

# RADIATIVE STABILITY AND SORPTION ABILITY OF CLINOPTILOLITE NANOPARTICLES

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The ion exchange of clinoptilolite nanoparticles by means of a radioactive isotope <sup>132</sup>Cs was studied. The caesium capacity for clinoptilolite nanoparticles at size 90 nanometers at reaching of an equilibrium was 55 mg/g.

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## 1. INTRODUCTION

The problem of practical use of natural minerals as the selective sorbents of various radioisotopes is explored throughout many years. Various objects of environment (bedrock, water, vegetative objects etc.) intensively absorb radioisotopes. It is known [1] that natural getter materials on the basis of zeolites possess high selectivity to some radioisotopes. The zeolites belong to high-silicon aluminosilicate and possess by high thermo- and chemical stability.

Getter properties of zeolites are being characterized by high cation-exchange capacity, an advanced surface, selectivity in relation to ions of strontium, caesium and radon [2]. The porous structure of zeolites allows to carry out a directional modification of water-cationic complexes, owing to their weak coupling with a crystalline skeleton. For example, aluminosilicate with bidimensional structure is less selective to radionuclide's of caesium and strontium. The caesium distribution coefficient change in the range from 10<sup>3</sup>-10<sup>4</sup> ml/g, strontium - from 340 to 500 ml/g depending on concentration of background.

It is necessary to notice that in many cases (atomic engineering, ecology, etc.) politest (clinoptilolite) is suitable for application only in fine-dispersed a state with the dimensions of particles from several unities to tens and hundred nanometers. For example, [3] in a new sorption-membranous technology the process of neutralisation of a liquid radioactive waste is possible only at use nano powder of clinoptilolite.

Variety of practical application of nanoclinoptilolite are caused by its structural singularities. One of the most remarkable of these singularities is crystalline skeleton with hollows and channels. In natural clinoptilolite they are filled up by crystalline hydrated water. The three-dimensional crystal of nanoclinop-

tilolite has a substratified constitution and bidimensional system of channels. The ions of Al<sup>3+</sup> and Si<sup>4+</sup> in elemental cell [(Si,Al)O<sub>4</sub>] are in tetrahedral coordinations relatively of oxygen and isomorphically substitutes Si<sup>4+</sup>. The perceptible hydration of clinoptilolite leads to weakening of electrostatic interaction of cations with a skeleton and, accordingly, to dropping of barriers of their migration [4]. The correct select of preliminary handling of a mineral is major factor of rising of cation activation [5,6]. For example, rise of temperature leads to development of diffusion mobility of molecules of water and cations. The barrier of diffusion of molecules of water in clinoptilolite is equal to 30±2 and 25±1 a kj/Mol, and is being characterized by great values of preexponential factors -(4±2)·10<sup>11</sup>. Apparently the process of molecular diffusion and of cation diffusion is caused thermoactivation ones of same equilibrium defects. The defect formation is connected with H-bond reorganization at temperature growth. The crystal-hydrated water is being released easily at slow warming. Dehydration process is accompanied by destruction of aquacomplex which freely move in skeleton vacuities. The liberated cations migrate to various crystallographic places of a lattice and connect with oxygen atoms of aluminosilicate tetrahedrons. The location of atoms near to planes of a crystalline lattice vary according to new locating of cations and formation of new connections with skeleton oxygen.

The cations of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, etc., are being substituted by cations of other metals (Cs<sup>+</sup> and Sr<sup>2+</sup>). Sorption of Cs<sup>+</sup> and Sr<sup>2+</sup> is caused by correlation between the dimension of vacuities and the ionic radii of Cs<sup>+</sup> - 0.69, and of Sr<sup>2+</sup> - 0.13 nanometers. The large ionic radius of Cs<sup>+</sup> cation is more preferable for structure of clinoptilolite As a result selectivity of clinoptilolite to Cs<sup>+</sup> is more than to strontium.

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The mutual relation between cations of clinoptilolite take place on a surface and on interphasic boundaries and appreciably depends on the dimension of particles of the mineral, properties of surface and interphasic boundaries [7]. The functional bond between structure and properties is specific for nanostructure systems. For the most part it concerns properties of exterior and interior diffusion processes. The diffusion coefficient for exterior processes is  $10^{-5}$  cm<sup>2</sup>/s, and for interior processes –  $10^{-11}$  cm<sup>2</sup>/s. According to this data the rate of ion exchange and the adsorption capacity of nanostructure clinoptilolite can be increased by means of augmentation of their specific surface area. The surface of nanoparticles have high density that gives the possibility to raise considerably capacity of volume unit [8,9].

In spite of the fact that the problem of getter ability of nanoparticles is widely researched, representations about influence on activity of cations of their dimension, densities, radioimmunity and quantity of an absorbed dose of ionising radiation from the radionuclide disposed in them till now remain obscure.

## 2. MATERIALS AND METHODS

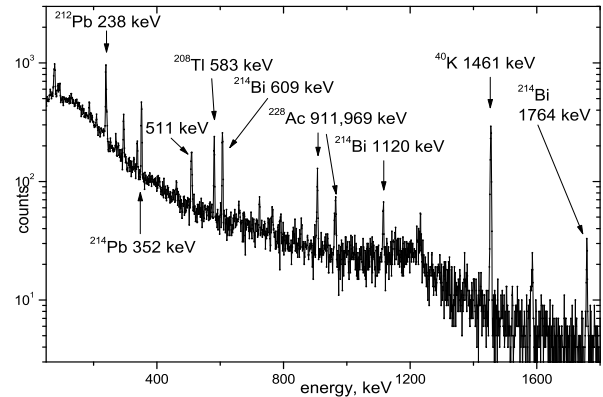
The high-silicon natural zeolite (clinoptilolite) out of the Sokirnitsky deposit with high content of SiO<sub>2</sub> (<70%) and Si/Al<sub>2</sub>O<sub>3</sub> ≥ 5 and by cationic capacity up to 2 mgeq./g was researched. This mineral is hydrated aluminosilicate with open wireframe structure (NaK)<sub>4</sub>CaAl<sub>6</sub>Si<sub>30</sub>O<sub>72</sub>·24H<sub>2</sub>O). The dimension of original fine-grained powder of clinoptilolite was ~3 mm. Procedure of deriving clinoptilolite in nano-size state was the following: the grinding of clinoptilolite in agate mortar for a long time, the precipitation of powder in the distilled water with the subsequent centrifugation. The velocity of subsidence of clinoptilolite particles was being determined out of equation:

$$V = \frac{2g(\rho - \rho_o)r^2}{9\eta}, \quad (1)$$

where  $\rho$ ,  $\rho_o$  - density of clinoptilolite particles and water, accordingly,  $g$  - acceleration of free falling,  $r$  - particle radius,  $\eta$  - dynamic viscosity of water. After 6 days of precipitation the solution was decanted and centrifuged. Velocity of turnovers of centrifuge was 12 thousands/s. In this case the sedimentation at a centrifugation was accomplished for diameter of clinoptilolite particles from 70 to 110 nanometers.

The spectrum of natural clinoptilolite (195 g) is shown on Fig.1. The gamma lines above than background and lines corresponding <sup>40</sup>K and families of <sup>238</sup>U, <sup>235</sup>U, <sup>232</sup>Th observed on Fig.1. The content of the following elements with using of intensity gamma spectrum were determined: U –  $2.75 \cdot 10^{-6}$ , Th –  $1.06 \cdot 10^{-5}$  and K –  $2.49 \cdot 10^{-2}$  g/g. These data are similar to the initial data of clinoptilolite sample from Sokirnitsky deposit: Th - 12 μg/g and K<sub>2</sub>O – 2.96%, ie  $1.2 \cdot 10^{-5}$  and  $2.45 \cdot 10^{-2}$  g/g, respectively. These results indicate that the content of U

and Th approximately coincide with the prevalence of these elements in the Earth's crust (Th  $1.0 \cdot 10^{-5}$  and U  $3.6 \cdot 10^{-6}$  g/g) and their ratio in the specimen (3.87) is slightly higher than the average in the Earth's crust (2.78).



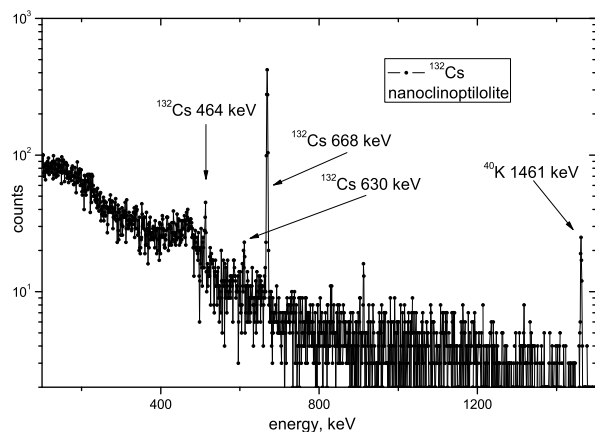
**Fig.1.** The gamma spectrum on natural clinoptilolite

The age of the mineral is more  $700 \cdot 10^3$  years (for  $T_{1/2} = 75.4 \cdot 10^3$  years for <sup>230</sup>Th) in case to take into consideration equilibrium isotope activity of a family of <sup>238</sup>U. Content of K in the sample coincides with its index in passport.

## 3. RESULTS AND DISCUSSION

CsNO<sub>3</sub> sample (30 mg) was irradiated by bremsstrahlung with  $E_{max} = 23$  MeV,  $I = 700$  μA. The nuclear reaction for activating cesium was <sup>133</sup>Cs(γ,n)<sup>132</sup>Cs. The active sample of CsNO<sub>3</sub> was dissolved in 250 ml of distilled water.

The sample of nanoclinoptilolite (3.7 mg) was placed in a solution of <sup>132</sup>CsNO<sub>3</sub>. The time of sorption was 24 hours. The caesium content in nanoclinoptilolite after 24 hours of a sorption was 55 mg/g (Fig.2). In our case according to [10] the time of stabilisation of equilibrium at level 0.95 for nanoparticles of clinoptilolite (100 nm) was 8 hours.



**Fig.2.** The gamma spectrum of nanoclinoptilolite sample after sorption from solution of CsNO<sub>3</sub>

It is known that the lattice parameter of nanoparticles depends on their size [10]. The critical size of nanoparticles can be calculated in the following way:

$$L_o = \sqrt{\frac{1.5}{km}} h(\theta_D)^{-1/2} = 230(\theta_D)^{-1/2}, \quad (2)$$

where – an Avogadro number, a Dirac constant, electron mass, accordingly. In the most cases the Debye temperature of nanoparticles is less, than for the same massive materials.

According to [11] the modification of lattice parameter of oxides can be observed up to 100 nanometers. The hydrated radius of caesium is less than the hydrated radii of sodium and potassium. Therefore exchange of ions of Na and K of Cs in nanoparticles will be more intense in comparison with exchange in massive material. Abovementioned the properties of nanoparticles promote of higher capacity of caesium in nanoclinoptilolite.

#### 4. CONCLUSIONS

1. Nanoparticles of clinoptilolite are chemically stable and have selectivity towards isotope of the caesium obtained in reaction  $^{133}\text{Cs}(\gamma, n)^{132}\text{Cs}$ .

2. The sorption ability of clinoptilolite nanoparticles towards of radiocaesium was studied. Equilibrium was reached after about 2 hours of sorption.

3. The ion exchange capacity of clinoptilolite nanoparticles ( $\sim 90$  nm) towards of  $^{132}\text{Cs}$  was 55 mgeq./g after reaching equilibrium.

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#### РАДИАЦИОННАЯ СТОЙКОСТЬ И СОРБЦИОННАЯ СПОСОБНОСТЬ НАНОЧАСТИЦ КЛИНОПТИЛОЛИТА

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Приведены результаты по сорбции цезия наночастицами клиноптилолита. Изучен ионный обмен в наноклинтоптилолите при помощи радиоактивного изотопа  $^{132}\text{Cs}$ . Емкость по цезию для наночастиц клиноптилолита размером около 90 нм при достижении равновесия составила 55 мг/г.

#### РАДІАЦІЙНА СТІЙКІСТЬ І СОРБЦІЙНА МОЖЛИВІСТЬ НАНОЧАСТИНОК КЛИНОПТИЛОЛІТУ

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Приведено наслідки з сорбції цезію наночастинками клиноптилоліту. Вивчено іонний обмін у наноклинтоптилоліті за допомогою радиоактивного ізотопу  $^{132}\text{Cs}$ . Ємність по цезію для наночастинок клиноптилоліту розміром близько 90 нм при досягненні рівноваги склала 55 мг/г.