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THE EFFECT OF RADIATION DOSES TYPICAL FOR HIGH-LEVEL WASTE ON THE PROPERTIES OF THE CEMENT MATRIX

Varlakov A. P.[1], Kapustin V. V.[1], Varlakova G. A.[1], Zherebtsov A. A.[2], Petrov V. G.[3], Shirshin E. A.[3], Kalmykov S. N.[3]

[1]JSC «A.A. Bochvar High-Technology Research Institute of Inorganic Materials», Moscow, Russian Federation

[2]ITCP "Proryv", Moscow, Russian Federation

[3]M. V. Lomonosov Moscow State University, Moscow, Russian Federation

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Radiation stability of Portland cement based compounds was studied under gamma irradiation at absorbed dose values up to 108 Gy, which is similar to the irradiation dose of high-level waste within the storage period. The results of investigation of their physical and chemical properties, morphological, structural and phase features demonstrated the ability of cement compounds to retain their characteristics under such irradiation doses.

Keywords: *cementation, radiation stability, irradiation doses, compressive strength, gas yield, structural properties.*

Introduction

Cementation is one of the most widespread method of radioactive waste conditioning. There are well-developed relevant technological processes and equipment. Cementation is used for conditioning of both liquid and solid radioactive waste with low- and intermediate-activity levels. The advantages of the method include its simple technology, inflammability and compression strength of the obtained matrix.

Currently the cement compound is not considered as a suitable matrix for immobilization of high-level waste (HLW). This is predominantly due to high dose loads on the cement stone in process of storage and high content of bound and free water and salts in the matrix. However, cement materials, especially Portland cement, are widely used for construction of storage pools and storage facilities for spent nuclear fuel [1], spent ionizing radiation sources, as radiation-protection materials in reactors, and, ultimately in containers for RW storage and disposal [2—4].

The cement itself is a radiation-stable material. Radiation degradation affects the water, hydrates and salts contained in the cement stone [5]. It is believed that radiation effects, in particular, radiolysis, may lead to the change of properties of cement compound, including: decrease of strength, fracturing due to gas generation, water resistance properties reduction and increase of radionuclide release rate. This compromises the reliability of the cement matrix, which should localize HLW for a long period of time comparable to the decay time of confined radionuclides or the preset storage time.

Understanding the mechanism of cement material hydration, formation and change of cement compound matrix in presence of RW is required in order to forecast the properties of compounds.

Solidification of cement compounds has a complex character: after strengthening there may be an abrupt drop or slowing of solidification with restoration of slow monotonous strength increase for up to 1 year with subsequent stabilization of strength

parameters. The general cause of strength drop in binding systems is connected to the inherent contradictory character of solidification processes, when the increase of structure strength is accompanied by processes leading to internal stress and degradation of the initially stabilized structure.

There should be noted the relatively small number of publications [6-8] dedicated to the issue of radiation stability of cement compounds with RW. At the same time, there are a number of studies where researchers indicate that there may be prospects of using cement materials for HLW immobilization [9,10]. There is a substantial lack of data of radiation testing for cement compounds, while the reasoning and conclusions were in most cases based on the general idea of cement stone properties.

The available works frequently considered separate parameters of cement compounds in irradiation conditions. For example, [11, 12] considered the change of mechanical strength and mineral composition of cement for dose values of 1 MGy. Only data on mechanical strength for doses up to 10^9 rad (equivalent of 10 MGy) [13] and 22 MGy [14] were given. Only phase composition and cement surface morphology evolution for doses up to 1409 MGy were studied in [15]; gas release for doses up to 2 MGy was studied in [16]. The works where the same object was studied systematically with respect to a number of parameters (cement stone strength, element leaching, gas release, etc.) have used irradiation doses of 1-2 MGy [10].

Reference analysis shows that cement-based compounds were considered to be resistant materials for exposure doses up to 10^6 Gy. For such irradiation dose there were no noticeable changes in the mechanical properties of cement materials, due to both negligible gas generation and sufficient gas permeability of cement stone. However, according to GOST R 50926-96 [17] HLW immobilization matrices should remain stable at doses up to $1 \cdot 10^8$ Gy (β- and γ-radiation)

In general, the predominant use of standard cement at nuclear facilities indicates the potential to implement immobilization of certain types of HLW in a cement matrix.

The goal of the current work was comprehensive assessment of regulated properties, phase composition and microstructure of cement compounds subjected to high ionizing radiation doses (up to 10^8 Gy) characteristic for high-level waste.

The goal of the current stage of works was to obtain initial information on the impact of gamma-radiation on traditional cement stone made from standard Portland cement and pure water. The results will subsequently be used for comparative analysis of the whole spectrum of radiation on the cement compound, including compounds with radioactive waste components.

Mechanical, physical, chemical properties, gas generation, structural and phase features of cement compounds were studied for absorbed dose values up to 10^8 Gy, which is similar to the irradiation doses of HLW over the storage period.

Research methods

The object studied in the current work was cement compound made of Portland cement PTs TsEM I 42.5B with water-cement (W/C) ratio of 0.5 with no additives. Characteristics of cement compound at solution stage are given in Table 1.

Table 1. Cement solution properties

Parameter name, unit	W/C	Density, g/cm^3	Spreadability, mm	Water gain, % of volume	Setting time, hours-min., beginning-end
Value	0.5	1.79±0.18	123±3	3.0±0.5	4-20±5 5-20±5

Spreadability of cement solution was determined using "AzNII KR-1" cone, and the binding time was determined using Vicat apparatus of OGTs-1 model.

Mechanical, physical and chemical properties of the compounds were measured at solidification stage: compression strength at solidification times of 7, 14, 28 days; low temperature resistance at 28 days; water resistance at 28 days (stability to long-term immersion in water during 28 days); radiation stability of the samples at solidification time of 28 days.

The methods used in cement compound tests corresponded to the methods recommended in relevant GOST standards. The tests were performed for samples having the form of bars 1×1×3 cm and cubes 2×2×2 cm.

Mechanical compression strength was measured using test facility manufactured by Testing Cybertronic with an appliance for pressing cement samples of bar and cube shapes. Low temperature stability of cement compounds was tested by periodic freezing and thawing of samples in a climate cell MK-53.

X-ray diffraction analysis (XDA) of cement compound was performed using x-ray diffractometer Ultima-IV manufactured by Rigaku. Operating mode: 40 kV 40 mA, CuK_a-radiation, nickel filter, measurement range 2—80° 2θ, scanning angle increment 0,02° 2θ, fixed system of focusing slits. Semiconductor detector DTex/Ultra was used to accelerate the imaging and enhance the quality of experimental data: scanning rate 5° 2θ/minute. Mineral composition diagnostics was performed by comparing experimental and reference spectra form the PDF-2 database of Jade 6.5 software produced by MDI.

Morphological characterization of the samples was performed using scanning electron microscope (SEM) JEOL JSM 6380 LA at accelerating voltage of 20 kV in the mode of secondary electrons. For SEM studies a thin slice of the sample studied was

Table 2. Strength parameters of unirradiated cement compounds

Mechanical compression strength, MPa (mean value for all measurements)						
Compound solidified in humid air conditions			In process of low temperature resistance tests		In process of water resistance tests	
7 days	14 days	28 days	Control compound at equivalent hardening time	Compound after 30 freezing/thawing cycle	Control compound at equivalent hardening time	Compound after 28 days of immersion in water
20.53±4.93	26.25±6.30	31.67±7.60	45.4±10.90	45.4±10.90	66.5±15.9	68.20±16.37

coated with gold. The samples were also studied using transmission electronic microscope (TEM) JEOL JEM 2100F.

The cement samples were irradiated in a gamma cell "Gamma-400" using a Cs-137 radiation source with an energy of 661 keV. Cement samples at 28 day of hardening were placed in a glass tube, the tube was sealed and irradiated in the gamma cell for the time sufficient to obtain absorbed doses of 10^6, 10^7, 10^8 Gy. The tubes with irradiated samples were used to determine gas release. Quantitative and qualitative analysis of gases released in cement compound irradiation was performed using LIBS — Laser-Induced Breakdown Spectroscopy. The advantage of the method with respect to the alternatives include simple implementation, universal application and fairly low detection threshold (at the level of 100 ppm of volumetric concentration).

Results and discussion

Studies of samples before and after irradiation with doses of 10^6, 10^7, 10^8 Gy were performed in order to obtain comparative assessment of cement compound properties.

Mechanical and physical properties of unirradiated compounds are given in Table 2.

Compression strength tests after 30 freezing/thawing cycles and after 28 days of immersion in water were carried out simultaneously with testing similar specimen with the same solidification time stored in humid air conditions.

Measurement results demonstrate traditional process of cement compound solidification, with compound strength increasing with time due to hydration processes in the cement stone.

In radiation stability tests the cement samples were placed in a sealed glass tube. After the opening of the tube, the specimen were measured with regards to mechanical strength, and compression strength of similar specimen stored in humid air conditions were performed simultaneously. The changes of phase composition, microstructure and surface morphology were studied by XPA, TEM, and SEM methods respectively.

Results of gamma-radiation impact on mechanical strength of cement compounds are given in Table 3.

No traces of mechanical degradation, i.e. chips, fractures were found in visual inspection of irradiated samples. Cement compounds retain high compression strength for irradiation dose increase from 10^6 to 10^8 Gy and conform to regulatory requirements. Their compression strength is 4—8 times higher than the regulatory requirement for immobilized RW (5 MPa).

Comparison of sample phase composition before and after irradiation for various absorbed dose values showed that no changes in the composition were manifested even for high irradiation doses (up to 10^8 Gy). Relative content of minor mineral phases changes insignificantly from sample to sample, however, this was likely caused by heterogeneity of the samples.

TEM images of mineral phase crystals before and after irradiation with absorbed dose of 10^8 Gy are shown in Fig. 1.

The structure of crystals indicates that crystals of the sample are not affected by irradiation. No visible changes in structure of separate crystal were observed.

SEM images showed no differences in sample surface morphology before and after irradiation (Fig. 2).

Comparative analysis of XPA, TEM and SEM results suggest that irradiation with doses of 108 Gy do not lead to changes in cement stone structure, newgrowths or defects. Apparently, the conditions (temperature, pressure, gas generation) formed by the respective irradiation doses were insufficient for destruction reaction in the cement stone or development of microfracture defect structure.

The results obtained indicate that compositions for immobilization of a wide spectrum of radioactive waste with high activity level can be based on cement.

Gas generation under irradiation. Studies of gas generation were performed by measuring the plasma spectrum obtained as a result of laser-induced optical breakdown in the volume of sealed glass tube. Sealed air-filled tubes were used for "blank experiment" in addition to tubes with irradiated samples. Spectra were recorded in wavelength

Table 3. Compression strength of irradiated cement compounds

Gamma-radiation, Gy	Mechanical compression strength, MPa
Reference sample	33.61±8.06
10^6	32.13±7.71
10^7	37.57±9.02
10^8	30.95±7.43

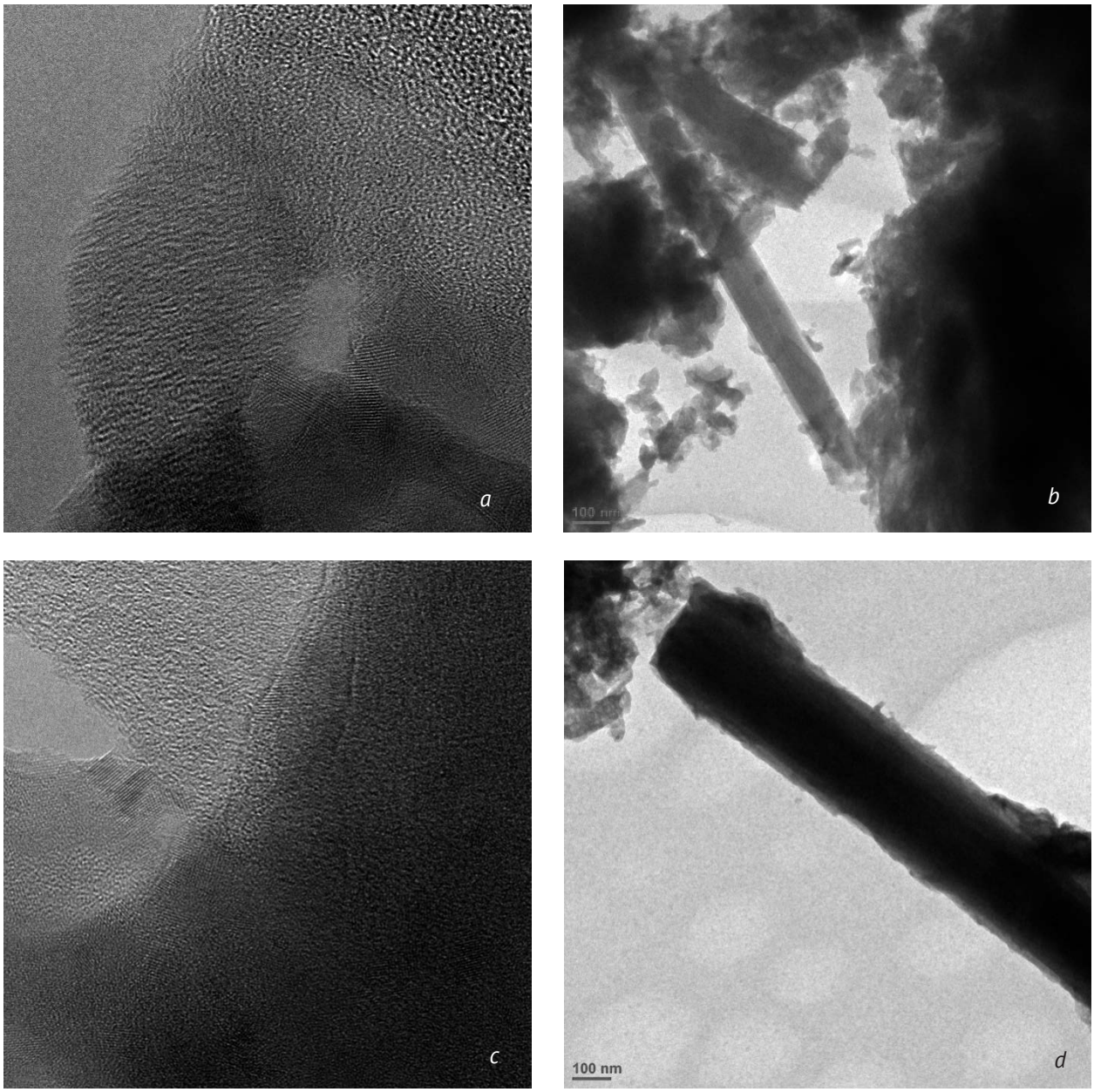

Fig. 1. Comparison of TEM images of cement compound before irradiation (a, b) and after irradiation (c, d) with absorbed dose $1 \cdot 10^8$ Gy

range of 640—770 nm (Fig. 3). Hydrogen emission was observed at 656 nm (water vapors), and nitrogen triplet was observed at 745 nm. Spectrum statistics obtained every (2—3) thousand laser pulses was collected for each of the samples. Hydrogen concentration in each experiment was assessed out of intensities of hydrogen and nitrogen lines, as the nitrogen concentration in the samples was constant. To increase accuracy, the ratio was assessed based on images with high hydrogen line intensity.

The obtained data on hydrogen concentrations and known glass tube volume were used to calculate the quantity of hydrogen generated in process of irradiation (Fig. 4).

The lines in Fig. 4 show experimental data approximation results in the dose range 10^4—10^8 Gy, with the following equation used as a mathematical model [18]:

$$n(H_2) = n_\infty (1 - e^{-kD}), \text{ mol/g}$$

where $n(H_2)$ — quantity of hydrogen released from a unit of sample mass as a function of irradiation dose, mol/g; n_∞ — quantity of hydrogen released for infinitely high irradiation dose, mol/g; D — exposure dose, Gy; k — hydrogen generation rate constant, Gy^{-1}. It should be noted that the equation does not explain the water radiolysis processes taking place in cement compound. Detailed models of such processes are described, e. g. in [19—21].

Nevertheless, such approximation allows assessing potential hydrogen generation for a given irradiation dose value. Experimental data demonstrated that maximum hydrogen generation does not exceed 10^{-3} mol/g (sample weight) for absorbed dose value of 10^8 Gy.

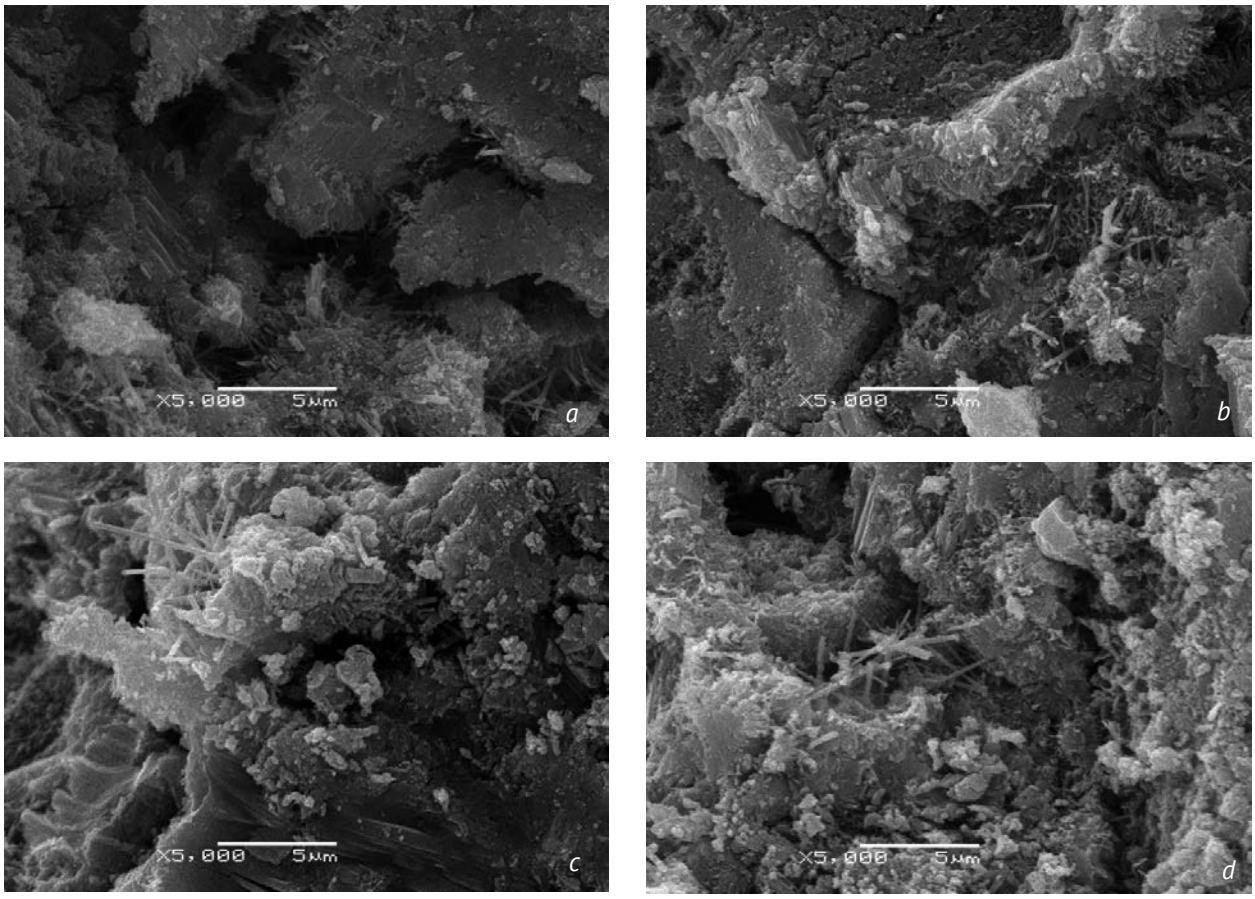

Fig. 2. Comparison of SEM images of cement compound before irradiation (a) and after irradiation with absorbed doses $1 \cdot 10^6$ Gy (b), $1 \cdot 10^7$ Gy (c), $1 \cdot 10^8$ Gy (d)

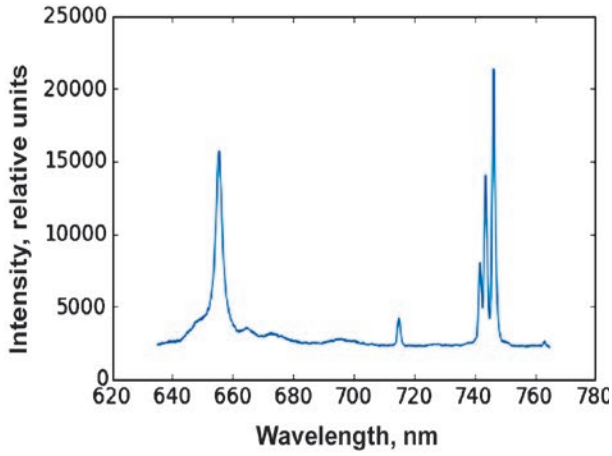

Fig. 3. Plasma emission spectrum for air in the glass tube

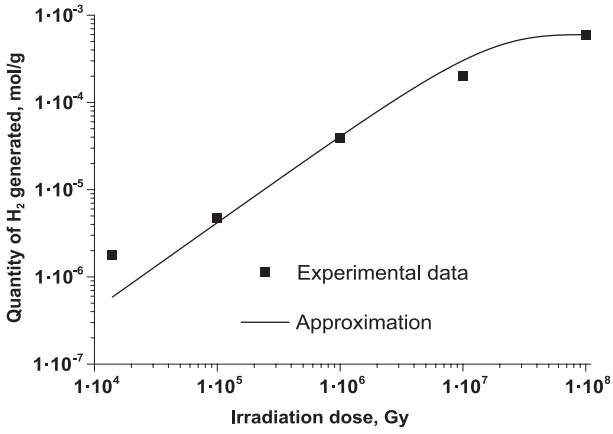

Fig. 4. Quantity of hydrogen released (mol) as a function of irradiation dose (Gy)

Conclusions

The studies carried out have demonstrated that cement compounds based on standard Portland cement are capable of retaining their physical and mechanical properties, phase composition and structure under irradiation conditions equivalent to radiation impact of HLW over the storage time, and, therefore, may be considered as a matrix for immobilization of not only medium-level, but also high-level waste.

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Information about the authors

Varlakov Andrej Petrovich, Doctor of Sciences, Director of Department, JSC «VNIINM» (5a, Rogova st., Moscow, Russia, 123060), e-mail: APVarlakov@bochvar.ru.

Varlakova Galina Andreevna, PhD, Main Specialist, JSC «VNIINM» (5a, Rogova st., Moscow, Russia, 123060), e-mail: varlakova@inbox.ru.

Zherebcov Alexander Anatolevich, PhD, Head of Department, ITCP «PRORYV», e-mail: zhala@proryv2020.ru.

Kalmykov Stepan Nikolaevich, Doctor of Sciences, Acting Dean of Chemical Faculty of MSU, Lomonosov Moscow State University (1, Leninskie gory st., Moscow, Russia, 119991), e-mail: stepan@radio.chem.msu.ru.

Kapustin Vitalij Vladimirovich, Lead Engineer, JSC «VNIINM» (5a, Rogova st., Moscow, Russia, 123060), e-mail: vit4022@gmail.com.

Petrov Vladimir Gennadevich, PhD, Associate Professor, Lomonosov Moscow State University (1, Leninskie gory st., Moscow, Russia, 119991), e-mail: vladimir.g.petrov@gmail.com.

Shirshin Evgenij Alexandrovich, PhD, Senior Research Officer, Lomonosov Moscow State University (1, Leninskie gory st., Moscow, Russia, 119991), e-mail: eshirshin@gmail.com.

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