

Characterization of Georgian, Kazakh and Armenian Natural Heulandite-Clinoptilolites

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Natural zeolites are recognized as a fairly effective filtering material for the purification of various special waste and municipal waters. The aim of the study was to characterize heulandite-clinoptilolite-type zeolites of Georgian, Kazakh and Armenian origin selected for the creation of new bactericidal zeolite filter materials for purification and decontamination of water from various sources. According to chemical composition and X-ray diffraction data, the sample from the Rkoni plot of the Tedzami-Dzegvi deposit, Georgia, is a sodium form of high-silica heulandite mixed with a small amount of chabazite, the zeolite from the Chankanay deposit, Kazakhstan, is a mixture of calcium heulandite and chabazite, and the zeolite from the Nor-Kokhb deposit, Armenia, is a typical calcium clinoptilolite. Powder X-ray diffraction patterns show a high content of zeolite phase (70-90%) and determine the main inorganic impurities; the presence of a developed system of micropores is confirmed by Fourier transform infrared spectra; the samples are also characterized by different developed systems of mesopores with a maximum diameter of 120 nm. © 2022 Bull. Georg. Natl. Acad. Sci.

heulandite-clinoptilolite, Tedzami-Dzegvi, Chankanay, Nor-Kokhb

Treatment of wastewater and water used for municipal and industrial purposes refers to the removal of suspended colloids and solids, as well as several dissolved substances. Among all avail-

able water treatment technologies, adsorption is considered the best option because of convenience, ease of operation, and simplicity of design [1]. Activated carbon, clay minerals, biopolymers, and

zeolites [2-7] have been widely used for adsorption of ions and organics in the tap water and wastewater treatment. Zeolites (aluminosilicates of general formula $M_x[Al_xSi_yO_{2(x+y)}]mH_2O$, $M^+ = Na^+, K^+, \dots, \frac{1}{2}Ca^{2+}, \frac{1}{2}Mg^{2+}, \dots$) have open, “framework” structure with cages and channels that determine molecular-sieve, sorption and other properties; zeolites adsorb a variety of heavy metals and ammonia, and remove a wide range of pollutants. Natural zeolites are usually characterized by a developed system of meso- and macropores in which large organic molecules, supramolecular aggregations, and even microorganisms can be adsorbed or immobilized. Previously [4], it was found that natural zeolites containing “usual” exchangeable ions M^+ are capable of inhibiting or stimulating the vital activity and viability of microbial organisms, and the nature of the effect depends on the nature and pretreatment of the sample, which changes the mesopore system.

Today it is recognized that natural zeolites outperform conventional granular materials in water purification, they are cost-effective, abrasion resistant, non-toxic and environmentally friendly, especially in the treatment of such special wastewater streams as acid mine drainage, landfill leachate, nuclear fallout, and urban runoff [5-8].

Among natural zeolites, heulandite-clinoptilolite is one of the most widespread in Nature, well studied and widely used as an adsorbent, ion exchanger and catalyst in industry [9], construction [10], medicine [11], agriculture [12] and environment protection [13].

The aim of this study was to characterize heulandite-clinoptilolite samples of Georgian, Kazakh and Armenian origin selected for implementation of the project “Scientific substantiation of the possibility of creating new bactericidal zeolite filter materials for purification-decontamination of water from various sources” granted by the International Scientific Technical Center.

Materials and Methods

Materials. Heulandite-clinoptilolite-containing rock from the Rkoni plot of Tedzami deposit (Eastern Georgia, [14]), the zeolitic tuff of Chankanay deposit (Kazakhstan, Almaty region [15]), successfully used in fish-breeding [16], and the tuff of Nor Kokhb deposit (Armenia, Noyemberian region [17,18]) were used as starting material.

Preparation of zeolite samples includes 1) grinding of rock using a standard crusher, 2) fractionation of obtained material using a set of sieves according to the standard requirements for filtering material for water purification (the particle size 1-1.4 mm or 14-16 mesh), 3) washing with distilled water or dilute HCl solution (0.025 N) to remove clay impurities and improve ion-exchange properties, and 4) drying of the prepared samples of the original zeolites under static conditions, first in air and then in a thermostat at a temperature of 95-100°C.

Characterization. Characterization of zeolite samples includes data on their chemical composition, structural features identified by the X-ray diffraction (XRD) patterns and Fourier transform infrared (FTIR) spectra, as well as characteristics of micro- and meso-porosity obtained from low-temperature nitrogen adsorption/desorption isotherms. Chemical composition of zeolites of the Georgian and Kazakh origin was calculated from the X-ray energy dispersive (XRED) spectra (scanning electron microscope JSM-6490LV equipped with INCA Energy 350 XRED analyzer), chemical composition of the Armenian zeolite was determined by classical elemental analysis methods. Powder XRD were obtained from a diffractometer D8 Endeavor (Bruker, Germany) employing the Cu-K α line ($\lambda = 0.154056$ nm); the samples were scanned in the 2θ range of 5° to 50° with a 0.02° step at a scanning speed of 1°/min. Infrared spectra were collected by a 10.4.2 (Perkin-Elmer, UK), a Prestige-21 (Shimadzu, Japan), and a Nexus (Thermo Nicolet, USA) spectrometer for samples of the Georgian, Kazakh and Armenian origin,

respectively, over the range of 400–4000 cm⁻¹ with a resolution of 2 cm⁻¹ using the KBr pellet technique for sample preparation. Nitrogen adsorption/desorption isotherms were measured at 77 K using ASAP 2020 Plus analyzer (Micromeritics, USA) for samples of the Georgian and Kazakh origin, and a NOVAe 2200 analyzer (Quantochrom, USA) for samples of the Armenian origin using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) models for data analysis.

Results and Discussion

Chemical composition. Heulandite-clinoptilolite belongs to the HEU group (crystal chemical data [Ca₄(H₂O)₂₄] [Al₈Si₂₈O₇₂]-HEU [19]), but the chemical composition of its varieties is characterized by remarkable changes in the Si/Al ratio (from 2.7 to 5.5) as well as in the content of exchangeable cations [20]. Chemical composition described by averaged empirical formulas of dehydrated zeolites is given in Table 1.

Table 1. Chemical composition of zeolite samples

Zeolite origin	Empirical formula of dehydrated zeolite
Rkoni plot of Tedzami deposit, Georgia	Na _{0.25} K _{0.06} Ca _{0.19} Mg _{0.15} [AlSi _{3.6} O _{9.2}]
Chankanay deposit, Kazakhstan	Na _{0.115} K _{0.079} Ca _{0.228} Mg _{0.175} [AlSi _{2.96} O _{7.92}]
Nor Kokhb deposit, Armenia	Na _{0.05} K _{0.07} Ca _{0.36} Mg _{0.08} [AlSi _{5.12} O _{12.24}]

According to the ratio of silicon and aluminum atoms in zeolite lattice and XRD data, the sample from the Rkoni plot is a high-silica heulandite (Si/Al=3.6) mixed with a small amount (≈10%) of chabazite (Si/Al=2) and containing relatively high content of sodium exchangeable ions. XRED spectra show the presence of titanium atoms in the crystal lattice (one Ti per 200±20 Si and Al atoms), as well as calcium and iron atoms composing amorphous or crystalline impurity inclusions. The zeolite from the Chankanay deposit is a mixture of heulandite (≈40%), chabazite (≈40%) and quartz

(≈20%) containing relatively high content of calcium ions, titanium is present in the amount of one atom per 110±10 Si and Al atoms, iron atoms constitute amorphous or crystalline impurity inclusions. The zeolite from the Nor Kokhb deposit is a typical calcium clinoptilolite (Si/Al=5.12) also containing 7% of kanemite (HNaSi₂O₅·3H₂O), 5% of quartz, 4% of natrolite ([Al₆Si₆O₂₄]-SOD) and 3% of sigma-2 zeolite ([Si₆₄O₁₂₈]-SGT); in its chemical composition is relatively large amount of iron atoms, as well as a small amount of titanium, phosphorus and sulfur atoms.

Structural features. Heulandite and clinoptilolite crystals are distinguished by their characteristic monoclinic appearance; idealized cell data: space group C2/m, a = 17.5 Å, b = 17.6 Å, c = 7.4 Å, β = 116.1° [19]. The heulandite-clinoptilolite framework (Fig. 1, left) is characterized by essentially two-dimensional system of open channels formed by 10- and 8-membered rings; channels parallel to [001] with elliptical 10-ring and 8-ring (Fig. 1, middle) apertures are interconnected at right angles by one-dimensional system of slightly smaller 8-ring channels (Fig. 1, right) parallel to [100].

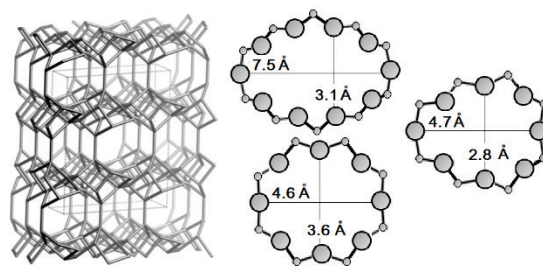


Fig. 1. Heulandite-clinoptilolite framework, 10- and 8-membered rings viewed along [001], and smaller 8-rings viewed along [100].

Identification of zeolites is based on the 2Θ (°) values of the three most pronounced low-angle reflections in the powder XRD pattern. According to simulated patterns for the HEU type zeolites [21], such three reflections for heulandite (Si/Al=2.88) are 9.85, 11.07, and 22.22°, for clinoptilolite (Si/Al=4.84) – 9.88, 11.19, and 22.49°, corresponding to the (020), (200), and (400)

reflections, respectively. Experimentally recorded XRD patterns generally coincide with the simulated patterns, the assignment of peaks to Miller indices is given in our recent publication [14].

The presence of a developed system of micropores is confirmed by the FTIR spectra in which, along with the bands typical of aluminosilicates (asymmetric stretching of OH groups at $\approx 3400\text{ cm}^{-1}$, bending vibration of H–OH at 1630 cm^{-1} and of bridging –OH–O– at 1460 cm^{-1} , internal at 1380 cm^{-1} and external at 1040 cm^{-1} asymmetric stretching), bands of external (780 cm^{-1}) and internal (720 cm^{-1}) symmetric stretching, as well as external tetrahedra double ring vibration (600 cm^{-1})

and a shoulder of internal tetrahedra bending vibration (440 cm^{-1}), characteristic of microporous zeolite structures, are observed; registered vibration bands with corresponding frequencies are listed in Table 2.

The band of external asymmetric stretching vibrations in the IR spectrum of Georgian heulandite has two maxima – at 1065 cm^{-1} , which usually is considered as characteristic of clinoptilolite, and at 1056 cm^{-1} , which is close to the characteristic value for heulandites (1050 cm^{-1}). The same band in the spectra of Kazakh heulandite and Armenian clinoptilolite is shifted to low frequency, 1010 cm^{-1} and 1040 cm^{-1} , respectively.

Table 2. The IR vibration bands (cm^{-1}) in spectra of heulandite-clinoptilolites

IR vibration band	Zeolite origin		
	Rkoni plot of Tedzami deposit	Chankanay deposit	Nor Kokhb deposit
Asymmetric stretching of OH groups	3400*	3420*	3407*
Bending vibration of H–OH	1630	1636	1634
Bending vibration of bridging –OH–O–	1500	1458	1451
Internal asymmetric stretching	1200**	1210**	1377
External asymmetric stretching	1056, 1065	1010	1040
External symmetric stretching	778	790	776
Internal symmetric stretching	724	675, 722	722
External tetrahedra double ring vibration	520, 600	536, 602	598
Internal tetrahedra bending vibration	450, 463, 470	470, 493	440

* maximum absorbance of broad peak; ** shoulder at broad peak

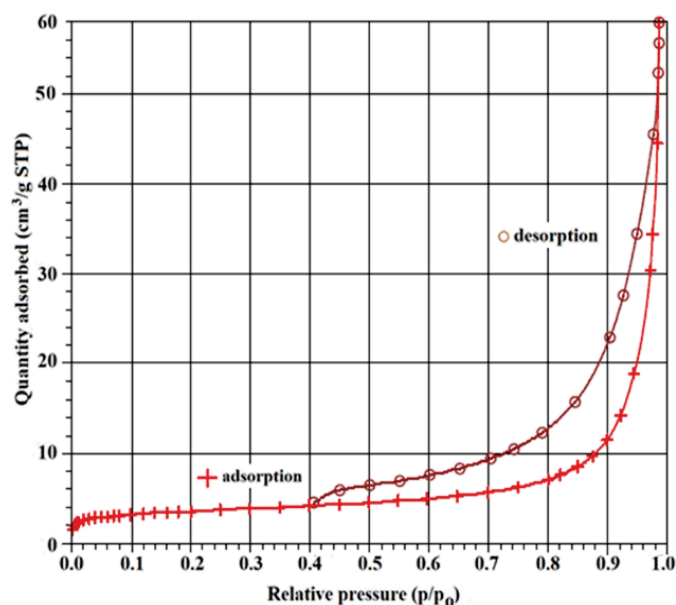


Fig. 2. N_2 adsorption-desorption isotherms on heulandite from Rkoni plot of Tedzami deposit.

Porous system. The low-temperature adsorption-desorption isotherms of nitrogen on studied zeolites (a typical isotherm is shown in Fig. 2) 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 mesopores.

The largest quantity of adsorbed nitrogen molecules was found in heulandites ($50-60 \text{ cm}^3/\text{g}$), in clinoptilolite it does not exceed $12 \text{ cm}^3/\text{g}$; the porosity parameters for heulandites are given in Table 3. Heulandite of Georgian origin is

characterized by high surface area of micropores ($>12 \text{ m}^2/\text{g}$) and a system of mesopores with an average diameter of 20 nm and a maximum diameter of up to 120 nm, heulandite of Kazakh origin has a relatively small BET surface area and a different mesopore system (see Fig. 3) with the same maximum diameter. Clinoptilolite of Armenian origin has surface area of micropores of $\approx 4 \text{ m}^2/\text{g}$ and reported high total BET surface area ($19.4 \text{ m}^2/\text{g}$, [18]), the dV/dD curve shows a broad distribution of mesopores in the range of 20-80 nm.

Table 3. Characterization of porosity in heulandites

Parameter	Zeolite origin	
	Rkoni plot of Tedzami deposit	Chankanay deposit
BET surface area, m^2/g	12.8	2.75
Total volume of pores less than 155 nm diameter, cm^3/g 177 nm diameter, cm^3/g	0.0895	0.0732
BET Adsorption average pore diameter, nm	28	106
BET Desorption average pore diameter, nm	28	106
BJH Adsorption average pore diameter, nm	38	66.3
BJH Desorption average pore diameter, nm	17.2	24.3

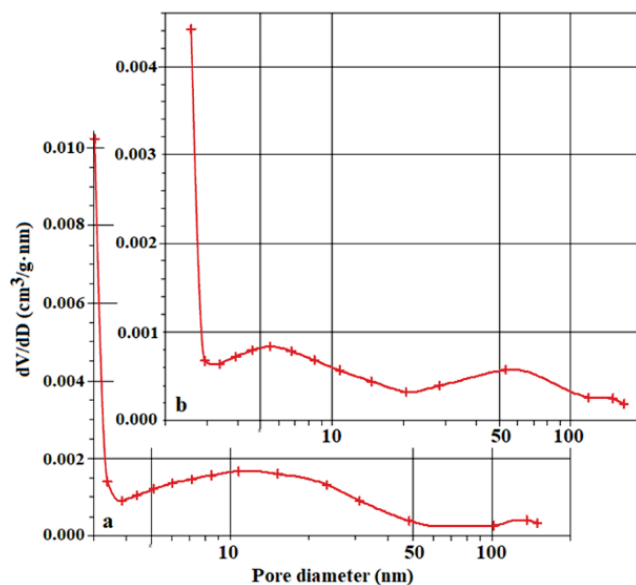


Fig. 3. Pore size distribution dV/dD curves for Georgian (a) and Kazakh (b) heulandites.

Conclusion

As a result of studies, carried out on zeolite tuffs of Georgian, Kazakh and Armenian origin, it was found that the zeolite from the Rkoni plot is high-silica heulandite ($\text{Si/Al}=3.6$) with an admixture of chabazite, the zeolite from the Chankanay deposit is a mixture of heulandite and chabazite with a high content of quartz, and the sample from the Nor Kokhb is a typical clinoptilolite ($\text{Si/Al}>5$). The presence of a developed system of micropores in all

three samples is confirmed by XRD patterns and FTIR spectra; the samples have different specific surface areas, as well as different mesopore systems with a maximum diameter of up to 120 nm.

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ფიზიკური ქიმია

საქართველოს, ყაზახეთის და სომხეთის ბუნებრივი ჰეილანდიტ-კლინოპტილოლიტის თვისებები

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ბუნებრივი ცეოლითები აღიარებულია, როგორც საკმაოდ ეფექტური მფილტრავი მასალა სხვადასხვა სპეციალური ჩამდინარე და საყოფაცხოვრებო წყლების გასაწმენდად. კვლევის მიზანი იყო სხვადასხვა წყაროდან მიღებული წყლის გამწმენდისა და დეზინფექციისთვის ახალი ბაქტერიციდული ცეოლითური მფილტრავი მასალების შესაქმნელად შერჩეული

ქართული, ყაზახური და სომხური წარმოშობის ჰეილანდიტ-კლინოპტილოლიტის ტიპის ცეოლიტების დახასიათება. ქიმიური შედგენილობისა და რენტგენული დიფრაქტოგრაფიების მიხედვით, ნიმუში საქართველოს თეძამი-ძეგვის საბადოს რკონის უბნიდან არის მაღალსილიციუმისანი ჰეილანდიტის ნატრიუმისანი ფორმა, რომელიც შერეულია მცირე რაოდენობით შაბაზიტთან, ყაზახეთის ჩანკანაის საბადოდან მიღებული ცეოლითი წარმოადგენს კალციუმისანი ჰეილანდიტისა და შაბაზიტის ნარევეს, ხოლო სომხეთის ცეოლითი ნორ-კოჰის საბადოდან, ტიპური კალციუმისანი კლინოპტილოლიტია. ნიმუშების ფხვნილის რენტგენული დიფრაქტოგრაფიები აჩვენებს ცეოლითური ფაზის მაღალ შემცველობას (70-90%) და განსაზღვრავს ძირითად არაორგანულ მინარევებს; მიკროფორების განვითარებული სისტემის არსებობა დასტურდება ფურიეს გარდაქმნის ინფრაწითელი სპექტრებით; ნიმუშებს ასევე ახასიათებს მეზოფორების განვითარებული განსხვავებული სისტემები მაქსიმალური დიამეტრით 120 ნმ.

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