## NANOSTRUCTURAL DEACTIVATING AGENTS SELECTIVE TO CAESIUM

N.P. Dikiy<sup>1</sup><sup>\*</sup>, A.N. Dovbnya<sup>1</sup>, Yu.V. Lyashko<sup>1</sup>, E.P. Medvedeva<sup>1</sup>, D.V. Medvedev<sup>1</sup>, V.L. Uvarov<sup>1</sup>, I.D. Fedorets<sup>2</sup>, N.P. Khlapova<sup>2</sup>, D.S. Bakay<sup>2</sup>

<sup>1</sup>National Science Center "Kharkov Institute of Physics and Technology", 61108, Kharkov, Ukraine

<sup>2</sup> V.N. Karazin Kharkov National University, 61077, Kharkov, Ukraine

(Received April 7, 2011)

The chemical reactivity of nanostructural clinoptilolite and  $\gamma$ -hematite which have highly selective for <sup>132</sup>Cs sorption from polyethylene surface and for liquid environments are studied. There are different components besides clinoptilolite and  $\gamma$ -hematite were chosen to examine as model of deactivation agents for <sup>132</sup>Cs sorption. Photon activation analysis was used for study of element composition in samples of natural clinoptilolite and hematite. The chemiluminescence method was used for definition of chemical reactivity of iron-exchanged form of the clinoptilolite to produce hydroxyl radicals from H<sub>2</sub>O<sub>2</sub> (Fenton reaction). The formation of volatile compounds in process of <sup>132</sup>Cs sorption was detected . The deactivation agent on basic of thermomodified clinoptilolite with  $\gamma$ -hematite nanoparticles was shown the highly synergistic effect for <sup>132</sup>Cs sorption from polyethylene surface and for liquid system.

PACS: 68.43.-h; 82.75.-z

#### 1. INTRODUCTION

Accumulation and distribution of radioactive pollution in an environment demands production of effective sorption materials for radionuclide extraction. The new sorbents should have high stability to leaching and stability to long radiating influence. Various sorption materials are already applied: natural and synthetic sorbents, complex-formative, composite materials. Inorganic sorbents find the increasing application for sorption of various kinds of pollution. These sorbents have higher chemical and radiation stability and show selectivity to the some radionuclides. For example,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> has high sorption ability in relation to uranium, plutonium, neptunium, americium; phosphates  $Ca_5(PO_4)_3(OH,F,Cl)$ - to uranium, thorium, americium, etc. [1,2]. Besides selectivity the sorption materials should provide high speed of substance extraction. Kinetic characteristics are determined by the nature and the form sorption material (granulated, fine-dispersed, fibrous, etc.) [3]. Such factors are necessary for taking into account convenience and good value of used sorbents for a choice of sorption material.

Zeolites are inorganic solids consisting of enclosed regular cavities or channel of well-defined size and shape, that are widely used in industry in separation processes, such as catalysts, and in nano-reactors [4,5]. Clinoptilolite with ratio Si/Al> 4 is widely used as natural sorbent [6]. Selectivity of ionic-exchange properties of clinoptilolite is used for sorption of caesium and strontium from radioactive waste on the atomic power station, for removal from waste waters  $\mathrm{NH_4}^+$ , and also for sorption from industrial emissions of amines and heavy metals [7]. In many cases (in medicine, atomic engineering, ecology and so forth) clinoptilolite is suitable to application only in finely divided condition, with the sizes of particles from several units up to tens and hundreds of nanometer [8]. For example, new technology of membranous sorption for neutralization of liquid radioactive waste is possible only with application crushed up to nanosize of powder clinoptilolite.

Various applications of clinoptilolite are caused by its structural features. Most remarkable of these features is presence in its crystal skeleton of emptiness and the channels filled in natural clinoptilolite by molecules of crystalline hydrate. The threedimensional crystal skeleton of clinoptilolite has legible sublayered structure and two-dimensional system of channels with the aperture  $0.3 \times 0.76$ ;  $0.33 \times 0.46$ and  $0.26 \times 0.47$  nm. Each atom of aluminium has one outskeleton cation (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, etc.) [9]. In many cases, activity outskeleton cations defines possibility of practical use clinoptilolite (Fig.1). The major factor of increase of cation activation is correct selection of conditions of preliminary processing of a mineral before its application [10]. Interest about nanoparticles is caused by a specific set of properties which correspond to nanosize conditions. One of such properties is multiple increase of surface to volume [11]. Influence on cation activity of their size, charge, density and distribution in porous structure, till now remain not clear. The high efficiency of caesium sorption is detected in clinoptilolite after superficial

<sup>\*</sup>Corresponding author E-mail address: ndikiy@kipt.kharkov.ua

PROBLEMS OF ATOMIC SCIENCE AND TECHNOLOGY, 2011, N3. *Series:* Nuclear Physics Investigations (55), p.35-41.



# Fig.1. Distribution of cations in the clinoptilolite channels

modification by nanoparticles of hematite [12,13].

In clinoptilolite there are 4 types of places of localization of the basic cations: M(1), M(2), M(3) and M(4)[14-17]. The M(1) is in the channel A (Fig.1, a), cation in this position is surrounded by two lattice atoms of oxygen and five molecules of water. In places of M(1) are located sodium and calcium cations, the M(2) represents a place of cation localization in the channel B with three lattice oxygen atoms and three molecules of water. The cations of sodium and calcium are located in this position, but population of  $Na^+$  ions in M(1) is higher, than in M(2). M(3) places of localization in the channel C(b), located along an axis a about the center of hexamerous rings. These places basically are populated cations of potassium and coordinated by six lattice atoms of oxygen and three molecules of water. The position of M(3) is

located near to M(1). The M(4) places are located in the channel A in the center of inversion. The ions of magnesium are usually located in these places and are connected with six molecules of water. Distribution and coordination of potassium ions in clinoptilolite is the factor determining thermal stability of zeolites of heulandite group.

The purpose of the given work consisted of development and approbation of deactivation agents on a basis of thermomodified natural clinoptilolite and nanohematite for caesium-132 sorption.

#### 2. MATERIALS AND METHODS

Clinoptilolite (NaK)<sub>4</sub>Ca[Al<sub>6</sub>Si<sub>30</sub>O<sub>72</sub>]·24H<sub>2</sub>O of the Sokirnitsky deposit (district "Sargich", Ukraine) and nanohematite (Fe<sub>2</sub>O<sub>3</sub>) (Alta Aesar, Germany) have been used. Optical properties and X-ray structural analysis of the initial and irradiated samples were investigated previously [18,19]. The size of clinoptilolite particle was of 110 nm,  $\gamma$ -hematite - 40 nm. Preliminarily clinoptilolite has been reduced to fragments in an agate mortar. For spherical particles of clinoptilolite sedimentation speed V in a gravitational field equals to:

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

where  $\rho$ ,  $\rho_o$  - density of clinoptilolite particles and water, accordingly, g-acceleration of free falling, rparticle radius,  $\eta$ -dynamic viscosity of water.



Fig.2. Gamma spectrum clinoptilolite

The sedimentation in water (within 6 days) and centrifugation at  $1,2\cdot10^4$  turn/min. has been realized for obtaining size 110 nm for clinoptilolite particles. The fraction of clinoptilolite nanoparticles has equaled 110 nm.

High-temperature processing of clinoptilolite nanopowder at 260°C has been executed. Photon activation analysis on the linear electron accelerator (LAE) with E=22 MeV and I=500  $\mu$ A has been used for determination of impurity of sam-

ples. Spectra of  $\gamma$ -radiation have been detected by means of Ge(Li)-detector, volume 50 cm<sup>3</sup> with the energy resolution 3.25 keV on line  ${}^{60}$ Co 1332 keV. Ge(Li)-detector was equipped by three-layer (Pb-Cu-Al) background protection. Fig.2 shows the  $\gamma$ -spectrum of the irradiated sample of natural clinoptilolite (195 g). The intensity of  $\gamma$ -lines of the clinoptilolite radiation exceeds those of the background, as well as those corresponding to  ${}^{40}$ K nuclide, and the families of the <sup>238</sup>U, <sup>235</sup>U and <sup>232</sup>Th. The content of elements in the clinoptilolite was U -  $2.75 \cdot 10^{-6}$ , Th - $1.06 \cdot 10^{-5}$  and K -  $2.49 \cdot 10^{-2}$  g/g. These data are close to the passport ones of the clinoptilolite from the Sokirny deposit: Th -  $1.2 \cdot 10^{-5}$  and K -  $2.45 \cdot 10^{-2}$  g/g, respectively. The capsulation of the clinoptilolite samples allowed to prevent the leakage of radon. In this case the constant intensity of  $\gamma$ -lines from the  $^{228}\mathrm{Ac}$  and  $^{40}\mathrm{K}$  radio nuclides was observed. At the same time the intensity of  $\gamma$ -lines from the <sup>214</sup>Pb, <sup>214</sup>Bi, <sup>212</sup>Pb, <sup>208</sup>Tl radionuclides increased and coincided for the two latter radionuclides with the activity of <sup>228</sup>Ac. This result is accounted by the volatilization from the open samples of 15...20% of the high mobility radon. The content of Th and U in the samples was approximately equal to the abundance of these elements in the Earth crust  $(Th \approx 1.0 \cdot 10^{-5})$ and U $\approx 3.6 \cdot 10^{-6}$  g/g) with their ratio (3.87) slightly

higher than the average one in the Earth crust (2.78).

The chemical compound and the trace element content of clinoptilolite according to data of the Sokirnitsky zeolitic factory of Ministry of Emergency Situations of Ukraine are shown in Tabl.1.

 
 Table.1 Chemical compound and the trace element content of clinoptilolite

| compound  | %,weight            | compound          | %,weight            |
|-----------|---------------------|-------------------|---------------------|
| $SiO_2$   | 66.7                | Na <sub>2</sub> O | 2.06                |
| $Al_2O_3$ | 12.3                | MgO               | 1.07                |
| $Fe_2O_3$ | 1.05                | $P_2O_5$          | 0.04                |
| FeO       | 0.78                | $K_2O$            | 2.96                |
| $TiO_2$   | 0.18                | $SO_2$            | 0.04                |
| MnO       | 0.19                | F                 | 0.03                |
| CaO       | 2.10                | $H_2O$            | 10.0                |
| element   | $\mu { m g}/{ m g}$ | element           | $\mu { m g}/{ m g}$ |
| Mn        | 242                 | Zn                | 45                  |
| Zr        | 235                 | Υ                 | 22                  |
| Ba        | 232                 | Nb                | 22                  |
| Rb        | 110                 | Ga                | 20                  |
| Ce        | 52                  | Th                | 12                  |

After activation of clinoptilolite and  $\gamma$ -hematite together with standards the element content in samples has been defined by analysis of  $\gamma$ -spectra (Fig.3).



Fig.3. Gamma spectrum hematite

High crystallinity level, lattice fluctuations character: Si-O-Al-links in tetrahedral positions of clinoptilolite and Fe-O-links in cubic structure of  $\gamma$ -hematite have been noted in all investigated samples - before and after  $\gamma$ -activation [9,18].

Chemical activity of nanostructure materials has been investigated by means of registration of intensity of Fenton-reactions on quantometer with PEM-140. Research of kinetics of quantum processes in the protective materials which were used for radionuclide sorption allows to study intermediate stages of chemical reactions. These reactions stipulate formation of excited particles. The method essence consists of the following: thermostatically controlled chamber at  $37^{o}$ C for measurement takes places above photocathode of photoelectronic multiplier with investigation object.

The spontaneous luminescence of the sample is

measured, then by means of the special channel in the cavity is added inductor. The typical kinetics of luminescence is being detected. The luminescence is detected in the form of the maximum intensity of flash in imp./sec, intensity of final value of a luminescence after 4 minutes of measurement and lightsum reactions for 4 minutes of supervision.



**Fig.4.** Gamma spectrum solution CsNO<sub>3</sub>

CsNO<sub>3</sub> salt has been preliminarily irradiated by bremsstrahlung with maximum energy E=23 MeV and I=700  $\mu$ A (reaction <sup>133</sup>Cs( $\gamma$ ,n)<sup>132</sup>Cs). Activity of CsNO<sub>3</sub> solution was equaled 6.5 · 10<sup>6</sup> Bk/l (Fig.4). Influence of pH on sorption efficiency of caesium has been checked by pH instrument-340.

### 3. RESULTS AND DISCUSSION

Deactivation is a process of removal of radionuclide from a surface for the purpose of decrease of level of radiating influence on the person. Following requirements have been considered at making of deactivating agents: 1. pollution kind; 2. material of a processed surface; 3. cost of spent works; 4. processing of waste; 5. not to render of destroying action and not to raise sorption ability of a surface.

Such thermodynamic properties should be considered: 1. surface characteristic; 2. superficial tension; 3. waterproof interaction; 4. superficial energy; 5. capillary pressure; 6. wettability and flowing; 7. dispersion; 8. selectivity of an ionic exchange; 9. concentration dependence of viscosity, etc.

Selection of auxiliary substances has been spent taking into account the above-stated requirements: 1. neutral salts of organic acids; 2. alkaline salts of weak acids; 3. solutions of organic acids of 0.3...0.4%; 4. surface-active substance 0.3%; 5. pyrophosphate of sodium - Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>10H<sub>2</sub>O; 6. salt of the higher fat acids RCOONa; 7. primary aliphatic alcohol; 8. complexing substances: trilon, sulfonic acids, hexmetaphosphate sodium.

Agents for deactivation of the polymeric surfaces <sup>132</sup>Cs polluted, offered by us, included following components:

1. Thermomodified clinoptilolite (technical conditions 21, USSR 485-90).

2. Synthetic zeolite NaA (technical conditions-U-320.00.15.8764-023-97).

3. Nanohematite (particles less than 40 nm), (EEC No:215-168-2, LOT AIITO16 Alfa Aesor).

4. Superficially active substances (State Standard 237708-88).

5. Synthetic washing-up liquid (technical conditions 2383-075-00204300-99).

6. Organic acid (party 20051012).

7. Distilled water.

The  $^{132}$ Cs solution has been put on plastic surfaces in amount of 5 ml and left before full drying. Then various variants of deactivating agents have been put on these surfaces.

1. Polyethylene surface with 5 ml of  $^{132}Cs +$  surface-active substance.

2. Polyethylene surface with 5 ml of  $^{132}$ Cs + thermomodified clinoptilolite + synthetic zeolite NaA + organic acid + surface-active substance.

3. Polyethylene surface with 5 ml of  $^{132}$ Cs + thermomodified clinoptilolite + nanoparticles of  $\gamma$ -hematite + organic acid + surface-active substance.

4. Polyethylene surface with 5 ml of  $^{132}\mathrm{Cs}$  + distilled water.

After drying during 20 hours the deactivating agents have been washed off by the distilled water. Residual  $^{132}$ Cs activity on a plastic surface and the washed off solutions has been measured by Ge(Li)-detector.

The received results have shown, that residual activity  $^{132}$ Cs on a plastic surface after deactivation equal  $0.99\pm0.006\%$ ,  $0.41\pm0.004\%$ ,  $0.13\pm0.003\%$  and  $0.42\pm0.005\%$ , accordingly.

The momodified at 260°C clinoptilolite which is enriched nanostructural  $\gamma$ -hematite are the most effective agents for deactivation of caesium-137. The intracrystal space of the momodified clinoptilolite is free from molecules of intraframe water. Therefore ratio of active centers on a sorbent surface changes. That is cause of improvement of their selectivity and kinetic characteristics for sorption <sup>137</sup>Cs. Also the sorption capacity of deactivating agents increases owing to use nanoparticles.

Oxidative processes on a surface of the developed sorbents strengthen as a result of use of such combination of components in deactivating agents and in consequence of oxidant formation.

For determination chemical reactivity this model system we focused on the ability of the ironexchanged forms of zeolites to produce hydroxyl radicals from  $H_2O_2$ . Fenton's reagent generates powerful oxidants called hydroxyl radicals (•OH) through the reaction of ferrous iron and hydrogen peroxide [20]:

 $\mathrm{Fe}^{2+} + \mathrm{H}_2\mathrm{O}_2 \rightarrow \mathrm{Fe}^{3+} + {}^{\bullet}\mathrm{OH} + \mathrm{OH}^{-}.$ 

It is one of the few methods available to generation these powerful oxidants without requiring light, additional energy or sophisticated equipment.

The method of chemiluminescence was used for determination intensity of the oxidative burst from different system. Light emission of decontamination agent with  $^{132}$ Cs was detected by photomultiplier-140 (range 350-750 nm).

Comparison of the levels of chemiluminescence of isolation components which are part of deactivating agents for  $^{132}$ Cs sorption are presented in Fig.5.



Fig.5. Intensity of the emission from solution

The highest chemiluminescence signal was registered in the system themomodified clinoptilolite with nanohematite. Obviously nanohematite plays an important part in the radical production. Natural clinoptilolite and artificial zeolite produce free radicals too. Even  $CsNO_3$  solution generate hydroxyl radicals as a result of initiated chemiluminescence. The small amounts of hydroxyl radicals produced in clinoptilolite +  $CsNO_3$ , artificial zeolite +  $CsNO_3$ and  $CsNO_3$  show low activity of Fenton reaction.

Generation of singlet oxygen was observed by the  $H_2O_2$  -  $OCl^-$  system [21,22].

The sodium hypochlorite (NaClO) has been received by means of electrolysis of sodium chloride (NaCl 0.9 %) before the beginning of experiment during hour. The anode material was pyrolitic graphite, and the cathode - spectroscopic pure graphite. Electrolysis carried out (I = 15 A/cm<sup>2</sup>, U = 3.5 V) in the quartz cell which was placed on magnetic mixer. Electrolysis time was 60 minutes. Primary processes on electrodes: on the anode  $2Cl^- \rightarrow Cl_2 + 2e$ ; on the cathode  $2H_2O + 2e \rightarrow 2OH^- + H_2$ . Hypochlorite and hypochlorous acid are formed at intermixing of anode and cathodic products:

 $Cl_2 + 2OH^- = ClO^- + Cl^- + 2H_2O;$ 

 $\mathrm{Cl}_2 + \mathrm{OH}^- = \mathrm{HClO} + \mathrm{Cl}^-.$ 

pH of sodium hypochlorite (NaClO) was 8.2. Formation of singlet oxygen  $(^{1}O_{2})$  was induced by reaction:

 $H_2O_2 + OCl^- = Cl^- + H_2O + {}^1O_2.$ 

Lifetime of singlet oxygen in a water phase is rather insignificant. The singlet oxygen lets out light quanta in visible and infra-red areas of a spectrum at transition in triplet condition. The quantum exit in a water phase is  $10^{-10}...10^{-12}$  (calculation data).

The interference filter (634 nm) for measurements singlet oxygen was placed above photomultiplier.

That system was able register single oxygen in different decontamination agents with  $^{132}$ Cs. It was shown, the level of spontaneous chemiluminescence in system nanoparticles  $\gamma$ -hematite and thermomodified clinoptilolite was the most high (I=11230±147 imp./sec).

The knowledge of the intensity of single oxygen in similar system is essential for an understanding of the mechanism of the oxidation process.

Sorption abilities of thermomodified clinoptilolite (260°C) have been studied at temperature 20°C and under the influence of VHF field with 10 % intensity at 65°C. For this purpose the samples were placed on incubation (24 hours) in alkaline solution NaOH (pH=8) with addition of activated solution of nitrate caesium. Centrifugation of solution has been realized after incubation. Solutions of leachate were transparent, did not contain suspensions and deposits, pH $\approx$ 8...8.5.

The sorption material deposits and leachate have been analysed on Ge(Li)-detector. The indicators of  $^{132}$ Cs sorption efficiency counted according to values of initial solution activity, leachate and deposits.

The comparative analysis of the investigated samples has shown, that at 20°C the rate of sorption of <sup>132</sup>Cs in a deposit (hematite + clinoptilolite) has amount 60%, in a deposit (themomodified 260°C clinoptilolite) - 81%, in a deposit (VHF themomodified clinoptilolite) - 79%. The rate of the contents <sup>132</sup>Cs in supernatant fraction has amount 1.1, 7.8 and 5.0%, accordingly. Discrepancy of total values (100%) of <sup>132</sup>Cs contents in solutions and deposits, in our opinion, can be explained by formation of volatile forms of <sup>132</sup>Cs. Besides it can be peroxide compounds of caesium Cs<sub>2</sub>O<sub>2</sub> and Cs<sub>2</sub>O<sub>3</sub> which are powerful oxidizers. The last vigorously incorporate to water, forming hydroxides CsOH which, in turn, cooperating with ozone and form volatile compounds.

The method of registration of high reactive products has been used as a express-estimation of action of an irradiation and influence of additional substances on physic mechanical properties of developed sorbents.

Features of induced by peroxide hydrogen of luminescence of the <sup>132</sup>Cs solution in different combinations of a solution of themomodified clinoptilolite without and with addition nanoparticles of hematite have been investigated. The carried out measurements have shown, that the maximal intensity of flash of a luminescence of the <sup>132</sup>Cs solution has made  $1563\pm63$  imp./s, intensity of final value 250 $\pm$ 24 imp./s, lightsum  $\Sigma$ =1066 $\cdot$ 10<sup>2</sup> imp.; for a sample of themomodified clinoptilolite with addition of the <sup>132</sup>Cs solution the maximal flash of a luminescence has made  $2460\pm58$  imp./s, intensity of final value  $324\pm28$  imp./s, lightsum  $\Sigma = 1800 \cdot 10^2$  imp.; for a sample of themomodified clinoptilolite with addition nanohematite and  $^{132}$ Cs the maximal flash of a luminescence has made  $3210\pm103$  imp./s, intensity of final value  $266 \pm 32$  imp./s, lightsum  $\Sigma = 2055 \cdot 10^2$  imp.

#### 4. CONCLUSIONS

1. Deactivating agents which included of natural clinoptilolite and nanoparticles  $\gamma$ -hematite is developed and approved.

2. Modified clinoptilolite is effective sorbent of  $^{132}\mathrm{Cs}$  with plastic surfaces.

3. The created deactivating agents has the improved selective and kinetic characteristics for sorption  $^{132}$ Cs out of the liquid medium.

4. High intensity of chemical Fenton reaction for  $^{132}$ Cs sorption by nanostructure materials with clinoptilolite + hematite was detected.

5. Formation of volatile compounds ( $Cs_2O_2$  and  $Cs_2O_3$ ) in process of <sup>132</sup>Cs sorption by nanostructure materials (hematite + clinoptilolite) is revealed.

## References

- G. Lujaniene, S. Meleshevych, V. Kanibolotsryy, et al. Synthesis and Characterization of Inorganic Sorbents and Their Application to Sorption of Radionuclides // Lithuanian Journal of Physics. 2008, v.48, N.1, p.107-114.
- A. Jain, N. Rawat, S. Kumar, et al. Sorption of Neptunium by Hematite Colloids // Radiochimica Acta. 2007, N.95, p.501-506.
- L. Sharygin, A. Muromskiy, M. Kalyagina. A Granular Inorganic Cation-Exchanger Selective to Cesium // J. of Nuclear Science and Technology. 2007, v.44, N.5, p.767-773.
- N.F. Chelishchev, B.G. Berenshtejn, V.F. Volodin. Zeolites - new type of mineral raw materials. M: "Nedra", 1987, 176 p, (in Russian).
- H.Van Bekkum, E.M. Flaningen, J.C. Jansen. Introduction to Zeolit Science and Practic. Amsterdam: "Elsevier", 1991, 355 p.
- P. Rajec, F. Macasek, P. Misaealides. Sorption of heavy metals and radionuclides // Natural Microporous Material in Environmental Technology. 2007, v. 362, Ser.E: Applied Sciences, p.353-363.
- A.M. Grancaric, A. Tarbuk, I. Kovacek. Nanoparticles of activated natural zeolite on textiles for protection and therapy // Chemical Industry & Chemical Quarterly. 2009, v. 15(4), p.203-210.
- N.K. Moroz, J.V. Seretkin, I.S. Afanasev, V.V. Bakakin. Structure and diffusion mobility extraskeleton subsystems in hydrated ammonium forms of zeolites clinoptilolite and chabazite // *Jour. Struct. Chem.* 2002, v. 43, p.642-648 (in Russian).
- N.P. Dikiy, E.P. Medvedeva, I.D. Fedorets, N.P. Khlapova. Thermoupdating nanopowder natural clinoptilolite // Vesnyk KNU Ser.: Physics. Nuclears, Particles, Fields. 2009, N.880, iss.4(44), p.84-90 (in Russian).

- D.T. Breck. Zeolites molecular sieves: structure, chemistry and use. New York: "John Wiley & Sons Inc.", 1974, 663 p.
- O.V. Salata. Application of nanoparticales in biology and medicine // Journ. Nanobiothechnology. 2004, v. 2:3, p.1-6.
- B. Dousova, T. Grygar, A. Martaus, et al. Sorption of AsV on aluminosilicates treated with FeII nanoparticles // J. Colloid. & Inter. Sci. 2006, v. 302, p.424-431.
- I. Melian-Cabrera, F. Kapteijn, J.A. Moulijn. Innovation in the synthesis of Fe-(exchanged)zeolites // Catal. Today. 2005, v. 110, p.225-263.
- K. Kayama, Y. Takeushi, Clinoptilolite: The distribution of Potassium atoms and its role in thermal stability // Z. Kristallogr. 1977, v.Bd.145, p.216-239.
- Th. Armbruster Dehydration mechanism of clinoptilolite and heulandite: Single crystal X-ray study of Na-poor, Ca-, K-, Mg-rich clinoptilolite at 100 K // Americal Mineralogist. 1993, v. 78, p.260-264.
- M. Jhonson, D. O'Connor, P. Barnes, at al. Cation exchange, Dehydration, and Calculation in Clinoptilolite: in Situ X-ray Diffraction and Computer Modeling // J. Phys. Chem. 2003, v. B107, p.942-951.
- A. Godelitsas, Th. Armbruster HEU-type zeolites modified by transition elements and lead // *Micropor. Mesopor. Mater.* 2003, v.61, p.3-24.
- N.P. Dikiy, E.P. Medvedeva, I.D. Fedorets, N.P. Khlapova. Structure and magnetic properties of gamma activated nanoparticles of magnetite // Vesnyk KNU Ser.: Physics. Nuclears, Particles, Fields. 2009, N.859, iss.2(42), p.89-94 (in Russian).
- 19. N.P. Dikiy, A.N. Dovbnya, E.P. Medvedeva, et al. Gamma activation and spectral analysis of element composition, structure and sorption activity of radiation synthesized magnetite and osmium nanoparticles // Vesnyk KNU Ser.: Physics. Nuclears, Particles, Fields. 2008, N.823, iss.3(39), p.78-84 (in Russian).
- How Rusting Iron Can Clean up Toxic Spills // Science. 2005, N.823, iss.3(39), p.19-21.
- S. Jockusch, J. Sivaguru, N.J. Turro, V. Ramamurthy. Direct measure of singlet oxygen lifetime in zeolites by near-IR phosphorescence // *Photochem. Photobiol. Sci.* 2005, N.4, p.403-405.
- R.L. Arudi, H.J. Bielski, A.O. Allen. Search for singlet oxygen luminescence in the disproportion of HO<sub>2</sub>/O<sub>2</sub><sup>-</sup>// *Photochem and Photobiol.* 1984, v.139, N.5, p. 703-706.

## СЕЛЕКТИВНЫЕ К ЦЕЗИЮ НАНОСТРУКТУРИРОВАННЫЕ ДЕЗАКТИВИРУЮЩИЕ СРЕДСТВА

## Н.П. Дикий, А.Н. Довбня, Ю.В. Ляшко, Е.П. Медведева, Д.В. Медведев, В.Л. Уваров, И.Д. Федорец, Н.П. Хлапова, Д.С. Бакай

Исследовалась химическая реактивность природного клиноптилолита и наночастиц  $\gamma$ -гематита, которые обладают высокой селективной сорбционной способностью в отношении <sup>132</sup>Cs. В качестве модели дезактивирующего средства для сорбции <sup>132</sup>Cs с полиэтиленовых поверхностей и водных растворов, помимо клиноптилолита и наночастиц  $\gamma$ -гематита были использованы дополнительные (вспомогательные) компоненты. Фотоактивационный анализ был использован для изучения примесного состава образцов природного клиноптилолита и активированного  $\gamma$ -гематита. Квантометрический метод применялся для определения интенсивности генерации свободнорадикальных продуктов в присутствии перексида водорода (Fenton reaction). Измерение с помощью Ge(Li)-детектора остаточной активности <sup>132</sup>Cs в твердой и жидкой фракциях дезактивирующих средств показало, что процесс сорбции <sup>132</sup>Cs сопровождается образованием летучих форм <sup>132</sup>Cs. Высокий синергетический эффект сорбции <sup>132</sup>Cs показан с использованием дезактивирующего средства на основе наноструктурного термомодифицированного природного клиноптилолита и наночастиц  $\gamma$ -гематита.

## СЕЛЕКТИВНІ ДО ЦЕЗІЮ НАНОСТРУКТУРОВАНІ ДЕЗАКТИВАЦІЙНІ ЗАСОБИ

## М.П. Дикий, А.М. Довбня, Ю.В. Ляшко, О.П. Медведева, Д.В. Медведев, В.Л. Уваров, І.Д. Федорець, Н.П. Хлапова, Д.С. Бакай

Досліджувалась хімічна реактивність природного кліноптилоліту та наночастинок  $\gamma$ -гематиту, які володіють високою здатністью до сорбції <sup>132</sup>Cs. У якості моделі дезактивуючого засобу для сорбції <sup>132</sup>Cs з поліетиленових поверхонь і водних розчинів, окрім клиноптилоліту та наночатинок  $\gamma$ -гематиту, були використані допоміжні стандартизовані речовини. Фотоактиваційний аналіз був використаний для вивчення домішкового складу зразків природного кліноптилоліту і активованого  $\gamma$ -гематиту. Квантометричний метод використовувався для визначення інтенсивності генерації вільнорадикальних продуктів при індукції пероксидом водню. Вимірювання за допомогою Ge(Li)-детектора залишкової активності <sup>132</sup>Cs в осадовій та рідкій фракціях дезактивуючих засобів виявило, що процес сорбції <sup>132</sup>Cs супроводжується утворенням летючих форм <sup>132</sup>Cs. Високий синергетичний ефект сорбції <sup>132</sup>Cs виявляється при умові, коли в складі дезактивуючого засобу присутні прирордний клиноптилоліт та наночастинки  $\gamma$ -гематиту.