CESIUM, STRONTIUM AND SODIUM DIFFUSION IN MAGNESIUM KALIUM PHOSPHATES SYSTEM

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(Received May 13, 2014)

Nuclear-physical methods have been used for determination of diffusion coefficient of Cs, Na, Sr and Ga in samples on the basis of Ceramicrete which contained simulators of a liquid radioactive waste of "Hanford-1", KW and KE Basin sludge, 10% wollastonite and 0.3% of boric acid. After an irradiation of investigated samples by electrons and brake radiation to a dose 100 and 1 MGy, accordingly, leaching was conducted at temperature 37°C. Values of diffusion coefficient of Cs, Sr, Na changed in process of leaching from units of 10^{-10} cm^2/s till 10^{-16} ... 10^{-17} cm^2/s, for Ga - from units of 10^{-13} cm^2/s to 10^{-16} cm^2/s. Decreasing of weight of ceramics in process of leaching during 858 hours irradiated by electrons to a dose 100 MGy, on 14.6 and 18.5% with simulators KE and KW is revealed, accordingly. Decreasing of weight of ceramics in process of leaching during 858 hours, irradiated brake radiation to a dose 1 MGy, on 19.9 and 21.6% with simulators KW and KE, accordingly is revealed. The sums of relations of diffusion coefficient of Na concerning Cs and Sr are in antagonistic dependence on the Cs and Sr content in a matrix on the basis of Ceramicrete.

PACS: 66.30.-h; 81.05.Rm

1. INTRODUCTION

The storage of the spent fuel assumes use of multibarrier protection that would allow to reliably isolate of radioactive waste in long-term storehouses. One of parts of this protection is materials which allow to prevent migration of radioactive isotopes into biosphere on the basis of phosphatic systems ($KMgPO_4$) [1-3]. Phosphates are extremely insoluble in groundwater and this would ensure their good isolating properties. The compound is formed under ambient conditions (room temperature) as a result of exothermic acid-base reaction between MgO and KH_2PO_4:

$$MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4 \cdot 6H_2O.$$

Possibility of sorption of a radioactive waste and, especially ^{137}Cs and ^{90}Sr, are intensively investigated. Application of Ceramicrete is more economic in comparison with other matrices for storage of a radioactive waste. The important characteristic of Ceramicrete materials for storage of a radioactive waste is level of leaching by underground waters. It is known that Ceramicrete has low enough values of leaching speed at room temperature in neutral or alkaline conditions. Use of accelerator base techniques allows to study extremely low values of leaching in conditions which are realized during long-term storage of the spent fuel.

One of methods which allows to check reliability of the radioactive sample and estimate storage conditions of radionuclide's is method of leaching. The liquid phase of leaching (filtrate) contains that part of the initial or radioactive sample which is liberated into a solution. Constant heating of sample in flask is realized. Speed leaching counted taking into account of a geometrical surface of the sample. This properties characterises directly matrix material, i.e. durability of deduction of leaching components, and also serves for an estimation of long-term stability of a matrix material and a way of reception of an end-product.

Physical and chemical parametres of reagents also can be changed easily. Usually processing of target was realised in the distilled water, i.e. in the neutral environment

In the paper the leaching of sodium, strontium, caesium and gallium from matrices on the basis of Ceramicrete which were irradiated by electrons and the brake radiation to a dose 100 MGy and 1 MGy, accordingly, was studied.

2. MATERIALS AND METHODS

Samples on the basis of Ceramicrete in aluminium containers with weight 10.32 g (with imitator "Hanford-1" KE basin sludge and 10%$CaSiO_3$+0,3%H_3BO_3), 12.588 g (with

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imitator "Hanford-1" KW basin sludge and 10%$CaSiO_3$+0,3%H_3BO_3), 16.67 g (with imitator "Hanford-1" KW basin sludge and 10%$CaSiO_3$), 6.273 g (with imitator "Hanford-1" KE basin sludge and 10%$CaSiO_3$+ 0,3%H_3BO_3) were irradiated by electrons and brake radiation to dose 100 MGy and 1 MGy, accordingly. Parametres of irradiation on the linear electron accelerator were: E_{max}=23 MeV, I=700 μA. After activation of samples and standards measurement of activity of the radioisotopes obtained in reactions ^{23}Na(γ,n)^{22}Na, ^{133}Cs(γ,n)^{132}Cs, ^{96}Sr(γ,n)^{95}Sr, ^{68}Ga(γ,n)^{67}Ga, ^{48}Ca(γ,n)^{47}Ca, ^{44}Ca(γ,p)^{43}K, ^{23}Na(n,γ)^{24}Na carried out by Ge(Li)-detector with volume 50 cm^3 and the energy resolution 3.2 keV in the area of 1332 keV (Figs.1, 2) [4-10].

In a spectrum of gamma radiation of the irradiated samples of ceramics before leaching lines of isotopes with a half-life period of some days are registered. The exception represents isotope of sodium-22 with a half-life period 2.6 years.

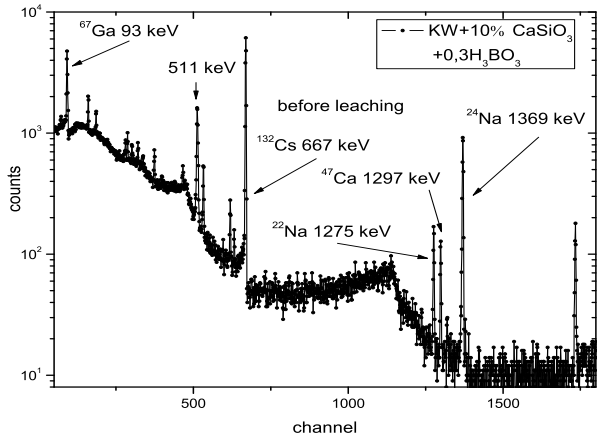

Fig.1. *Energy spectrum of the sample of ceramics after an irradiation on the electronic accelerator before leaching*

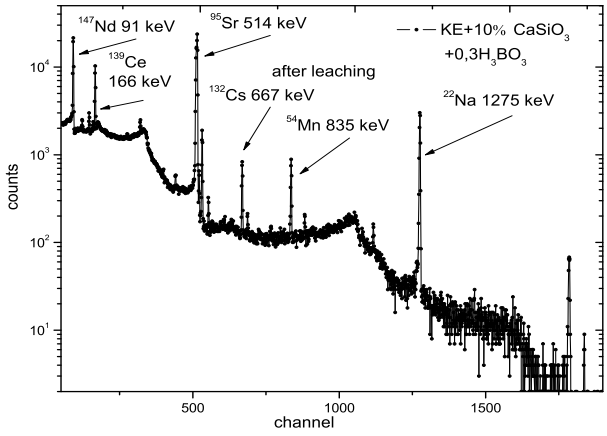

Fig.2. *Energy spectrum of the sample of ceramics after an irradiation on the electronic accelerator after leaching*

Gamma lines of isotopes with a half-life period more than 10 days are registered in a spectrum of radiation of the irradiated samples of ceramics after leaching. The isotope of sodium-22 with a half-life period of 2.6 years is most strongly shown. After the process termination of leaching in samples of ceramics the gamma lines from isotopes neodymium ^{148}Nd(γ,n)^{147}Nd, 91 keV), cobalt (^{58}Ni(γ,p)^{57}Co, 122 keV), chrome (^{52}Cr(γ,n)^{51}Cr, 320 keV), manganese (^{55}Mn(γ,n)^{54}Mn, 835 keV), cerium (^{140}Ce(γ,n)^{139}Ce, 165.8 keV), rubidium (^{85}Rb(γ,n)^{84}Rb, 881.5 keV), zinc (^{66}Zn(γ,n)^{65}Zn, 1115 keV) etc. are detected.

After an irradiation the leaching of samples were realised in the distilled water (volume of 100 ml) at temperature 37°C in the thermostat. The leaching was realised in 8 cycles during 3, 16, 29, 67, 76.33, 116, 195 and 335.66 hours. After certain time of leaching the solution was decanted. The solution was filtered for an exception of small fragments of Ceramicrete before measurement of radioactive waste in it. Fig.3 shows samples of Ceramicrete.

Fig.3. *The samples on basis Ceramicrete for conditioning of radioactive waste*

The pH determination of infiltrated waters is necessary regularly. This indicator, as a rule, remained invariable. Infiltrated waters with which the mobile phase of leaching was taken out, remained transparent throughout all experiment.

Table 1. *The content of elements in samples*

Elements	KW-basin at.%	KW-basin wt.%	KE-basin at.%	KE-basin wt.%
Na	12.06	12.64	11.7	12.09
Mg	12.06	13.36	10.31	11.27
P	12.06	17.03	9.62	13.4
K	4.7	8.37	3.85	6.77
Cl	2.68	4.33	3.85	6.13
S	1.34	1.96	3.64	5.25
O	52.76	38.45	52.94	38.07
Si	0.54	0.69	0.41	0.52
Al	1.23	1.51	2.4	2.91
Ca	0.054	0.099	0.096	0.17
Cr	0.0027	0.0064	0.0055	0.013
Mn	0.0013	0.0033	0.0055	0.014
Fe	0.4	1.018	0.99	2.48
Ga	0.06	0.19	0.082	0.26
Cs	0.0056	0.034	0.026	0.16
Nd	0.047	0.31	0.076	0.49

In the course of carrying out leaching the pH of solution of leaching on pH-meter-340 has been executed. pH of solution of leaching was 9.5.

The chemical compound of studied samples of matrixes for storage of radioactive waste is resulted in Table 1.

3. RESULTS AND DISCUSSION

The diffusion coefficients Na, Cs, Sr and Ga in samples of matrix for storage radioactive waste on basis of Ceramicrete were calculated from expression:

$$q = \frac{2}{\sqrt{\pi}} c_o \sqrt{Dt}$$

where D - diffusion coefficient, c_o - concentration of a studied element in substance (Figs. 4-10).

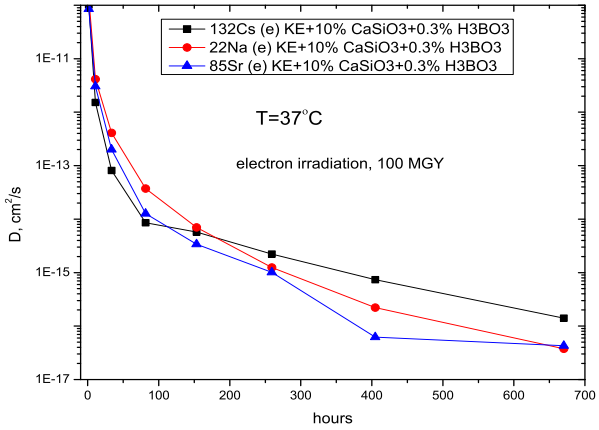

Fig.4. *Diffusion coefficients of Cs, Na and Sr in samples on basis of Ceramicrete with imitator Hanford-1 KE basin sludge, 10% of wollastotine and 0.3% of boric acid irradiated by electrons, dose 100 MGy*

Reactions in which firm substances and pure water take part only, can be considered as reaction between firm substance because activity of water is constant. To obtain the data about speed of carrying out of soluble ions from the radioactive sample, it was necessary to make weighing of the sample. The weight of samples of ceramics before and after leaching is resulted in Table 2. It is possible to see that substance ablation at leaching is more for the samples, irradiated by gamma radiation. Stronger radiating influence on irradiated samples by electrons leads to structural transformations to a matrix on the basis of Ceramicrete and, accordingly, to decrease of values leaching and can be a possible explanation of such behavior of degree leaching.

The matrices on basis of Ceramicrete loses to 20...25% of the weight when the temperature rises above 70°C, which is caused by loss of crystal water from the sample and the change in the initial structure of the material. In leaching process may also occur degradation of the original crystalline structure and consequent formation of magnesium oxide, and the remaining components arrive in solution leaching. It is known that sodium and nitrates arrive in a solution appreciably at temperature of leaching 20°C: sodium up to 40%, sulphates up to 15%, nitrates completely – 100%. Also phosphates considerably leave matrixes on basis of Ceramicrete: about 9% [3].

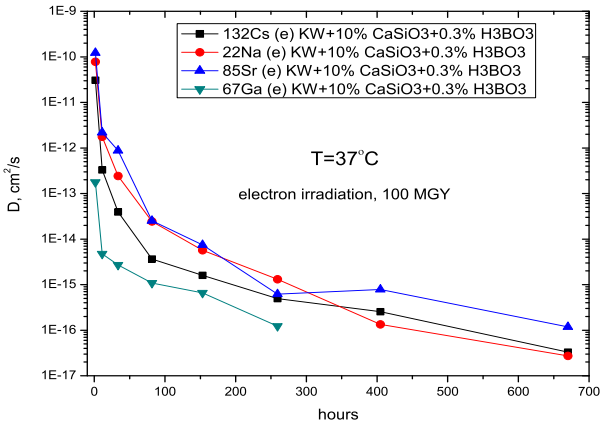

Fig.5. *Diffusion coefficients of Cs, Na, Sr and Ga in samples on basis of Ceramicrete with imitator Hanford-1 KW basin sludge, 10% of wollastotine and 0.3% of boric acid irradiated by electrons, dose 100 MGy*

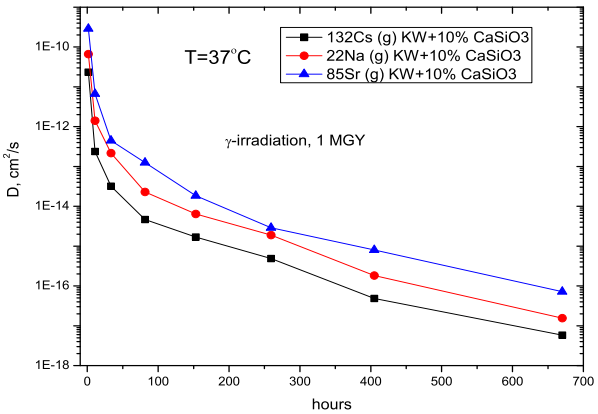

Fig.6. *Diffusion coefficients of Cs, Na and Sr in samples on basis of Ceramicrete with imitator Hanford-1 KW basin sludge and 10% of wollastotine irradiated by bremsstrahlung, dose 1 MGy*

Table 2. *The weight of ceramics samples before and after leaching*

Leaching samples	Weight before leaching, g	Weight after leaching, g	Ablation	Irradiation
KE+10%$CaSiO_3$+0.3%H_3BO_3	10.32	8.815	14.6%	e^- 100 MGy
KW+10%$CaSiO_3$+0.3%H_3BO_3	12.59	10.26	18.5%	e^- 100 MGy
KW+10%$CaSiO_3$	16.67	13.35	19.9%	γ 1 MGy
KE+10%$CaSiO_3$+0.3%H_3BO_3	6.273	4.915	21.6%	γ 1 MGy

The diffusion coefficients of sodium in ceramics for all samples regardless of the conditions of exposure and leaching show high similarity. Therefore, given the sum of values of relations sodium diffusion regarding cesium and strontium largely characterize the behavior of the latter. It can be seen that the strontium content is more than the higher diffusion coefficient in the matrix of the cesium in samples on the basis of Ceramicrete (Tab.3). On the other hand, the greater the amount of cesium, the greater diffusion coefficient of strontium in ceramics on the basis of Ceramicrete. Note that a strong mutual opposite effect occurs for strontium. In other words, strontium is less isomorphic admixture in matrix on the basis of Ceramicrete.

Table 3. *The sum of ratios of the diffusion coefficients of sodium relative to cesium and strontium and content of cesium and strontium in the ceramic samples*

	KE+10%$CaSiO_3$ +0.3%H_3BO_3 electrons, 100 MGy	KW+10%$CaSiO_3$ +0.3%H_3BO_3 electrons, 100 MGy	KW+10%$CaSiO_3$ γ-radiation, 1 MGy	KE+10%$CaSiO_3$ +0.3%H_3BO_3 γ-radiation, 1 MGy
$\sum D_{Na}/D_{Cs}$	15.87	28.3	34.6	14.7
$\sum D_{Na}/D_{Sr}$	15.76	5.98	2.56	32.7
content Cs, g/g	$1.6 \cdot 10^{-4}$	$5.25 \cdot 10^{-4}$	$5.15 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$
content Sr, g/g	$9.97 \cdot 10^{-3}$	$4.63 \cdot 10^{-3}$	$4.37 \cdot 10^{-3}$	$1.09 \cdot 10^{-2}$

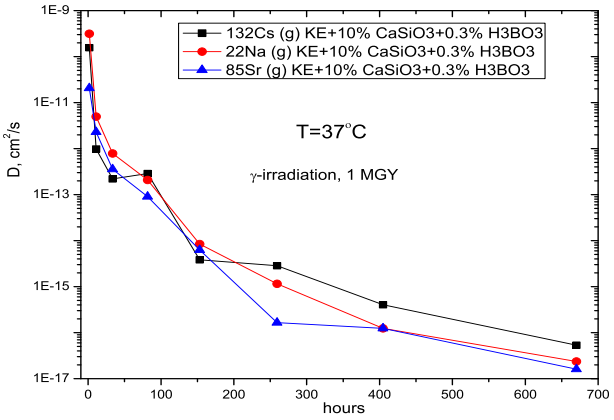

Fig.7. *Diffusion coefficients of Cs, Na and Sr in samples on basis of Ceramicrete with imitator Hanford-1 KE basin sludge, 10% of wollastotine and 0.3% of boric acid irradiated by bremsstrahlung, dose 1 MGy*

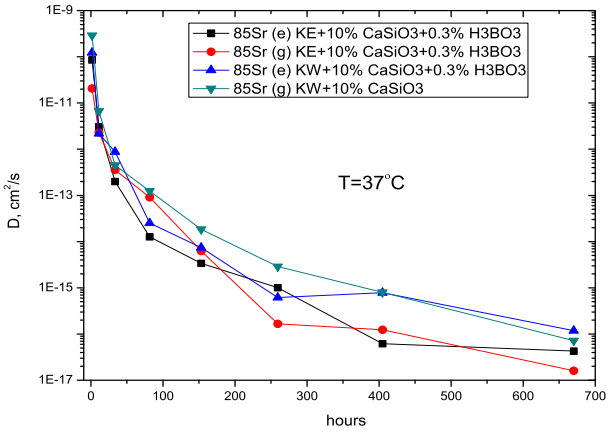

Fig.9. *Diffusion coefficients of Sr in samples on basis of Ceramicrete with imitator Hanford-1 KE and KW basins sludge*

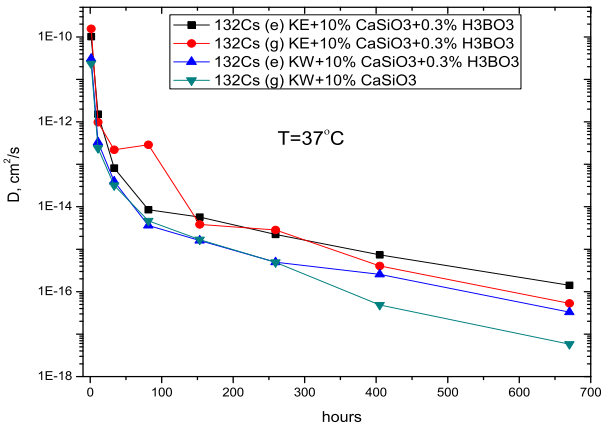

Fig.8. *Diffusion coefficients of Cs in samples on basis of Ceramicrete with imitator Hanford-1 KE and KW basins sludge*

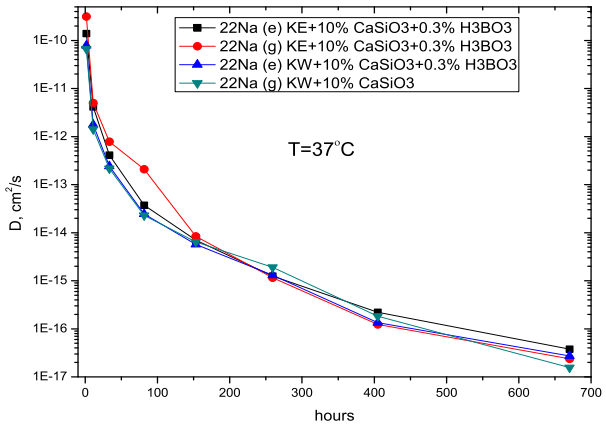

Fig.10. *Diffusion coefficients of Na in samples on basis of Ceramicrete with imitator Hanford-1 KE and KW basins sludge*

The diffusion coefficients of gallium in the irradiated electrons to a dose of 100 MGy of sample KW +10%$CaSiO_3$+0.3%H_3BO_3 has significantly lower values compared with cesium, strontium and sodium, which can be explained by the different valence concerning twice charged atoms of strontium and magnesium. The data on the diffusion of gallium can be use for some assumptions about the diffusion of aluminum, which is similar to gallium by means of close ionic radius.

4. CONCLUSIONS

1. Diffusion coefficients of cesium, strontium, sodium and gallium are measured during the leaching in distilled water at 37°C from matrices on basis of Ceramicrete in 8 cycles during 3, 16, 29, 67, 76.33, 116, 195 and 335.66 hours for the samples irradiated by electrons and gamma rays to a dose of 100 and 1 MGy, respectively. Diffusion coefficients of cesium, strontium and sodium changes from units 10^{-10} cm^2/s to 10^{-16} ... 10^{-17} cm^2/s in the process of leaching. Gallium diffusion coefficients changes from units 10^{-13} cm^2/s to 10^{-16} cm^2/s during leaching.

2. Decreasing of weight of ceramics irradiated by electrons to dose 100 MGy in process of leaching within 858 hours on 14.6 and 18.5% for samples with imitator Hanford-1 KE and KW basins sludge with 10%$CaSiO_3$+0,3%H_3BO_3, accordingly, is discovered. Decreasing of weight of ceramics in process of leaching within 858 hours, irradiated by bremsstrahlung to dose 1 MGy, on 19.9 and 21.6% for KW and KE samples with 0%$CaSiO_3$ and 10%$CaSiO_3$+0,3%H_3BO_3, accordingly, is discovered.

3. It is discovered that the sums of ratio of diffusion coefficients of sodium concerning caesium and strontium are in antagonistic dependence on the caesium and strontium content in a matrices on the basis of Ceramicrete. The more of the content of strontium correspond to the more of diffusion coefficient of caesium in a matrix on the basis of Ceramicrete. The more of the caesium content correspond to the more diffusion coefficient of strontium in ceramics.

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ДИФФУЗИЯ ЦЕЗИЯ, СТРОНЦИЯ И НАТРИЯ В МАГНИЙ КАЛИЙ ФОСФАТНОЙ СИСТЕМЕ

Н.П. Дикий, А.Н. Довбня, Ю.В. Ляшко, Е.П. Медведева, Д.В. Медведев, О.А. Репихов, С.Ю. Саенко, В.А. Шкуропатенко, Р.В. Тарасов, И.Д. Федорец, Н.П. Хлапова

Ядерно-физические методы были использованы для определения коэффициентов диффузии Cs, Na, Sr и Ga в образцах на основе керамики Ceramicrete, которые содержали имитаторы жидких радиоактивных отходов "Хенфорд-1", KW и KE Basin sludge, 10% волластонита и 0.3% борной кислоты. После облучения исследуемых образцов электронами и тормозным излучением до дозы 100 и 1 МГр, соответственно, было проведено выщелачивание при температуре 37°C. Значения коэффициентов диффузии цезия, стронция, натрия изменялись в процессе выщелачивания от единиц $10^{-10}0$ см^2/с до 10^{-16} ... 10^{-17} см^2/с, для галлия – от единиц 10^{-13} см^2/с до 10^{-16} см^2/с. Обнаружено уменьшение веса керамики в процессе выщелачивания в течение 858 часов, облученных электронами до дозы 100 МГр, на 14,6 и 18,5% с имитаторами KE и KW, соответственно. Обнаружено уменьшение веса керамики в процессе выщелачивания в течение 858 часа, облученной гамма-квантами до дозы 1 МГр, на 19,9 и 21,6% с имитаторами KW и KE, соответственно. Обнаружено, что суммы отношений коэффициента диффузии натрия относительно цезия и стронция находятся в антагонистической зависимости от содержания цезия и стронция в матрице на основе Ceramicrete.

ДИФУЗІЯ ЦЕЗІЮ, СТРОНЦІЮ І НАТРІЮ В МАГНІЙ КАЛІЙ ФОСФАТНІЙ СИСТЕМІ

М.П. Дикий, А.М. Довбня, Ю.В. Ляшко, О.П. Медведєва, Д.В. Медведєв, О.О. Репіхов, С.Ю. Саєнко, В.А. Шкуропатенко, Р.В. Тарасов, І.Д. Федорець, Н.П. Хлапова

Ядерно-фізичні методи були використані для визначення коефіцієнтів дифузії Cs, Na, Sr і Ga в зразках на основі кераміки Ceramicrete, які містили імітатори рідких радіоактивних відходів "Хенфорд-1", KW і KE Basin sludge, 10 % волластоніту і 0.3% борної кислоти. Після опромінення досліджуваних зразків електронами і гальмівним випромінюванням до дози 100 і 1 МГр, відповідно, було проведено вилуговування при температурі 37°C. Значення коефіцієнтів дифузії цезію, стронцію, натрію змінювалися в процесі вилуговування від одиниць 10^{-10} см^2/с до 10^{-16} ... 10^{-17} см^2/с, для галію – від одиниць 10^{-13} см^2/с до 10^{-16} см^2/с. Виявлено зменшення ваги кераміки в процесі вилуговування протягом 858 годин, опромінених електронами до дози 100 МГр, на 14,6 і 18,5% з імітаторами KE і KW, відповідно. Виявлено зменшення ваги кераміки в процесі вилуговування протягом 858 години, опроміненої гама-квантами до дози 1 МГр, на 19,9 і 21,6% з імітаторами KW і KE, відповідно. Виявлено, що суми відносин коефіцієнта дифузії натрію до цезію та стронцію знаходяться в антагоністичної залежності від вмісту цезію та стронцію в матриці на основі Ceramicrete .