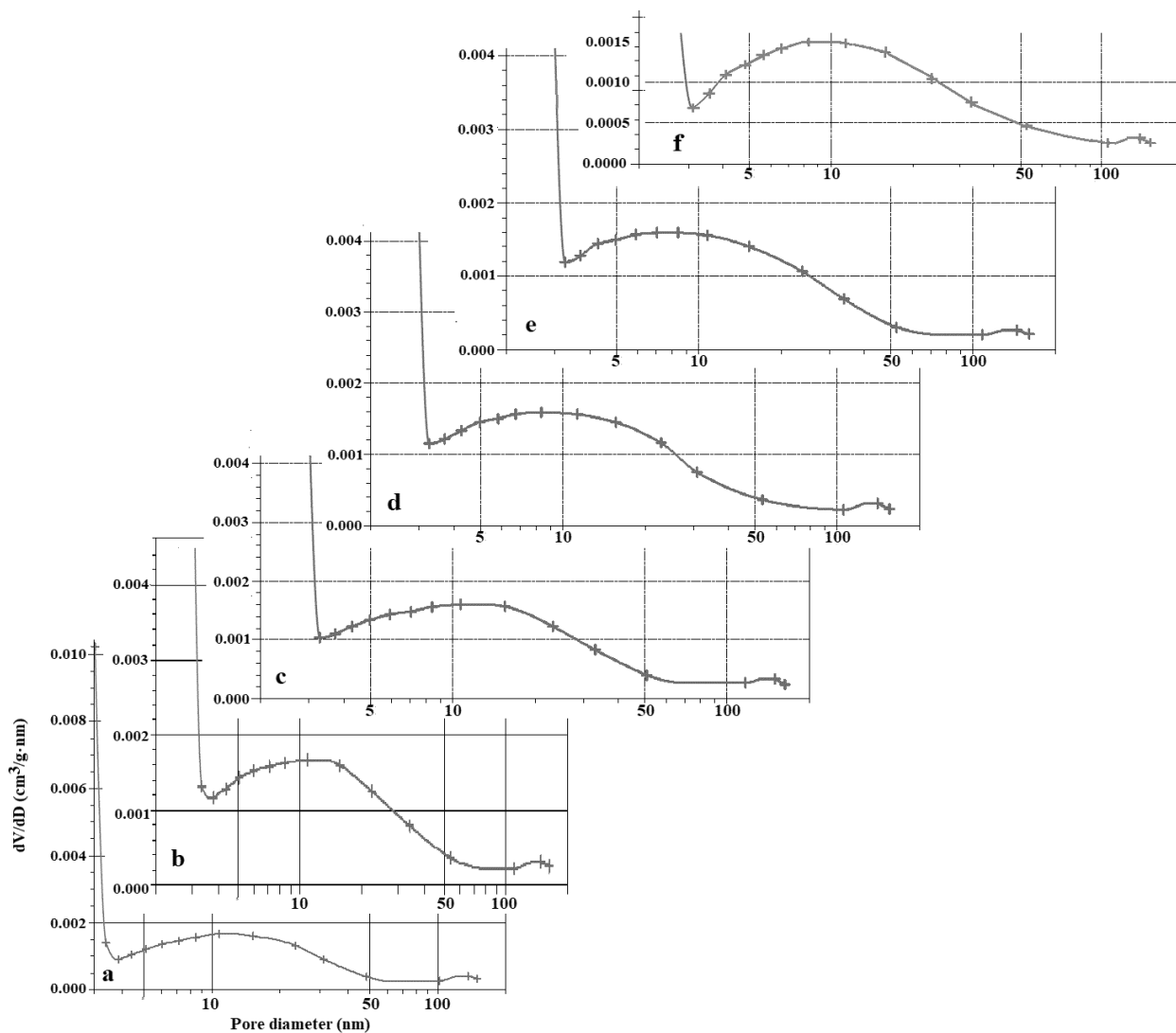
The average mesopore diameter  $D_{BJH}$  slightly changes as a result of calcination, and as the pore size distribution curves  $V(D)$  (see Fig. 10) show, the volume of mesopores decreases, although the difference between the distribution of mesopores in samples calcined at 400 and 800 °C is insignificant. The nature of the pore size distribution (maximum at  $\approx 12$  nm) remains the same, and this is clearly seen in Fig. 11, which shows the differential pore size distribution curves  $dV/dD$  for heulandite calcined at different temperatures.



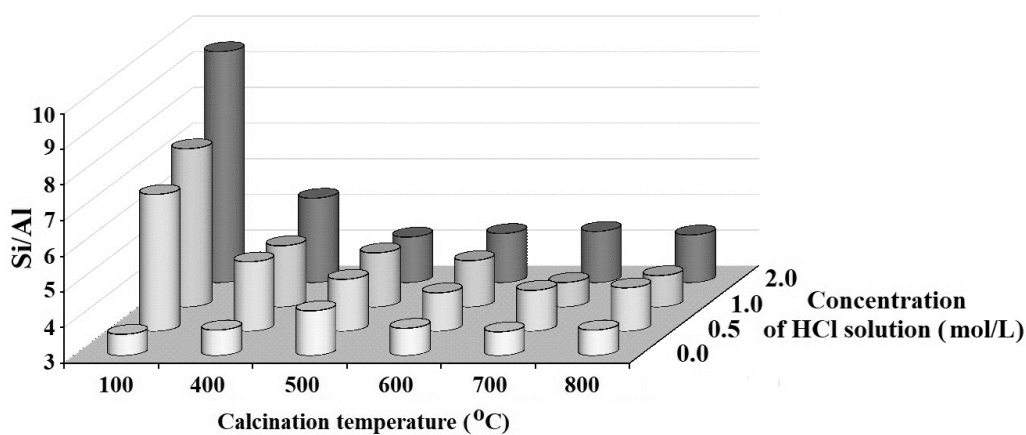
**Fig. 9.** Pore size distribution volume  $V$  vs. pore diameter  $D$  (left) and differential  $dV/dD$  vs. pore diameter (right) curves calculated by BJH model for original heulandite (0) and its acid-treated forms



**Fig. 10.** Pore size distribution curve volume vs. pore diameter  $V(D)$  calculated by BJH model for original (0) and calcined at 400 °C (a) and 800 °C (b) heulandite samples



**Fig. 11.** Pore size distribution  $dV/dD$  curves calculated on the basis of the BJH model from desorption isotherms measured on Georgian heulandite calcined at 100 (a), 400 (b), 500 (c), 600 (d), 700 (e) and 800 °C(f)



**Fig. 12.** The Si/Al molar ratio calculated from XR-ED spectra in samples calcined at different temperatures and treated with HCl solutions of various concentrations



Thus, heat treatment does not lead to significant changes in systems of micropores and mesopores, but causes significant structural changes in heulandite. According to measured changes in the Si/Al molar ratio in samples subjected to calcination and then treated with hydrochloric acid solutions (see Fig. 12), such pre-heat treatment significantly reduces the degree of dealumination, especially for samples amorphized by high-temperature calcination.

Perhaps these results are not of practical importance, since at an annealing temperature of 600 °C and above, the corresponding samples lose their adsorption properties, but the structure and properties of the calcined and acid-treated samples require further study and consideration.

### CONCLUSIONS

Acid treatment leads to significant dealumination and decationization of heulandite-containing tuff from the Tedzami-Dzegvi deposit, Eastern Georgia, without amorphization, sharply increases the surface area and volume of

micropores available for large molecules, and causes changes in the mesoporous system, leading to the prevalence of pores with a diameter up to 4 nm. Heat treatment causes dehydration continuing up to 800 °C, amorphization starting at 200 °C, formation of wairakite at 500 °C, and does not lead to significant changes in pore systems. Heat treatment increases the acid resistance of heulandite by reducing the degree of dealumination after the sample is treated with hydrochloric acid solution. The results obtained show the possibilities of obtaining effective molecular sieves, adsorbents and ion exchangers by modifying natural heulandite.

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## Кислотна та термічна обробка природного гейландиту

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*Кислотна обробка природних цеолітів вважається ефективним методом «поліпшення» їхньої структури та властивостей, серед яких особливе місце припадає термостійкість, особливо для каталітичного застосування цеолітів. Досліджено вплив розчинів соляної кислоти концентрацією до 2 mol/L та прожарювання при температурах до 1100 °C на структуру та властивості гейландитмісного туфу грузинського родовища Дзегві-Тедзамі, відібраного для створення нових бактерицидних цеолітових фільтрувальних матеріалів для очищення та знезараження води з різних джерел, досліджували рентгенівськими енергетичними дисперсійними спектрами, дифрактограмами та термічним аналізом, а також адсорбційними методами води, бензолу та азоту. Встановлено, що кисле середовище призводить до значного dealюмінівання (молярне відношення Si/Al зростає з 3.6 до 9.5) та декатіонізації (сумарний заряд іонів металу на атом Al зменшується з 1 до 0.68) зразка; розчини соляної кислоти не призводять до аморфізації мікропористої кристалічної структури цеоліту, а поступово розчиняють її. В результаті кислотної обробки також різко збільшується об'єм мікропор, доступних для великих молекул (від  $\approx 7$  до  $80\text{--}90$  мм<sup>3</sup>/г) і площа поверхні (від  $\approx 13$  до  $120\text{--}175$  м<sup>2</sup>/г), а також зміни мезопористої системи, що призводять до переважання пор діаметром до 4 нм. Нагрівання гейландиту призводить до ступінчастої дегідратації, що триває до  $\approx 800$  °C, аморфізації, починаючи з  $\approx 250$  °C, і структурних змін: перехід у фазу метастабільного гейландиту В при  $\approx 340$  °C не фіксується, але при  $\approx 500$  °C утворюється вайракіт (Ca(Al<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>)<sub>2</sub>·2H<sub>2</sub>O), при температурах вище  $\approx 1000$  °C аморфний алюмосилікат містить кристалічні включення кристобаліту (поліморф SiO<sub>2</sub>),  $\alpha$ -кварцу, альбіту (Na(AlSi<sub>3</sub>O<sub>8</sub>)), гематиту (Fe<sub>2</sub>O<sub>3</sub>) та магнетиту (FeO·Fe<sub>2</sub>O<sub>3</sub>); викликані нагріванням зміни мікро- та мезопорових систем незначні. Показано також, що термообробка підвищує*

кислотостійкість гейландиту, що виражається в зниженні ступеня dealюмінівання після кислотної обробки прожарених зразків. Таким чином, кислотна і термічна обробка гейландиту дають змогу отримати матеріали з різними сорбційними та іонообмінними властивостями.

**Ключові слова:** гейландит, dealюмінівання, декатіонізація, дегідратація, аморфізація

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