INVESTIGATION OF GRANITE ROCKS RADIATION-CHEMICAL DURABILITY

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Gamma-activation analysis is used to study dynamics of leaching of various elements from granite samples. The sample preliminary irradiation and activation was carried out in the field of bremsstrahlung of electron accelerator. With the use of Ge(li) detector concentration of sodium, cesium and manganese isotopes in the leachant as well as the dependence of diffusion coefficient are determined.

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1. INTRODUCTION

Managing spent nuclear fuel supposes it to be kept in water pools and dry storage facilities at the nuclear plants for 10-50 years with the following placing in the geological repositories. During disposal in the geological structures the long-living isotopes of nuclear fuel fission has particular importance: ^{99}Tc (period of half-decay $T_{1/2}$ makes up to $2{,}1\cdot10^5$ years), ^{129}I ($T_{1/2} = 1{,}6\cdot10^7$ y), ^{135}Cs ($T_{1/2} = 2{,}3\cdot10^6$ y), ^{93}Zr ($T_{1/2} = 1{,}5\cdot10^6$y), ^{126}Sn ($T_{1/2} = 10^5$ y), ^{79}Se ($T_{1/2} = 6{,}5\cdot10^4$ y), ^{137}Cs ($T_{1/2}$= 30,2 y), ^{90}Sr ($T_{1/2}$= 28 y) and actinides: ^{239}Pu ($T_{1/2} = 2{,}4\cdot10^4$ y), ^{240}Pu ($T_{1/2} = 6{,}5\cdot10^3$ y), ^{242}Pu($T_{1/2} = 3{,}8\cdot10^5$ y), ^{241}Am ($T_{1/2}$= 432 y), ^{244}Cm($T_{1/2}$ = 18 y). The most ecologically dangerous from these elements are ^{137}Cs, ^{135}Cs, ^{129}I, ^{99}Tc. They are dissolved in the water and can easily get into the biological cycle. From the total amount of materials intended for disposal, the volume containing these elements is up to 90% [1].

In Ukraine, the repositories for long-term disposal of radioactive wastes (RAW) are supposed to place in geological structures of the Ukrainian Crystalline Shield (UCS) [2]. Therefore, the investigation of durability of UCS rocks as a geological barrier under the condition of radiation effect is a topical problem. It is also stipulated by the possibility to use the component of the UCS rocks to immobilize RAW. Of particular interest is the study of long-living radionuclides migration during corrosion processes in the mountain rocks.

Applying nuclear-physical methods is rather an efficient means to research radionuclides diffusion and leaching processes [3-6].

The purpose of the work was developing the method of researching the diffusion processes of leaching materials and Mn (Tc analogue in chemical properties) in non-organic materials under the terms of the combined (radiation and corrosion) effect as well as demonstrating the possibilities of this method on the example of the granite samples.

2. THE METHODS OF EXPERIMENT

For the investigation granite samples of UCS Dneprovskiy deposit made in the shape of parallelepiped with the size 10x10x10.5 mm and mass (2,8-2,9) g were chosen. The samples were irradiated in the field of bremsstrahlung of the electron accelerators at two stages: first – at the value of upper boundary of the photon energetic spectrum $E_{\gamma\ max}$=10 MeV up to the value of the absorbed dose (AD) $1{,}7\cdot10^7$ Gy, after that the samples were activated at $E_{\gamma\ max}$=23 MeV during 7 days up to the summary value of AD $3{,}0\cdot10^7$ Gy. Then the samples were kept for some days to reduce the level of the induced radioactivity, ground up into granules with the size less than 0.83 mm which allowed to increase their surface area from 6,2 to 59 cm^2 and underwent dynamic tests on leaching in the plant based on Soxhlet extractor [7] by methods described in work [8].

Soxlet extractor is traditionally used in geological research to carry out prolonged experiments simulating the process of natural weathering.

The temperature of the leachant in the cylinder of the extractor was 72°C. The leachant was discharged every 1,5, 3,5, 30, 105 and 113 hours. After each discharge of the leachant its activity was measured by Ge(Li) spectrometer with power identification 2,8 keV (on the line E_γ=1333 keV). This approach made it possible to study dynamics of leaching the various chemical elements from the investigated samples with high sensitivity.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Gamma-activation analysis of samples showed that the feature of the element composition of the studied granite is the increased content of uranium – 10 μg/g 3 times exceeding its characteristics clark value. The content of Zr and Nb in the sample was also higher than characteristic values.

The typical spectrum of gamma-radiation of the granite sample after activation is given on Fig.1. On the spectrum the lines from photo-nuclear reaction on the matrix and microelements of granite can be definitely see: $^{48}Ca(\gamma,n)^{47}Ca \rightarrow ^{47}Sc$, $^{23}Na(\gamma,n)^{22}Na$, $^{23}Na(n,\gamma)^{24}Na$, $^{93}Nb(\gamma,n)^{92m}Nb$, $^{85}Rb(\gamma,n)^{84}Rb$, $^{89}Y(\gamma,n)^{88}Y$, $^{133}Cs(\gamma,n)^{132}Cs$, $^{55}Mn(\gamma,n)^{54}Mn$, $^{238}U(\gamma,n)^{237}U$. The element and crystal-optic analysis of the samples allowed defining the granite composition (see the table).

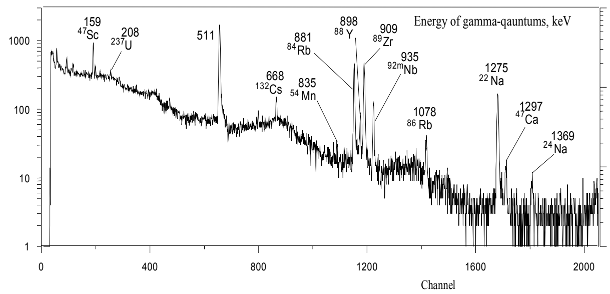

Fig. 1. *γ-spectrum of granite sample after activating by bremsstrahlung*

Chemical and mineralogical compositions

Chemical composition		Mineralogical composition	
Oxide	%, mas	Mineral	%,mas
SiO_2	72,9	Quartz (SiO_2)	25-30
Al_2O_3	14,1	Potassium feldspars (orthoclase, microcline) $K(Na)AlSi_3O_8$	55-60
Fe_2O_3 FeO	2,2		
CaO	1,4	Acid plagioclases, albite $Na(Ca)AlSi_3O_8$	<10
MgO	1,0	Color mica, biotite $K(Mg,Fe,Mn)_3\cdot[AlSi_3O_{10}(OH,F)_2]$	10-12
K_2O, Na_2O	8,4		
		Muscovite $2[K_2Al_4(Si_6Al_2O_{20})(OH,F)_4]$	<1
TiO_2	< 0,1	Accessory: garnet, zircon, apatite, monazite and ore minerals: magnetite, hematite	<1

3.2. The leachant spectrum after 113 hours of leaching is showed on Fig.2. Its analysis shows that sodium, rubidium and calcium are leached from granite most intensely. There was no noticeable release of uranium and yttrium from this sample.

3.3. Amount *q* of substance of passed through the unity of the sample surface for time *t*, in our case can be expressed like that [9]:

$$q = (2/\pi^{1/2})\, c_o\, (Dt)^{1/2}, \qquad (1)$$

where C_0 – concentration of the element under investigation in the granite sample, D – coefficient of diffusion of this element in the sample. Using the values of stream densities (rates of leaching) Na, Rb, Cs and Mn obtained during the experiment, their coefficients of diffusion were calculated from the equation (1). Dependencies of diffusion coefficients of these elements on the logarithm of the leaching time are given on Fig. 3.

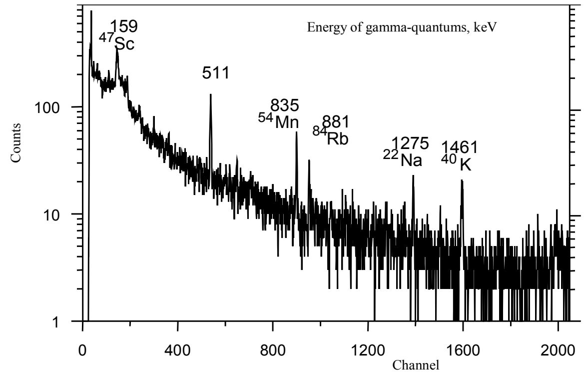

Fig. 2. *γ-spectrum of leachant*

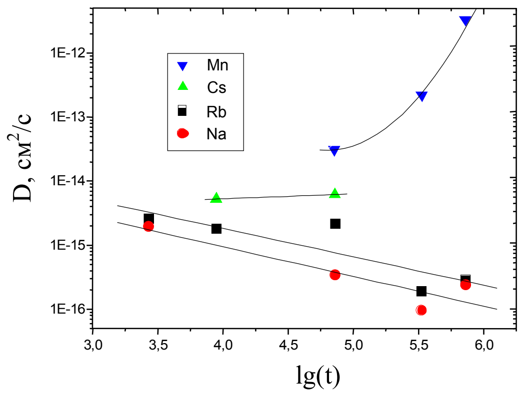

Fig. 3. *Coefficients of diffusion of alkaline elements and Mn*

3.4. As it follows from the data obtained, coefficients of diffusion Na and Rb reduce depending on the time of leaching while coefficient of diffusion Cs in the studied interval of time remains the constant value. Coefficient of diffusion Mn increases considerably which might be stipulated by forming the hydro oxides layer on the surface [10-12]. The fact that Mn is similar to ^{99}Tc in chemical properties is significant during choosing the places for RAW long-term disposal in geological structures.

It is noteworthy that coefficient of diffusion Na are the lowest. Higher values are observed for Rb and the highest for Cs. Ion radii Na, Rb, Cs and K make up 0,098; 0,149; 0,165 and 0,133 nm correspondingly. Potassium feldspars and plagioclase amount 65-70% of mass in the granite under study. Rb and Cs being a part of them have bigger ion radii as compared to potassium thus causing due to elastic deformation g the crystalline lattice the essential change of pre-experimental (frequency) factor D_0 in the expression for coefficient of diffusion D:

$$D=D_0 exp(-Q/RT), \qquad (2)$$

where Q – energy of activation, R – gas constant, T – absolute temperature.

D_0 is stipulated by physico-chemical properties of the crystal. In the first approximation the noticeable change of the frequency of atom fluctuation ω:

$$\omega = (1/\pi)(K/M)1/2, \quad (3)$$

where M – mass of isotope, K – coefficient of the elastic increasing force for particle moving in the potential well $V(x)=V(x_0)+0{,}5K(x-x_0)^2$. As calculation shows [13] the frequency factor for Cs is 5 times as high as for Na in NaCl. Isomorphous substitution of a certain part of potassium by sodium in the potassium feldspars does not cause deformation of the crystalline latter, sodium being included in plagioclase as mineral forming component. Therefore coefficients of diffusion Na have minimum values.

Coefficients of diffusion of leaching metals and manganese in granite samples of UCS, which are not irradiated, are 30% less relative to the irradiated ones [10,14,15].

CONCLUSIONS

1. There has been developed the method of investigation of the radiation and chemical stability of non-organic materials that can be used for choosing perspective environments for deep geological disposal of the radioactive wastes. The method includes dynamic tests on leaching the samples of materials which underwent the combined irradiation in the field of bremsstrahlung of the electron accelerator with the following analysis samples gamma-irradiation and leachant. Sensitivity of the method is by factor of value higher than that of the traditionally used chemical methods of the leachant analysis.

2. Possibilities of the granite of Dneprovskiy deposit of the Ukrainian Crystalline Shield. The obtained coefficients of diffusion Na, Rb and Cs depending on the time of leaching allow to prognose durability of the granite as a geological barrier relative to the release of radionuclides under the condition of radiation and corrosion effect.

3. Behaviour of Mn in the system granite-water under these conditions requires further specification and studying.

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