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Structural and Ion-Exchange Properties of Natural Zeolite

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1. Introduction

Intensive studies of natural and synthetic zeolites properties are being held from the middle of 60-70-ies. Among the various examples of zeolites application it is sufficient to mention emission and purification of normal paraffin hydrocarbons, catalytic reactions of hydrocarbons, extraction of radioactive isotopes, obtaining carriers for catalysts, release of enzymes and removal of impurities polluting the atmosphere [1-3]. The interest of researchers towards such alumosilicates is connected with unique properties of zeolites: an extremely high adsorption capacity, catalyzing action, thermal stability and resistance in different chemical environments. The relative simplicity along with relatively low cost thereof stipulates for a significant availability for mass application.

Zeolitic rocks are widely distributed in the territory of Kazakhstan and are economically and ecologically cost-efficient raw material for creating unique ion-exchange sorbents with selective properties. Development of natural zeolites modification methods opens a possibility of purposeful construction of chemically modified inorganic sorbents able to substitute synthetic analogues and of obtaining new compositions with a prospect of widening the range of ion-exchange materials. The results of the study of structural, physicochemical and ion-exchange properties of natural alumosilicates allow developing the theoretical bases for the directed alternation of the complex of useful properties of natural minerals, meeting the main criteria required for sorption materials.

2. Investigation of physico-chemical properties of natural zeolite

Natural zeolites fields explored in Kazakhstan determine the intensive development of studies in different application areas. In spite of the numerous publications, the physicochemical properties of natural zeolites are still not sufficiently studied.

A quick diagnosis of natural zeolites can be significantly enhanced through a combination of such methods of analysis as X-ray phase and thermographic study. Recording the diffraction pattern makes it possible to state a presence of zeolites isostructural to heulandite even in the mixtures [4]. Analysis of thermogram allows determining the species within this group qualitatively. To that effect you can use the low-temperature area up to 400⁰C. According to XRF data, the main phase of zeolite tuff studied is clinoptilolite-heulandite (Figure 1). The distinct peaks 9,58; 8,68; 7,42; 5,69; 5,07; 4,58; 4,37; 3,69; 3,62; 3,45; 3,23 ; 3,03 Å typical for clinoptilolite appear on natural zeolite's diffraction pattern. There are montmorillonite, plagioclase and quartz among other phase components. Comparison of the results with literature data obtained for monophasic clinoptilolite shows that the material in question is close to clinoptilolite according to the composition but it has higher sodium, calcium and iron contents (Table 1). The study thereof showed that it was characterized by Si/Al ratio equal to 3,83.

As a result of the studies held it was stated that zeolite tuff of Shankhanai field of Kazakhstan contained up to 70% of the plate-like shape main product with high ratio between silica and aluminum oxides (heulandite – clinoptilolite). Brown-red colouring thereof specifies to the presence of fine iron oxides.
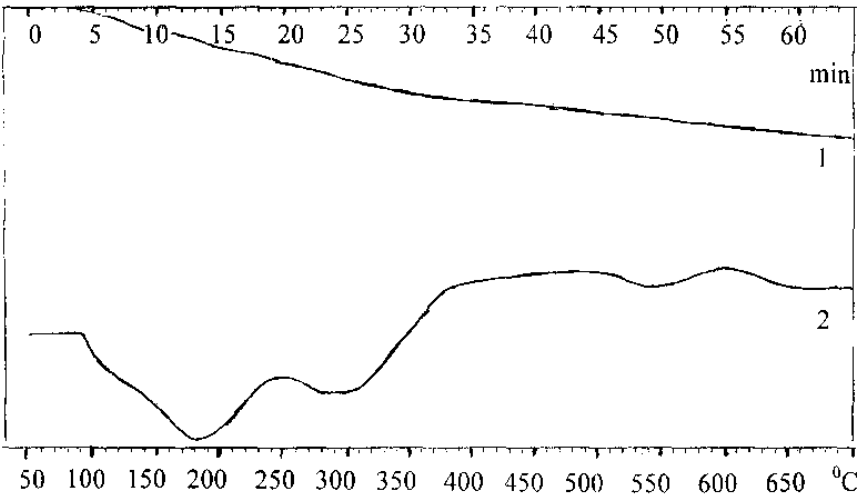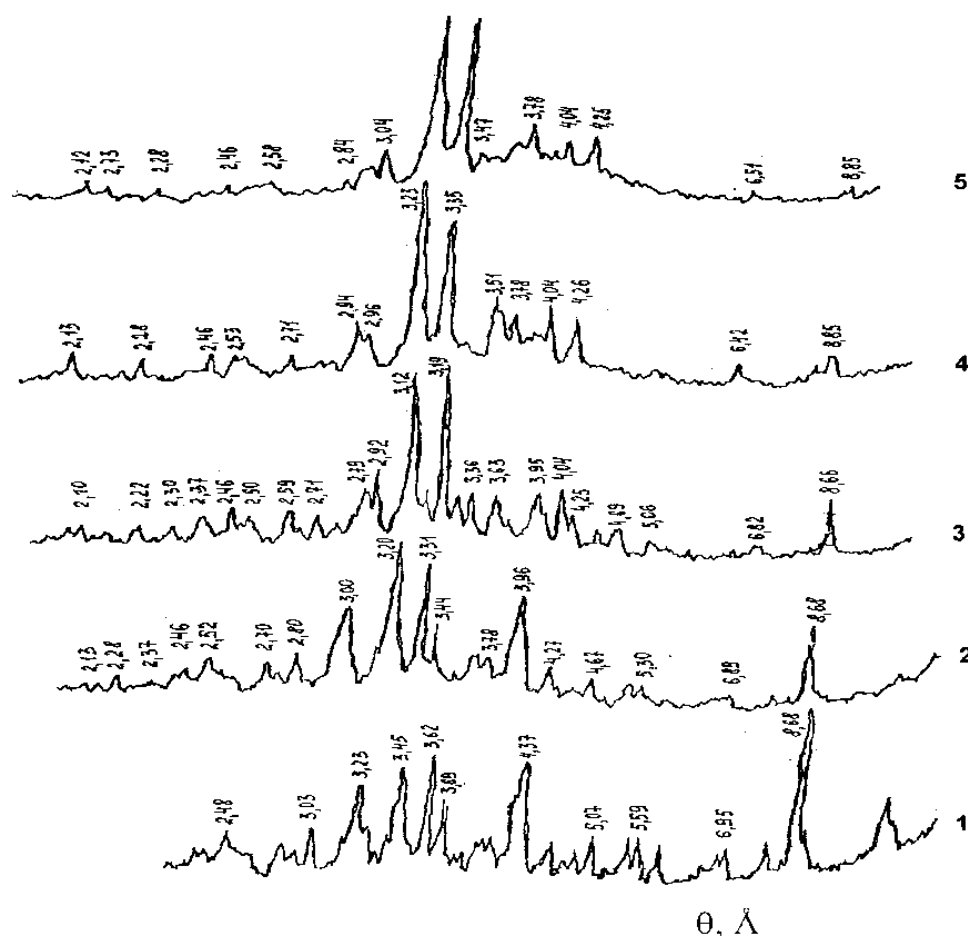

Figure 1. Derivatogram of natural zeolite. 1 – TG; 2 – DTA.

№	HCl, N	The composition of clinoptilolite, %							SiO₂/
		SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	Fe_2O_3	Al_2O_3
1	---	58,08	15,16	2,30	1,42	4,92	2,53	5,95	3,83
2	3 (20-22⁰C, 24 h)	58,19	15,09	1,75	1,27	4,02	2,28	5,60	3,86
3	12 (20-22⁰C, 24h)	58,86	15,05	1,77	1,25	4,05	2,34	5,54	3,91
4	1,5 (96-98⁰C, 6h)	69,16	15,43	1,67	1,18	2,24	1,41	4,95	4,48
5	Concentration (96-98⁰C, 6h)	79,10	6,20	1,24	1,01	0,58	0,29	0,70	12,80

Table 1. Changing the chemical composition of clinoptilolite.

The results of thermographic studies are given in the Figure 2. Differential thermal analysis (DTA) data show that the dehydration of clinoptilolite-containing tuff begins from the

lowest temperatures, approximately from 60°C, and proceeds continuously over a broad temperature range up to 400°C. The mass loss at this temperature reaches 3,3%. The total mass loss while heating zeolite up to 700°C is 6,7%. Water release in zeolite proceeds continuously and smoothly, as evidenced by the mass loss (TG) curve. The DTA curve of the raw zeolite exhibits several endothermic effects with minimums at 100; 180; 280; 550 and 660°C. The character of DTA and TG curves over the entire temperature range of 50–700°C is indicative of several forms of bound water in minerals [4]. The presence of two endothermic effects due to the release of adsorbed water indicates that active sites in clinoptilolite microcavities are inhomogeneous in energy. The natural zeolite heating curve shows the loss of weakly bound adsorption water and capillary-condensation water at 100°C. The energy of interaction of water molecules with potassium ions is lower, and the endothermic effect at 170°C is due to the desorption of water molecules bound as K^+, as well as due to zeolite oxygen framework. Weakly expressed endothermic effects displayed by zeolitic rock thermograms are caused by foreign impurities. At 550°C it is stipulated by the detachment of hydroxyl groups. As follows from the given experimental data, the initial natural zeolite exhibits a fairly high thermal stability (above 700°C).

1 –natural zeolite (№1); after treatment: 2 – 3 N HCl solution, 22-25⁰C (№2); 3 – 12 N HCl solution, 22-25⁰C (№3); 4 – 1,5 N HCl solution, 96-98⁰C (№4); 5 – concentrated solution of HCl, 96-98⁰C (№5)

Figure 2. The diffractograms of the zeolite samples

It is known that in the process of natural mineral sorbents treatment with acids their pore structure develops. Therefore, we tested different ways of acid processing of natural zeolite with hydrochloric acid. From the standpoint of environmental friendliness of the process (simplicity of purification and regeneration of spent solutions), HCl was used as a modifying acid for sorbent treatment, since the wastes of dilute hydrochloric acid are much easier to purify of leaching products and to neutralize.

In the experiments, we varied the acid concentration, temperature and duration of processing. The effectiveness of activation was evaluated in terms of the total porosity of a sorbent and specific surface area thereof.

Activation typically involves three stages: removal of exchangeable cations, framework dealumination and formation of an amorphous silicon-oxygen phase. The sequence and intensity of the stages are determined by processing conditions and the specific features of zeolites. Acid modification of the investigated zeolite with 3 and 12 N HCl solution within the day (№ 2 and №3) at room temperature showed that the value of silica modulus (Table 1) was not changing essentially. More stringent processing conditions lead to a sharp increase in the silica modulus (Si / Al). At modification by 1,5 N HCl solution by heating (№ 4) clinoptilolite is subject to dealumination and removal of cations without significant destruction of the crystal lattice in comparison with the treatment thereof under the same conditions with a concentrated acid (№ 5). In the latter case the amorphous phase of zeolite forms. These results confirm the XRF data (Figure 1). Comparison of natural and modified samples radiographs indicates to a decrease in the intensity of main reflection characteristics of the mineral up to complete disappearance due to the amorphization of the structure and changes in zeolite cation composition after mineral acid treatment.

The obtained results show that removal of cations and dealumination are insignificant under milder conditions of acid processing. More severe activation conditions result in intensification of these processes. The removal of exchangeable zeolite cations and occupation of the free sites by protons have an effect on the cationic density of the framework and can change the sizes of channel windows. The removal of aluminum from mineral framework also results in partial degradation of zeolite crystal structure.

Location and exploration of large deposits of natural zeolites in different regions of Kazakhstan creates significant scientific-technical prospects for the complex use of natural sorbents, especially for the creation of nanomaterials on their basis.

For the study of morphology of the porous structure of natural zeolites and those ones, activated by acidic treatment, adsorption-desorption measurements have been carried out (Table 2). Natural zeolite (sample №1) is characterized, by the isotherm data, by mesoporosity. It also contains some micropores, because nitrogen vapors are absorbed to some degree at low pressures (p/p_s less than 0,1). Its treatment with a 3 N HCl solution (№2) pracically does not change the surface characteristics of the sorbent, and the treatment by a 12 N HCl solution (№3) results in an increase in the total pore volume by a factor of about 2. Porocity increases considerably with the activation with a 1,5 N HCl upon heating (№4). For the initial sample the total pore volume constitutes 0,019574, whereas for the activated ones – 0,19611 (№2);

0,031348 (№3); 0,064101 (№4); 0,122297 (№5) cm³/g. Chemical treatment increases porosity of zeolite by a factor of 6. Differential curves of the pore size distribution have shown that the studied samples possess mainly mono- and bi-dispersion structures. Natural zeolite possesses the mono-dispersion structure with a large maximum in the area of mesopores d ~ 30 Å. For the sample №3, besides, an increase in the field of d~ 20 Å is observed, i.e. the activation of the mineral with 12 N acid in the usual conditions results in the development of micropores, the volume of which increases more than 5 times (Table 2). Differential dimensional spectra of such samples are characterized by the narrow distribution. The sample №4 is characterized by bioporosity, the volume of mesopores increases by a factor of 1,5 and microporosity – by a factor of 217. The further activation of zeolite also leads to an increase in the micro- and mesoporous structure with an extension of the range of the mesopores (№5).

№ sample	$S_{БЭТ}$, m²/g	St-diagram, m²/g	Vmicropores, cm³/g	Vmesopores, cm³/g	ΣVpores, cm³/g
1	5,8714	7,8482	0,000162	0,019412	0,01957
2	6,8487	8,1363	0,000379	0,019232	0,019611
3	9,8917	9,9675	0,000841	0,030507	0,031348
4	108,5298	21,8786	0,035250	0,028851	0,064101
5	181,8055	47,9273	0,050992	0,071305	0,122297

Table 2. Surface area and porosity of the zeolite samples

In the NMR spectra of the zeolite samples № 4 and №5 alongside with the signals from aluminum atoms in the tetrahedral coordination (56 ppm), show the signals with the size of chemical shift of 3 and 11 ppm., characteristic for the atoms of aluminum in the octahedral medium by oxygen (Figure 3). With an increase in decationation their intensity increases. An increase in decationation of zeolite leads to an increase in the intensity of the signal from the atoms of alluminum in the octahedral coordination. On the whole the predominant part of aluminum atoms remains in the structure of the carcass also after removal of cations of zeolite.
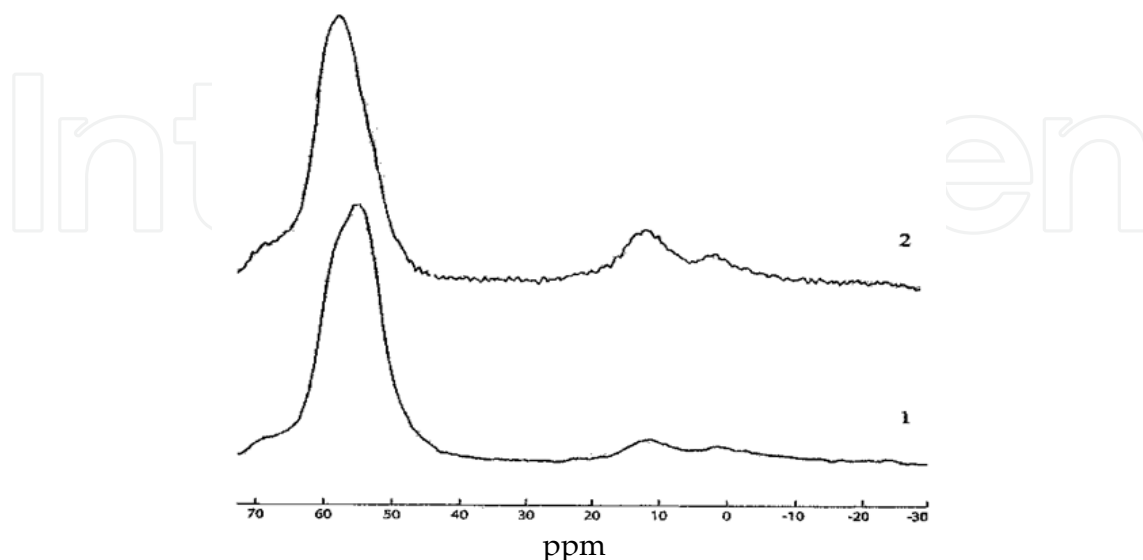

Figure 3. ²⁷Al NMR spectra of zeolite after acid treatment. 1 - sample №4 (1,5 N solution of HCl, 96-98⁰C); 2 - sample № 5 (conc. solution of HCl, 96-98⁰C)

3. Investigation of ion-exchange properties of natural zeolite

The intensive use of zeolites in various fields of science and practice is based largely on their ion exchange properties, which are one of the main parameters that characterize their sorption and technological properties. The use of zeolites as selective sorbents can solve a number of important problems of technology and environment (Table 3). In this regard, commercial development of deposits of natural zeolites, which due to low cost can be applied in various fields where the use of synthetic analogues is marginal, is required.

Method of application	Zeolite	Fields of application
Without regeneration	clinoptilolite mordenite	Cleaning of waste water from the radioactive ions ^{137}Cs, ^{90}Sr, followed by burial of the zeolites. Treatment of domestic wastewater from ammonium nitrogen with followed by the use of zeolite as ammonium fertilizer
	clinoptilolite	Purification of wastewater from the nonferrous metals using zeolites as a flux
With the self refresh	clinoptilolite mordenite	The use of zeolites as filter material for water treatment
	clinoptilolite	The introduction of zeolites in the soil to increase the duration of fertilizer
Regeneration with solutions	clinoptilolite mordenite	Concentration and separation of alkali metals from technological solutions and natural waters
	clinoptilolite	Concentration of Sr from the waste and natural waters
	clinoptilolite mordenite	Concentration of non-ferrous metals from technological solutions, waste and natural waters

Table 3. Use of natural zeolites in ion-exchange process

Acid resistance is crucial to the technological application of clinoptilolite. The study of the conditions for maintaining its crystallinity allows creating a basis to obtain the samples intermediate in the degree of cations removal and dealumination which have acidic properties.

It is established [5] that two stages of acid activated cation removal - ion exchange and dealumination – are observed as a result of zeolite reaction with dilute solutions. The former may be connected with polycationicity of mineral. In the latter case, the divalent cations Ca^{2+} are harder replaced by hydrogen than monovalent ones. In processing zeolites with more concentrated acid solutions there is a shift to the solution of aluminum from tetrahedron with the formation of high-silicon core. The crystal structure thereof can be preserved up to a very high degree of cations removal and dealumination.

In practice, in most cases, clinoptilolite containing material is rarely used in its natural form and it is usually subjected to additional chemical pre-treatment to improve its sorption,

mainly ion-exchange properties. The most common method of zeolite adsorbent targeted modification is a cation-exchange modification, consisting in the transfer of polycationic natural material into one of monocationic form (H-, Na, Ca, NH4-, etc.).

When processing high-silicon zeolites with strong acids a sequential substitution of cations hydroxonium ions [6] occurs. Hydrogen forms of zeolites can be regarded as solid crystalline alumosilicic polyacids. Therefore, the method of potentiometric titration with alkaline solutions which allows evaluating the active groups' acidity usual for ion exchanger may be used for hydrogen forms of zeolites. For high-silicon natural zeolites (clinoptilolite, mordenite) with enhanced stability in acidic solutions in comparison with other zeolites, the hydrogen forms can be obtained directly by treatment of acid solutions. The high stability of clinoptilolite to heating and acids can be explained by an increase in the stability of skeleton associated with a decrease in the number of weaker bonds Al-O (1,66 Å) and an increase in the number of strong bonds Si-O (1,62 Å).

To study the acid-base properties of the investigated zeolite air-dried sample, previously modified with 3 N hydrochloric acid was being treated with 0,1 N alkali solutions within one day at room temperature. Analysis of the potentiometric titration curve (Figure 4) shows that the hydrogen forms of zeolite obtained by treatment with acid are titrated with KOH solution. At alkali charge 0,5 mg-eq / g there is a clear inflection point.

Consequently, the hydrogen forms of zeolites obtained by treatment with HCl have a more acidic hydroxyl grouping. The other exchange centers are subacid and uniformly distributed in the mineral structure. The static exchange capacity of the activated zeolite is 2,7 mg-eq /g.
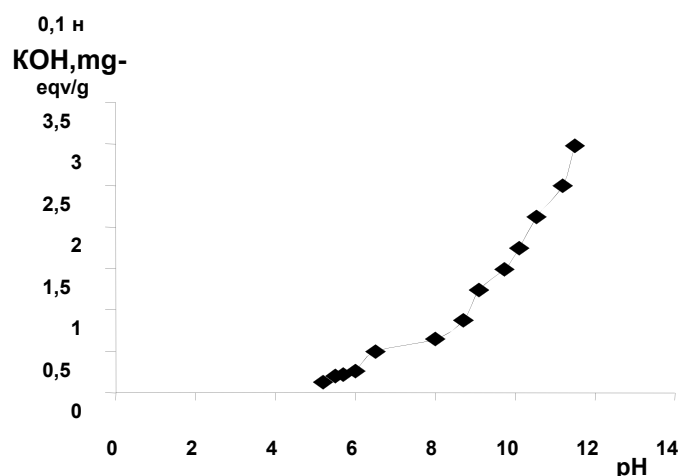

Figure 4. Potentiometric titration curve of the H $^+$ form of zeolite.

The capacity for chemical modification of natural zeolites gives the possibility of obtaining a large variety of adsorbents, catalysts and other fine general-purpose bodies. The results of these studies contribute to the establishment of limits of clinoptilolite in the presence of acidic reagents, and in addition, the identification of opportunities for obtaining the modified forms with novel properties. The successful implementation of technology of

sorption metal extraction is realized by a comprehensive study of the processes occurring in a complex system ion exchanger-solution. The study of adsorption on decationed and dealuminated clinoptilolite samples revealed their ability to selective adsorption of large cations [7,8]. This is apparently due to the proximity of the ions sizes and the kinetic diameters of clinoptilolite channels, which defines a strong Coulomb interaction with structure of the zeolite. In addition, it may be due to the presence of stronger acid sites and stabilizing role of the major cations in conditions of a significant reduction in their number in the internal space stipulated by a decrease in tetrahedral aluminum content.

Analysis of the kinetic curves of lead ions sorption in zeolite under study showed that the time to reach equilibrium decreased as the concentration of original solution increased and the grain size [8] decreased. The obtained results indicate that the rate of exchange of lead ions on the H-form of clinoptilolite is controlled by internal diffusion mechanism of the process. The effective diffusion coefficient depends linearly on the radius of the incoming ion and does not depend on the concentration of external solution.

The problem of waste water treatment is largely due to the lack of low-cost multifunctional sorbents stable during operation. Existing industrial sorbents with high sorption capacity are economically unfeasible due to their high cost. The results of experiments with investigated zeolite show that sorption of phenol on the natural sample and aminated form thereof happens with high degree of extraction from dilute solutions [9]. Modification of the PAV sorbent allows adsorbing phenol from aqueous solutions to the level of MPC and increasing the efficiency of the process in the presence of organic impurity compounds.

The presence of commercial deposits of clinoptilolite and experience of its application in various sorption processes make it possible to use it in the process flow sheets designated to extract a number of metal cations from solutions and wastewater. Significant amounts of the latter require the methods of treatment to have low cost and high efficiency. Addressing these issues is also associated with an additional yield of these metals which are being irretrievably lost currently.

One of the criteria of the waste water condition is nonferrous and heavy metal ions content in it. The latter are contained in waste water of nonferrous and ferrous metallurgy enterprises, concentration plants, galvanizing rooms of plants. There are different methods either physical or chemical which enable to retrieve ions of metals from solutions and industrial waste. The treatment of this sewage by ions isolation in the form of hydroxides cannot provide the required drop of concentration of the latter in sewage. Metals deposition in a form of sulphides is connected with the use of toxic reagents such as Na_2S and H_2S. The effective sewage treatment can be obtained by the sorption process which is easy to control and allows reducing relative detection limits.

The sorption of copper ions (II) under static conditions at different concentrations of mother solution, pH medium and in presence of various metals ions was conducted on investigated natural zeolite.

The effectiveness of sorption in many respects is determined by kinetics of the process. The curves of copper ions sorption are presented in the Figure 5. The equilibrium in distribution

of metal ions among the sorbent and solution at room temperature is established within short period of time (30 min). Short time of process is determined by the presence of chemically active groups in surface layers and high selectivity of sorbent toward metal ions. The results of conducted studies showed that natural zeolite has high activity at sorption of Cu^{2+} even in lower concentrations (0,125 g/l). Within 30 minutes the degree of recovery/extraction is 92% and it reaches 95% with increase of content of metal ions up to 0,5 g/l. At sorption of Cu^{2+} in areas of ions metal concentrations in natural waters 0,001-0,0005 mg/l high degree of recovery/extraction (90%) for 30 minutes is also reached, that shows the effectiveness of used sorbent. Hyperactivity of the latter at low contents stipulates for the suitability of use of metal ions for extraction of trace contaminants.

Due to the fact that waste outlet waters may contain both different composition and variable acidity, there is a need to study the influence of pH degree on sorption of copper ions. The curves of recovery degree dependence on acidity of solution under constancy of concentration Cu^{2+} (0,25 g/l) show (Figure 6) that the degree of metal ions recovery in studied conditions decreases with increase of acidity of solution due to competitive effect of hydrogen ions. Thus, in pH<4 area the extracting ability of zeolite falls to 10%. With increase of pH medium to more than 4-5 the sediments of basic salts and hydroxides delayed by ionite are generated and sorption occurs additionally due to adhesion of generated sediments (recovery is 90-91%). Under collective concentration of Cu^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+} with cumulative content of metals ions 0,5 g/l (concentration of each ion is 0,125 g/l) sorption of copper ions occurs with delayed kinetics (Figure 7). The maximum degree of recovery is 67% for 120 minutes. According to the obtained data under accepted conditions natural zeolite equally sorbs copper and lead ions.

It is determined that ratio of the solution volume to sorbent mass influences recovering ability thereof. Growth of zeolite content in the solution from 0,5 g to 2 g (V=50 ml) leads to increase of recovery effectiveness by 3%. Degree of sorption reaches 97% within 30 minutes.
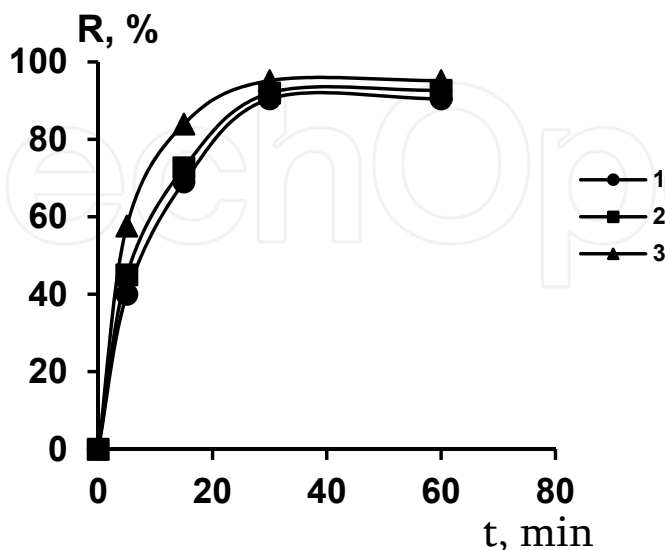

Figure 5. Degree Cu^{2+} by natural zeolite as a function of the process duration t. Cs: 0,125 (1); 0,25 (2); 0,5 (3); $C_{Cu^{2+}}$=0,5 g/l; V=50 ml; m=0,5 g.
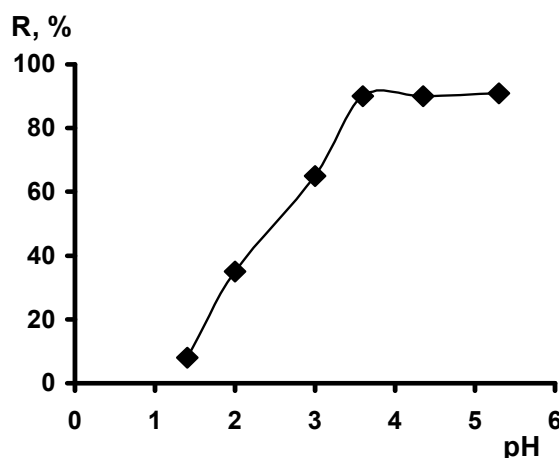
Figure 6. Degree of Cu^{2+} by natural zeolite as a function of the pH. $C_{Cu^{2+}}$=0,25 g/l; V = 50 ml; m = 0,25 g / l; τ= 30 min.
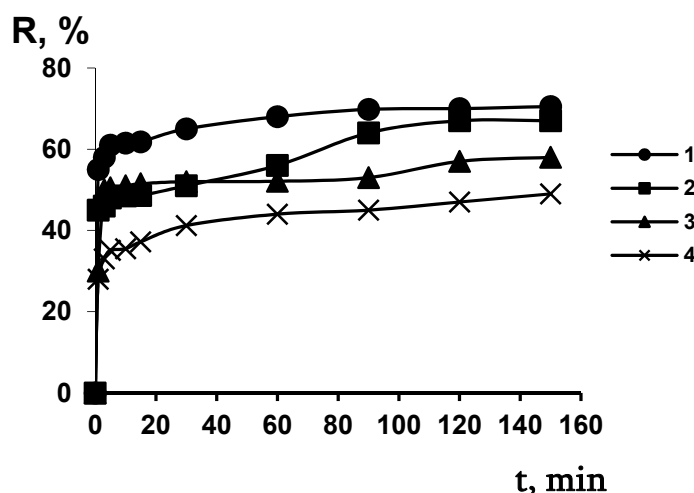

Figure 7. Degree Pb^{2+} (1); Cu^{2+} (2); Co^{2+} (3); Ni^{2+} (4) by natural zeolite as a function of the process duration t. $\Sigma C_{Me^{2+}}$=0,5g/l; V=50 ml; m=0,5 g.

Thus, the suggested sorbent effectively recovers copper ions from model solutions within short periods of time. Cheap natural zeolites may be used in the processes which do not provide regeneration of ionites. The opportunity of its one-time use with subsequent burial provides application thereof in such spheres where synthetic zeolites or ion-exchange polymers cannot be used under economical reasons.

4. Features of the sorption of various substances vapors by activated forms of natural zeolite

The comparative ease of zeolites chemical modification opens up wide possibilities for controlled changes in their structure and properties. This makes them very convenient objects for studying the nature of sorption interactions, molecular-sieve effects. The vast majority of these studies were conducted with synthetic zeolites. The natural forms of such minerals which are multicomponent systems complex and variable according to

composition are much less known. Their physicochemical properties essentially depend on the content of zeolitic phase in the rock, such as cation exchange form and nature of impurities. Even with the same content of the zeolitic phase in the rock a mismatch in the properties of individual samples may be observed. Natural zeolites are biporous systems; the primary porosity of them is determined by the micropores of crystals, and the secondary one – by the transitional pores and macropores. The latter are the main transport arteries for the supply of a substance; they determine the absorption of relatively large molecules and play an important role for a number of sorption and catalytic processes.

Hydrophilic inorganic sorbents, which include zeolites, are practically useless for adsorption of many organic substances from aqueous solutions since water molecules interact with the OH - groups to form strong hydrogen bonds (5-10 kcal/mol) energy of which exceeds the energy of adsorption of most organic molecules [10]. In this connection, it is important to study the sorption of vapours of various substances on the surface of such minerals.

We used acidoactive (processing for twenty four hours by 3 and 12 N hydrochloric acid solution) air-dried and dehydrated (600ºC) natural zeolite samples as the adsorbate. Sorption was determined by the increase in mass of the sorbent (initial sample 1 g) placed in open weighing cup over liquid adsorbate in a desiccator under normal conditions.

Porous crystals of zeolites are of great interest as highly specific adsorbents both on the molecular sieve effect and also on the nature of their channels' surface. Adsorption peculiarities are connected with the fact the delicacy of the crystal structure creates a large adsorption volume (up to 0,54 cm^3/g for faujasites), and its geometry determines the molecular sieve properties. The presence of acceptor centers (cations, the Lewis acid centers) firmly holding the electron donors, or OH - groups, strongly binding bases (Bronsted centers), causes strong interaction of adsorbed molecules with the adsorbent.

Depending on the nature of these molecules, various types of interactions may occur between them and zeolites. The specificity of zeolites with respect to the molecules of this adsorbate is determined by the values of the interaction energies of different types. In case of the heteropolar adsorbent, the polarization of the adsorbate molecules occurs by its electrostatic field. High adsorption energy of zeolite by molecules capable for specific interaction with cations having a peripheral dipoles (water, aether), the large quadrupoles and π-electron bonds (nitrogen, olefins, benzene) are typical for zeolites. The energy of dispersive attraction makes decisive contribution to the specificity of the process. For zeolites, the prevalence of the energy may be due to the dense environment of adsorbate molecules by the atoms of oxygen frame. Therefore, it is very high energy of adsorption of organic molecules with peripheral functional groups having atoms with free electron pairs and π-bonds for them.

The ratio of Si/Al in natural zeolites can be improved by chemical treatment of the crystals, resulting to the removal of part of aluminum from the frame. Herewith, dealumination can occur without significant changes in their characteristic structural features. A simple option

thereof is the treatment of crystals with acid solutions. The result of this chemical action is the artificial increase of the adsorption volume and the effective pores' size.

The curves of the kinetics organic solvents vapours sorption on dehydrated and non-dehydrated zeolite samples are given in the Figure 8. For each of them, they are close to each other, and according to the value of weight gain of the solvent they are in the following order: acetone>toluene>carbon tetrachloride. This range correlates with the size of Vander Waals molecules. Not less important role is played by well-known sorption activity of the polar solvent (acetone). For molecules of hydrophobic solvents water sorbed and bound with cations in the crystallographic positions of the mineral blocks the entrance windows in its cavity. It is shown [11] that the sorption of carbon tetrachloride vapours occurs only on the outer surface of both natural and activated clinoptilolite, and sorption of acetone – in the micropores of the latter. If we assume that water molecules are completely desorbed in zeolite pores dehydrated at 600^0C, then the process of sorption of these compounds on the active sites of sorbent runs with displacement of pre-sorbed water.

The results of acetic acid and water vapours sorption on zeolites treated with 3 and 12 N hydrochloric acid are given in the Figure 9. A slight difference in the values of weight gain of the substance on the original forms of mineral is shown in this Figure; a small difference in weight gain of water and organic acid on non-dehydrated and dehydrated zeolites treated with 3 N solution of mineral acid is due to insufficiently developed micro porosity of the mineral. Specific adsorption of water molecules by zeolite is mainly represented by interaction of free electron pairs of oxygen atoms with cations of zeolite cavities surface. The polar molecules of water penetrating into its micropores are sorbed, including as a result of ion-dipole interaction with the active centers (cations, compensating the excess charge of zeolite frame). Water molecules bond with the cations and the frame is predominant in the case of natural zeolites [12]. The adsorbate-adsorbent interaction completely determines the process.
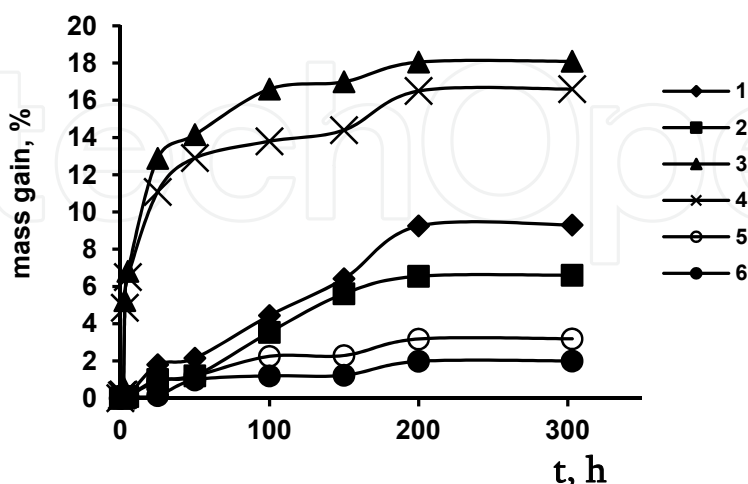

Figure 8. Degree of the mass gain of solutions as a function of the process duration t. sample №2: **dehydrated zeolite 1 –** toluene; 3- acetone; 5- carbon tetrachloride. **air-dry zeolite** 2- toluene; 4- acetone; 6- carbon tetrachloride.
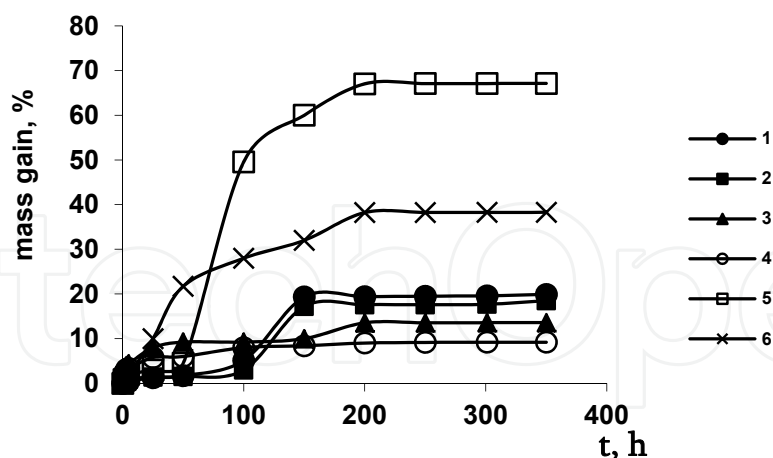
Figure 9. Degree of the mass gain of acetic acid and water as a function of the process duration t. **acetic acid: (**sample №2) 1 - dehydrated zeolite; 2 - air-dry zeolite; (sample №3) 5 - dehydrated zeolite; 6 - air-dry zeolite; **water:** (sample №2) 3 - dehydrated zeolite; 4 - air-dry zeolite

Large scale polarizability (in comparison with water) and low dielectric permeability of the organic acid that increase the binding energy of the cation-fixed ion create preconditions for more effective development of the dispersion forces which play an important role in the mechanism of weak organic acid absorption by ionites.

Acid treatment of zeolite samples with 3 N hydrochloric acid under normal conditions practically does not lead to significant changes in the structural properties of the sorbents, as it is shown above (Table 2). The values of specific surface area for them according to BET and t-graphic have small differences [4]. However, increase of acid concentration under comparable conditions leads to an increase of micro- and mesopores volume. Therefore, zeolite activated by 12 N acid has a higher sorption capacity. Such treatment fosters the expansion of the input windows of mineral channels, and water allocation on ignition contributes to the displacement of cations inside and improvement of primary porosity which depends on the nature of zeolite. This effect seems to be the result of changes in the chemical nature of adsorption sites and porous structure of the mineral in the process of activation. This condition is caused by changes in relative positions of aluminum-oxygen and silicate-oxygen tetrahedrons of the core.

It is shown by example of acetic acid (Figure 9, 10) that there is an evident divergency between the curves of sorption of vapours of the studied substance on non-dehydrated and dehydrated zeolite. Study of the kinetics process showed that for 200 h there is a saturation of natural mineral and sorption volume, is 47 and 89 mmol/g, accordingly.

Increasing of activating acid concentration leads to development of micro-cavities and channels interconnected within the frame of zeolite free of exchangeable cations that promotes the growth of the volume of adsorbed acetic acid. The latter circumstance indicates that the activation process in comparison with the amorphization of zeolite prevails under these conditions; this characterizes the studied mineral as an acid-resistant.
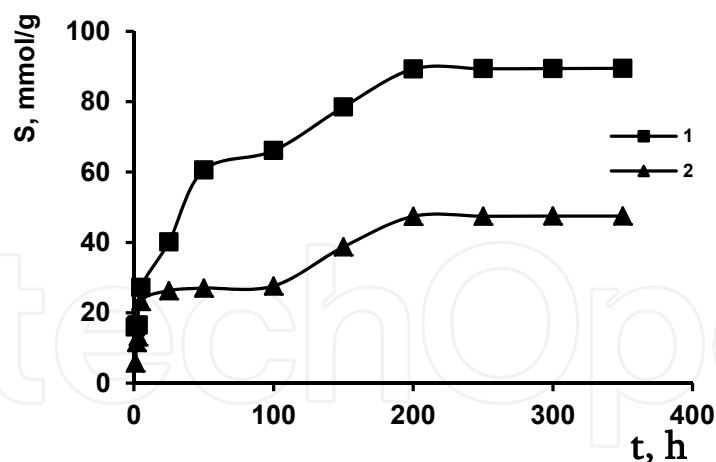
Figure 10. Degree of the sorbtion S of acetic acid vapors by natural zeolite as a function of the process duration t. 1- dehydrated zeolite; 2- air-dry zeolite

The results of spectroscopic (Figure 11) and X-ray studies of natural zeolite activated by 3 and 12 N hydrochloric acid solutions give evidence of preservation of mineral crystal structure due to acid resistance thereof.
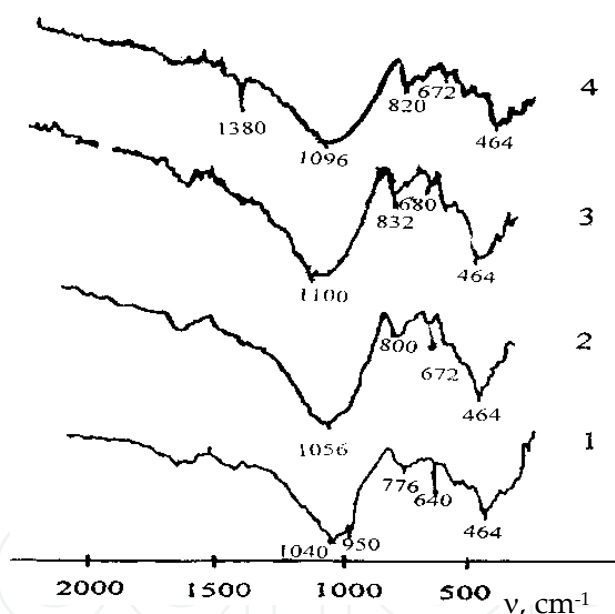

Figure 11. IR spectra of zeolites. 1 - natural zeolite; 2 - activated 3 N hydrochloric acid; 3 - activated 12 N hydrochloric acid; 4 - after the sorption of acetic acid vapors.

The absorption bands at 464, 640, 776, 950 cm^{-1} typical for Si-O-Al intratetrahedral deformative and symmetric valence vibrations are prescribed in original zeolite spectrum. When treating it by 3 and 12 N hydrochloric acid, all the characteristic frequencies become more apparent. The position of the peak at 464 cm^{-1} is kept and there is a shift of the absorption bands at 640 and 776 to the long-wave area (672; 680 and 800;832 cm^{-1}, accordingly) without changing the intensity of the spectrums. This gives evidence of preservation of samples crystallinity degree after activation. In the spectrums of zeolite

saturated by acetic acid vapours frequencies of adsorbate molecules methyl groups vibrations appear at 1380 cm^{-1} and the absorption band broadens at 1640 cm^{-1} due to overlap of the deformation vibrations of water molecules and asymmetric COO$^-$ valent groups.

Dealumination is accompanied by rupture of Si-O-Al bonds and the resulting shift of asymmetric valent intratetrahedral vibrations frequency from 1040 to 1056 and 1100 cm^{-1}.

The studies showed that an increase in acid concentration leads to an increase in sorption ability of mineral connected with an increase of mineral porosity in the cation removal process. Thus, depending on the nature of adsorbate and adsorbent type, the appropriate modes of activation can be selected.

5. Investigation of mechanochemical modification of natural zeolite with various substances

Diversity of centers formed in zeolites explains the fact that zeolites can be used in a wide range of chemical and technological processes. One of the effective ways of intensification of processing different types of mineral raw materials is mechanical activation, which determines the formation of a significant number of defects in the structure of minerals, which should lead to a change in surface properties of the constituent particles [13, 14].

Mechanochemical modification allows, first of all, intensifying the process of solids dispersing. As a result, the chemisorbed polymer layer passivates the surface of dispersed particles and lyophilized highly dispersed filler is formed. At the same time, the conditions for emergence of chemical interaction at the interface of filler-polymer are created, that leads to a deeper change in the surface.

Environmental cleanness and the possibility of simplifying the process flow sheet determine the prospects for such studies. In this regard, we conducted mechanochemical modification of natural zeolite with aminoacetic acid and epoxy resin for the first time ever.
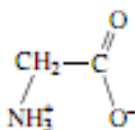
5.1. Solid-phase interaction of natural zeolite with aminoacetic acid

Layered silicates and zeolites are characterized by the presence of both basic and acid active sites on their surface [4,15]. The solid-phase interaction of these sites with amino acids is of interest [16]. In the sorption on solid supports, amino acids containing two functional groups can form different surface complexes. The structure and chemical properties of the surface and also theoretical and practical aspects of adsorption and catalysis on zeolites are studied by various methods. Widely used spectral methods provide valuable information on the structure and properties of supports [16].

The aim of this work was to study the interaction of α-aminoacetic acid (α-glycine) with natural zeolite during their mechanochemical activation. Natural aluminosilicate, zeolite from Shankhanai deposit (Kazakhstan), was used. To remove nonstructural impurities readily washed out with acids, zeolite was preliminarily activated with a 10% HCl solution for a day. Aluminosilicate samples were dried at 130°C for 2 h; α-glycine was used without

additional purification. The mechanochemical activation of initial compounds (the amount of glycine was 30% of that of the zeolite) was performed in an agate mortar for 30 min. The IR absorption spectra of powders pressed into pellets with optically pure KBr were recorded on a UR-20 spectrophotometer.

α-Glycine has a layered crystal structure [14]. Glycine molecules are present in crystals as zwitterions, which are bound with each other by relatively short (therefore strong) N–H···O hydrogen bonds and form antiparallel layers,

Scheme 1. Scheme 1

The spectra of the samples are presented in the Figure 12. Carboxylic acids form very strong hydrogen bonds; therefore, OH group stretching vibration frequencies are characteristic frequencies. A broad absorption band and several weaker peaks are observed over the range 3000–2500 cm^{-1}. In the spectra of aminoacetic acid and its activated mixture with zeolite, the main peak is observed at 3000 cm^{-1}, and weaker peaks, at 2720, 2616 and 2700, 2600 cm^{-1}, respectively; these peaks can be assigned as combination tones corresponding to C–O (1420 cm^{-1}) and O–H (1300 cm^{-1}) vibrations [17]. The band of stretching vibrations shifts toward lower frequencies, 3488; 3424 cm^{-1}. A pronounced secondary band at 2175 cm^{-1} in the spectrum of α-glycine is evidence of the presence of a bipolar ionic structure; in the modified sample, this band is observed at 2170 cm^{-1}.

Both samples exhibit absorption in the range 1420–1340 cm^{-1}, which is assigned to C–O vibrations closely related to planar bending vibrations of OH groups. In the spectrum of the modified sample, vë=é and antisymmetric stretching vibrations in α-glycine(1720–1540 cm^{-1}) and Si–O stretching vibrations in zeolite (1060 cm^{-1}) are shifted toward longer wavelengths (1700–1500 and 1040 cm^{-1}, respectively). Absorption in the range 1700–1500 cm^{-1} can also be assigned to hydrogen bonds of aminoacetic acid with OH surface groups. This assignment is based on the results obtained for the intra- and intermolecular association of carboxylic acids [18].

Thus, the NH^{3+} stretching vibration and COO^{-} antisymmetric vibration frequencies shift toward lower frequencies. Similar results were obtained in the mechanochemical activation of caolinite and the amino acid with the formation of a salt with the NH$_2$CH$_2$COO^{-} [14].

It is known [16] that, along with the absorption band of the ionized carboxyl group (1600–1550 cm^{-1}), all amino acids containing the group exhibit two characteristic bands at 1600–1500 cm^{-1}. One of these is observed at 1640–1610 cm^{-1}. For the amino acid under study, bending vibrations occur at 1640 and 1608 cm^{-1}. These bands are also present in the spectrum of the modified zeolite sample; the band at ~1640 cm^{-1} is, however, broadened. This band is a superposition of antisymmetric stretching vibrations of COO^{-} groups and bending vibrations of water molecules and NH$_2$ groups. The other characteristic band of
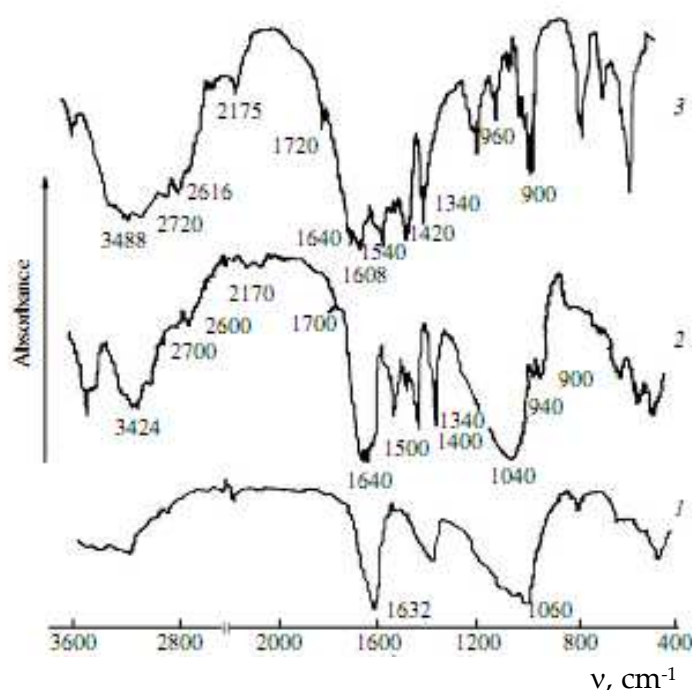
Figure 12. IR spectra of (1) natural zeolite, (2) activated mixture, and (3) aminoacetic acid.

amino acids (1540–1420 cm⁻¹) is, as a rule, more intense than the first characteristic band. In the zeolite activated with the amino acid, this band is shifted toward lower frequencies (1500–1400 cm⁻¹). A similar result was obtained in [14]; however, in the spectra of activated caolinite samples, the absorption band of NH₂ groups was observed at 1550–1450 cm⁻¹ and had a low intensity or even disappeared against the background of the maximum at 1640 cm⁻¹.

The absorption band in the frequency range 960–900 cm⁻¹ is assigned to OH group bending vibrations. In the spectrum of the modified zeolite sample, this band is narrowed and is observed at 940–900 cm⁻¹.

To summarize, the solid-phase neutralization reaction in the mechanochemical activation of zeolite and the amino acid results in the formation of chemical bonds between carboxyl groups of the acid and basic sites of the aluminosilicate and also coordination bonds between aluminum atoms in the zeolite lattice and nitrogen atoms of amino acid molecules.

5.2. Mechanochemical modification of natural zeolite with epoxy resin

The joint dispersion of fillers with polymers of different nature leads to the breakdown of macromolecules with formation of free radicals, which react with the active centers of minerals to form surface chemical compounds [19].

The specific features of zeolite structure, its high affinity to polar groups, the developed surface area, adsorption capacity determine the possibility of combining the filler with high-

molecular compounds. Herewith, the additional intermolecular bonds form and the ability to structure the macromolecule as a result of adsorption at the interface appear. In this regard, the results of the study of the joint dispersion of natural aluminosilicate with an industrial epoxy resin ED-20 [20] were considered.

The results of the study of dependence of the value of epoxy resin weight gain on the surface of zeolite on its concentration showed that epoxy cycles open and the chemisorption of free radicals (Figure 13) takes place. Resin content change from 1 to 20 mass % in the process of dispersion system for 0,5 h leads to an increase in the value of the polymer grafting from 3,2 to 5,7%.

Modification of zeolite for 1 h contributes to a sharp increase in polymer weight gain on the surface, which reaches 7,5% at 1:10 mass parts components ratio (Figure 11). The maximum for these conditions dispersion of zeolite in the presence of ED-20 occurs within the first hour of grinding (Figure 14).
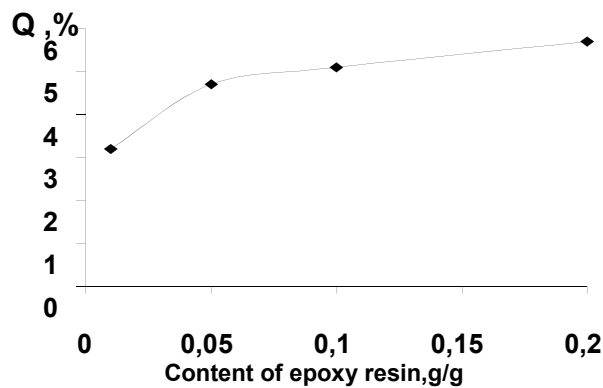

Figure 13. Degree of the grafting of polymer (Q) on the surace of zeolite) as a function of the content of epoxy resin (dispersion for 0,5 h)
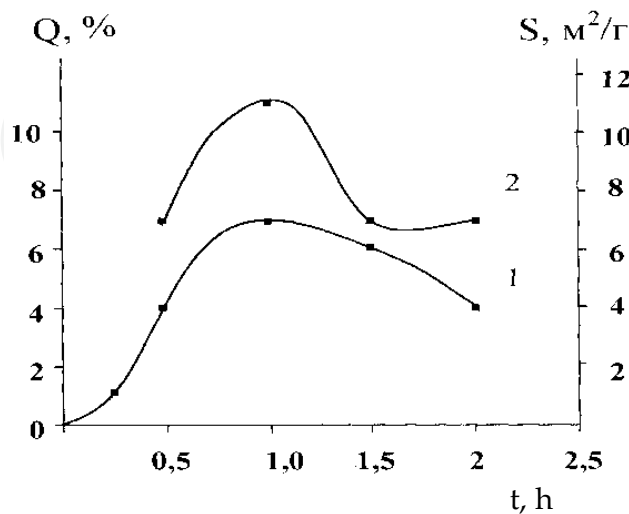

Figure 14. Degree of the grafting of epoxy resin (Q) and the specific surface area (S) minerals (2) as a function of the process duration t. (Resin: Zeolite = 1:10 mass part by weight)

The data obtained shows that at mechanochemical interaction of natural aluminosilicate with an epoxy resin a number of transformations with the components of the system take place. Spectroscopic studies found the significant changes in the chemical structure of polymer as a result of the modification. It is observed that with the increase of process duration a decrease in the intensity of absorption band at 832 cm^{-1} and disappearance of frequency at 916 cm^{-1} are observed, characterizing the epoxy groups' vibrations (Figure 15). This indicates the mechanochemical activation of the latter. Free radicals formed as a result of disclosure thereof contribute to the dispersion and intensify the process of grafting, which affects certain increase in polymer weight gain. Thus, with increasing of grinding time up to 1 h, zeolite specific surface increases and the grafting of polymer (Figure 14) takes place. The process is intensified due to the interaction of freshly formed surface with products of mechanodestruction of macromolecules and its modification as a result of epoxy resin free radical grafting. A further increase in the duration of system dispersion up to 2 h leads to a decrease in the specific surface of modified aluminum silicate stipulated by the grafted layer of polymer the amount of which at this time is the maximum.
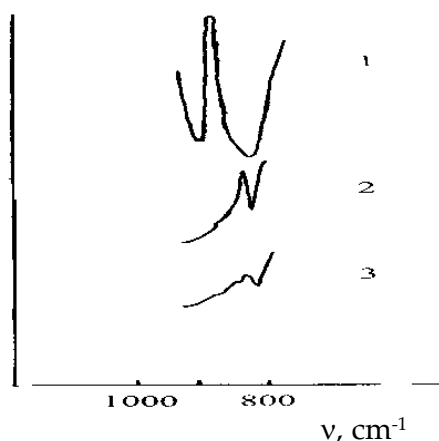

Figure 15. IR spectra of epoxy resin. 1 - in the absence of dispersion; 2 - dispersion for 0,5 h; 3 - dispersion for 1 h.

Extraction data of polymer-zeolite system showed the physical and chemical nature of the adsorption bonds between molecules of resin and aluminum silicate surface. Herewith, the contribution of chemisorption bonds varies depending on the ratio of the components and process duration.

Thus, a modified aluminum silicate which can be used effectively to create a variety of organo-mineral systems with a complex of valuable properties was obtained by combined dispersion of natural zeolite and epoxy resin.

6. Conclusion

The study of sorption activity of natural and modified sorbents has made it possible to substantiate the decisive role of the nature of the acid-base properties of a mineral in the

process of extraction, as well as the influence of the porous structure upon sorption of organic compounds (acetone, toluene, acetic acid) and inorganic ions (the ions of nonferrous metals).

Physico-chemical study of the composition and thermal stability of natural zeolite allowed to determine the ratio of Si / Al as a 3,8, a high thermal stability, and to find optimal conditions for acid activation of the zeolite with the aim further modification of the samples with epoxy and amine reagents. It is shown that, depending on the nature of adsorbate and adsorbent type can be selected appropriate modes of activation of natural zeolite as a result of vapor sorption studies of various organic solvents, water and acetic acid.

It has been shown for the first time by the method of IR-spectroscopy that a chemical interaction takes place between the main centers of natural zeolite and carboxylic groups of aminoacetic acid in the process of their mechanic-chemical activation, as well as the formation of a coordination bond between the aluminum atoms of its lattice and nitrogen of aminoacid. Stereoscopic studies have established considerable changes in the chemical structure of the polymer as a result of mechanic-chemical modification of natural zeolite by epoxy resin. The extraction data of the system polymer-zeolite testify to the physical and chemical nature of adsorption bonds between the molecules of resin and the surface of alumosilicate. Incidentally, the contribution of chemosorption bonds is different in dependence of the ratio of the components and duration of the process.

Development of methods for modification of natural zeolite by various oligomers and functional materials opens up the possibility of synthesis of chemically modified materials for ion-exchange technology. Therefore, an interest is evoked by a profound research of the processes, proceeding on the surface of the modified natural sorbents, the state of engrafted compounds and creation of methods of purposeful alternation of the structure of the engrafted layer and the properties of the modified sorbents, connected with this structure, as well as establishing of a possibility to use them in the modern sorption processes, creation of new competitive technologies for the extraction of metal ions from technological solution.

The profound theoretical and practical studies of the methods of modification of natural sorbents will result in the development of available methods of obtaining of organomineral sorbents as the most problematic aspect of the development of the modern ion-exchange technology and related fields. And the achievements in this field should be connected, first of all, with the physical-chemical approach to the assessment and generalization of the existing vast experimental and theoretical material.

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