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CALCULATION OF THE ABSORBED DOSE BY A BOROSILICATE GLASS MATRIX AND ITS SIMULATED IRRADIATION[†]

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The state of liquid radioactive wastes (LRW) management at Ukrainian Nuclear Power Plants (NPPs) is characterized by the lack of a completed technological cycle from processing to obtaining the final product suitable for further long-term storage or disposal. As a result, the storage tanks for bottoms residue (BR) are 65-75% full (Zaporizhzhia and South-Ukrainian NPPs), and the resource for placing molten salt at Zaporizhzhya NPP (92.7%) is close to exhaustion. Therefore, the development of technologies and materials for NPP LRW solidification is an urgent need and aims to ensure the processing of LRW to a solid state that will meet the acceptance criteria for disposal in centralized storage facilities. One of the effective methods of LRW solidification is their vitrification. The main advantage of vitrification is that during the vitrification process the volume of waste is reduced by several times and this saves expensive storage space. The purpose of this work is to calculate the absorbed dose that borosilicate glass matrices with included bottoms residue will accumulate over 300 years of storage, and to study the effect of simulated X-ray irradiation on their physical and mechanical properties.
Keywords: liquid radioactive wastes, bottoms residue, borosilicate glass matrices, absorbed dose, numerical simulation.
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INITIAL CONDITIONS

In Ukraine today, more than 19 000 m^3 of liquid radioactive waste has been accumulated at nuclear power plants. Due to the lack of technical solutions that ensure the receipt of the final product acceptable for disposal for disposal, with the current dynamics of LRW receipts, the resource of LRW storage tanks is close to exhaustion [1]. It is believed that the most optimal method of LRW solidification is their vitrification followed by storage in surface storage facilities [2, 3].

The following data were taken for calculations through the article: specific activities of isotopes ^{137}Cs, ^{134}Cs and ^{60}Co in BR are given in Table 1. The half-lives and decay constants of these isotopes are given in Table 2. The chemical composition of borosilicate glass is given in Table 3

Table 1. Initial data

Parameters	Value
Specific activity of isotopes:	
^{137}Cs, 10^{-6} Ci/l	52
^{134}Cs, 10^{-6} Ci/l	28
^{60}Co, 10^{-6} Ci/l	6,1
Period of simulation, years	300

Table 2. The half-lives and decay constants ^{137}Cs, ^{134}Cs and ^{60}Co

Isotope	Half-lives, days	Decay constant, λ
^{137}Cs	11000±90	0.0000630
^{134}Cs	754±0.7	0.0009197
^{60}Co	1925.3±0.4	0.0003601

Table 3. The chemical composition of borosilicate glass

Name of oxide	Content, mass. %	Density, kg/m^3
B_2O_2	11.49	2460
Na_2O	27.64	2300
MgO	0.43	3600
Al_2O_3	0.98	3950
SiO_2	45.67	2648
P_2O_5	0.072	2390
SO_2	0.45	2619

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Name of oxide	Content, mass. %	Density, kg/m^3
Cl_2O_3	0.21	1600
K_2O	3.55	2300
CaO	0.94	3340
TiO_2	0.037	4230
Fe_2O_3	0.36	5240
Cu_2O	0.036	6000
Cs_2O	0.58	4650
PbO	7.55	9640

DESCRIPTION OF THE SAMPLES PREPARATION AND THEIR IRRADIATION

Samples of the borosilicate glass matrix were obtained by preliminary melting of a mixture of a calcined solution – simulator of NPP LRW condensate with VVER-1000 reactors with the addition of glass-forming silicon oxide, in the form of sand, and 10 wt. % lead oxide (SK45-Pb10) or calcium fluoride (SK45-CF10), followed by melting and pouring glass into metal molds. At the same time, it was taken into account that since the content of Na and B in the bottom residues of LRW from nuclear power plants with VVER reactors is quite high, there is no need to add these elements to obtain borosilicate glass matrices [4]. According to the results of XRD and SEM studies, it was determined that the resulting glass matrices are X-ray amorphous, do not have crystalline inclusions, and are characterized by a dense and homogeneous structure.

Simulated X-ray irradiation of samples of the borosilicate glass matrix was carried out on a linear electron accelerator LU-10 (NSC KIPT) using bremsstrahlung radiation. The average energy of photons is 10.4 MeV. The dose rate is equal 1.09 kGy per hour.

Taking into account the fact that the activity of bottom residues of NPP LRW can differ markedly depending on the methods of LRW processing used at individual NPPs, and, moreover, the distribution of radionuclides in the matrix can be uneven, which can increase the dose of self-irradiation of individual glass blocks, simulation irradiation was carried out with an increased absorption dose – 10 kGy and 100 kGy.

DESCRIPTION OF THE NUMERICAL SIMULATION

For calculation of absorbed dose received by borosilicate glass matrices with included bottoms residue we used software toolkit GEANT4, a toolkit for the simulation of the passage of particles through matter. Its areas of application include high energy, nuclear and accelerator physics, as well as studies in medical and space science [5–7]. To use GEANT4 the following aspects should be defined:
– the geometry of the system;
– the materials and chemical elements involved;
– the fundamental particles of interest;
– the physical processes of interest;
– the generation of primary events;
– the response of sensitive detector components.

The geometry of the system

The geometry of the systems involves the dimensions of the objects and their location. For the calculation three types of setups were chosen:

Setup 1. The cube with dimensions 2 cm × 2 cm × 2 cm with radioactive sources as spheres with diameter 0.5 mm located inside the cube with following coordinates: 1st source (^{137}Cs) – {0; 2 mm; 2 mm}, 2nd source (^{60}Co) – {0; 0; 0}, 3^{d} source (^{134}Cs) – {0; -2 mm; -2 mm}. The absorbed dose was calculated for whole cube.

Setup 2. The absorbed dose was calculated for the cube with the dimensions 10 cm × 10 cm × 10 cm located in the center of a cylinder (height – 812 mm, radius – 560 mm) which consist of a borosilicate glass (Fig. 1). Radiation sources are uniformly dispersed through the cylinder.

Setup 3. The dose map was calculated for cross-section of the same cylinder as item 2 (Fig. 2). Radiation sources are uniformly dispersed through the cylinder.

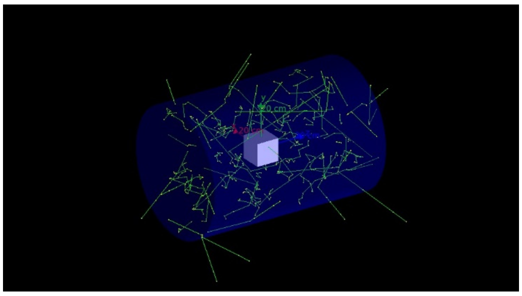


Figure 1. Setup No 2 (see text)

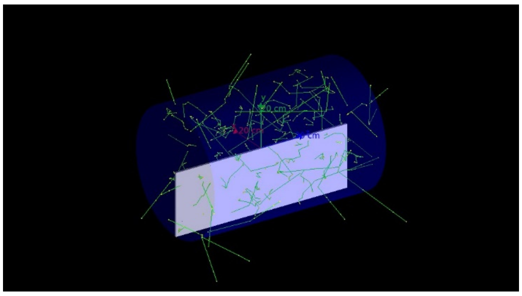


Figure 2. Setup No 3

The materials and chemical elements involved

The following materials are involved into the simulation:
– borosilicate glass matrix (chemical composition is given in Table 3);
– radioactive isotopes ^{137}Cs, ^{134}Cs, ^{60}Co.

The fundamental particles of interest

According to the physical laws during gamma irradiation following elementary particles take part:

– gamma rays;
– X rays;
– electrons;
– positrons;
– anti-neutrinos.

Anti-neutrinos are not included into simulation because these particles can pass through the matter without any collisions with the matter.

The physical processes of interest

Seven major categories of processes are provided by GEANT4:

1. electromagnetic;
2. hadronic;
3. decay;
4. photolepton-hadron;
5. optical;
6. parameterization;
7. transportation.

In the simulation, the 1st, 3^{d} and 7th processes were chosen.

The generation of primary events

Generation of initial gamma rays are generated from ^{137}Cs, ^{134}Cs and ^{60}Co isotropically according to specific activities given in Table 2. Built-in GEANT4 General Particle Source (GPS) class is used for this purpose. The decay of isotopes (see Table 2) is taken into the account in the simulation.

The response of sensitive detector components

To record and output data from simulations, a process called "scoring", must be implemented, specifying what should be measured and where.

In the simulation absorbed doses were calculated for the borosilicate glass itself: for Setup1 absorbed dose was calculated for whole cube; for Setup 2 absorbed dose was calculated for cube inside cylinder; for Setup 3 absorbed dose was calculated for half of cross-section. All values of absorbed dose are referenced to the water.

RESULTS OF NUMERICAL CALCULATION

Calculations were performed on personal computer equipped with AMD Ryzen™9 3900xt (24 threads, 12 cores) processor, 48 GB RAM.

Amount of simulated events was 10^7. For every half of year activities of isotopes recalculated according to the following radioactive decay law

$$I - I_0 e^{-\lambda t} \tag{1}$$

where, I_0 – initial activity, Ki; λ – decay constant; t – time elapsed since the initial moment of time, days. Absorbed dose calculated according to the following formula

$$D = \frac{k \cdot d \cdot \sum I \cdot V}{n_0} \tag{2}$$

where k = 3.7·10^7 – number of decays per 1 second (corresponds to 1 Ci); d – calculated absorbed dose; ΣI – total activity of all radioactive sources at the time of calculation (taking into account radioactive decay), Ci/m^3; V – volume of the target being modeled, m^3; n_0 – the number of decays (10^7) that was modeled. The results of calculations for 300 years of long-term storage of nuclear waste are given on Fig. 3. The initial data are given in the Tables 1 and 2. The absorbed dose in cylinder (height - 0.8 and radius - 0.28 m) is equal to 627.9 Gy for 300 years.

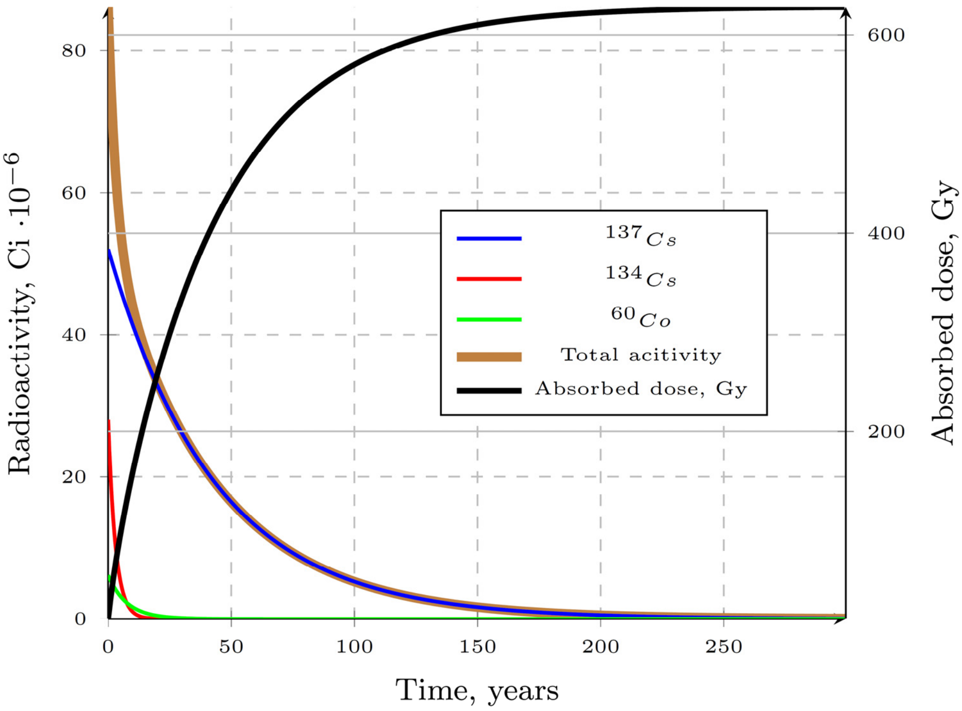
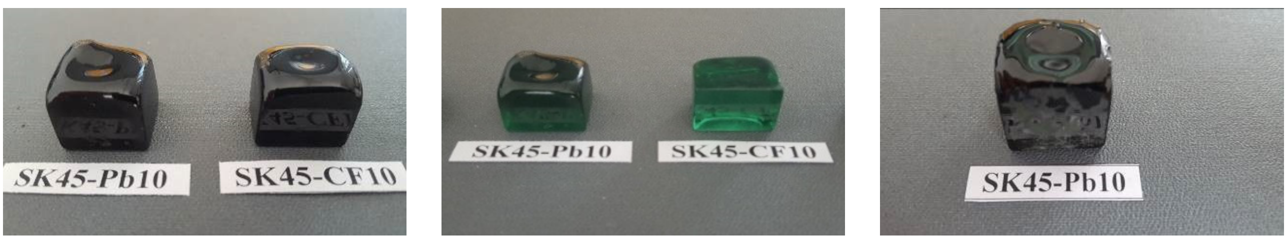


Figure 3. Radioactivities of ^{137}Cs, ^{134}Cs, ^{60}Co, total radioactivity, absorbed dose vs time

RESULTS OF THE SIMULATED IRRADIATION

Simulated irradiation of samples of the borosilicate glass matrix was carried out on a linear electron accelerator LU-10 (NSC KIPT) using bremsstrahlung X-ray radiation. The average energy of photons is 10.4 MeV. The rate of collection of the absorbed radiation dose is 1.09 kGy per hour.

After the simulated irradiation, the structure and phase composition of the SK45-Pb10 and SK45-CF10 glass matrix samples were studied. As can be seen from Fig. 4, the appearance of the samples of borosilicate glass matrices SK45-Pb10 and SK45-CF10 irradiated with X-ray did not differ from the samples before irradiation, except for color. Samples for irradiation have a green transparent colour, while after irradiation their colour has changed to opaque black. As is known, most types of glass lose their transparency under the influence of X ray irradiation. Exposure to this type of radiation leads to colouration of the glass throughout its entire thickness.



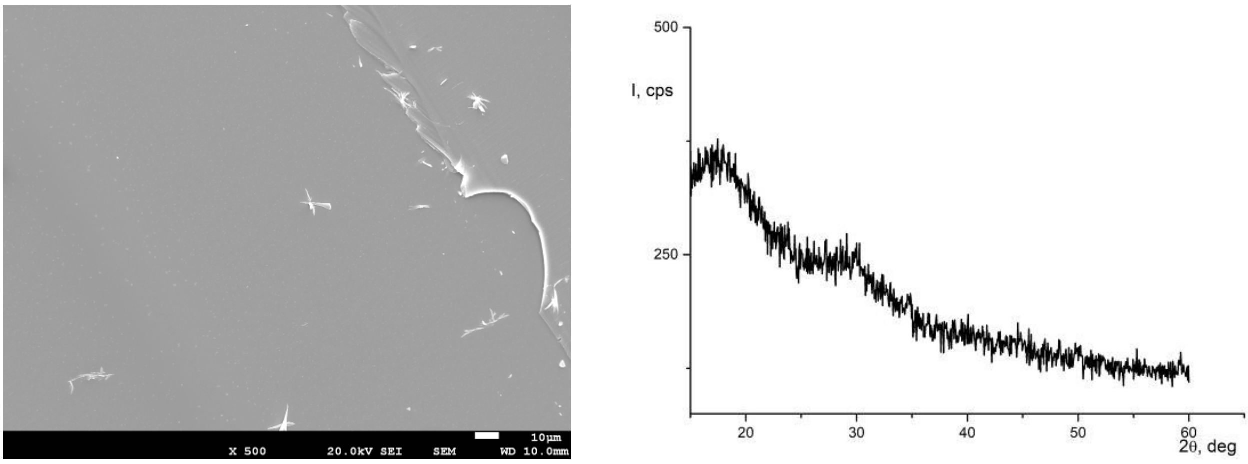
(a) **(b)** **(c)**

Figure 4. Samples of glass matrices SK45-Pb10 and SK45-CF10
a – before irradiation, b – after 10 kGy irradiation, c – after 100 kGy irradiation

There are no signs of destruction and the appearance of cracks and other defects on the samples after irradiation. Also, no changes were observed in the structure (Fig. 5a) and phase composition of the SK45-Pb10 glass matrix samples after irradiation to an absorbed dose of 100 kGy (Fig. 5b). The glass matrix material remains X-ray amorphous without the appearance of crystalline phases.

Small differences were found in the IR spectra of glass matrix samples before and after simulated irradiation. An IKS-29 IR spectrophotometer (LOMO) was used to record absorption spectra in the IR range.

The IR spectra of the SK45-Pb10 glass matrix sample before and after irradiation with X-rays up to an absorbed dose of 10 and 100 kGy are shown in Fig. 6 and 7. Before irradiation, the IR spectrum of the SK45- Pb10 glass matrix has a broad band in the region of 470 cm^{-1} and a broad doublet band with weak maxima at 980 and 1020 cm^{-1}. These bands refer, respectively, to the bending and stretching vibrations of O-Si-O in the silicon-oxygen glass network. The spectrum shows a weak peak at 700 cm^{-1} associated with symmetric stretching vibrations of the Si-O-Si bridges, as well as a peak at 1590 cm^{-1} (deformation vibrations of OH in water molecules) and a doublet at 3400 and 3450 cm^{-1}, caused by the presence of two types of H_2O: structurally bound and absorbed (Table 4).



(a) (b)

Figure 5. Structure and phase composition of SK45-Pb10 glass matrix samples after irradiation
a – SEM image, b – diffraction pattern.

As a result of irradiation to an absorbed dose of 10 kGy, the intensity of the main bands associated with Si-O-Si vibrations decreases, and their shift to the low-frequency region is observed due to a decrease in the degree of coupling of the silicon-oxygen framework. The bands of both structurally bound and adsorbed water completely disappear. When the dose is increased to 100 kGy, no significant changes in the spectrum occur, except for the appearance of a weak band of adsorbed water in the region of 3360 cm^{-1}.

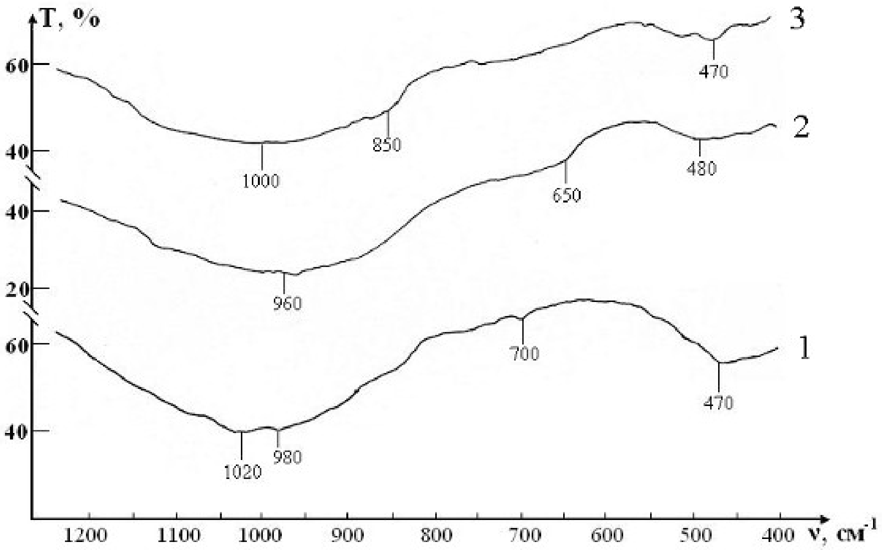


Figure 6. IR absorption spectra of SK45-Pb10 glass samples in the range 400-1200 cm^{-1}
1- before irradiation, 2- irradiation (10 kGy), 3- irradiation (100 kGy)

The IR absorption spectra of the SK45-CF10 glass in the initial state and after irradiation with X-rays up to 10 kGy are shown in Figs. 8 and 9. In the spectrum of the original glass, there are a number of broad bands with diffuse maxima due to bending and stretching vibrations of the Si-O bonds (Table 5). The presence of a weak peak at 3390 cm^{-1} in the spectrum indicates that the initial glass contains a small amount of adsorbed water.

As a result of irradiation with a dose of 10 kGy, the shape and intensity of the main bands in the IR spectrum does not change, but the appearance of a low-frequency shoulder (940 cm^{-1}) on the band in the region of 1000 cm^{-1} is noted.

This indicates the beginning of depolymerization of the silicon-oxygen network [8]. In addition, the occurrence of an inflection in the region of 1350 cm^{-1} indicates the formation of some amount of boron in triple coordination.

Thus, according to the data of IR spectroscopy, as a result of X-ray irradiation of SK45-Pb10 glass to a dose of 10 kGy, the degree of bonding of the silicon-oxygen skeleton of the glass begins to decrease and both structurally bound and adsorbed water are lost. When the dose is increased to 100 kGy, no significant changes occur. Irradiation of SK45-CF10 glass up to 10 kGy leads to the onset of depolymerization of the silicon-oxygen network of the glass and the formation of boron in triple coordination. However, the detected minor changes in the IR spectra do not affect the composition, structure and chemical bonds of the obtained glass matrices, and, accordingly, their insulating properties. That is, the resulting SK45-Pb10 and SK45-CF10 glass matrices have sufficient radiation resistance, which can ensure its integrity and stability during long-term storage.

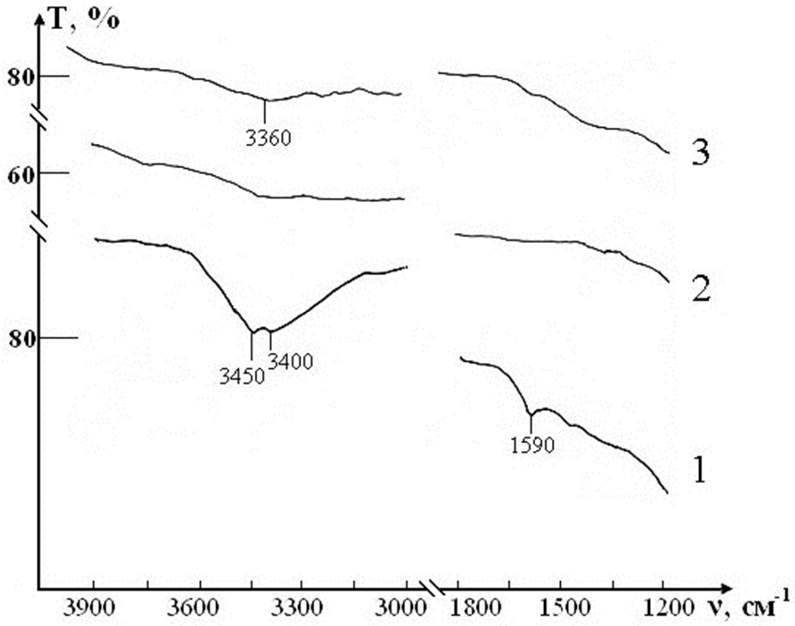


Figure 7. IR absorption spectra of SK45-Pb10 glass samples in the range 1200-4000 cm^{-1}
1- before irradiation, 2-irradiation (10 kGy), 3-irradiation (100 kGy)

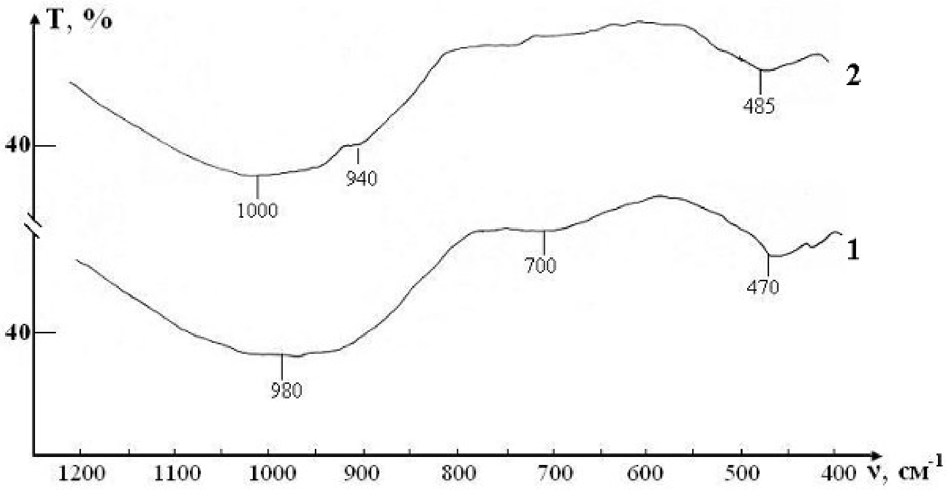


Figure 8. IR absorption spectra of SK45-CF10 glass samples in the range 400-1200cm^{-1}
1 – before irradiation, 2 – Irradiation (10 kGy)

CONCLUSION

Radiation testing of glass matrix samples was carried out using simulated X-ray irradiation at the linear electron accelerator LU-10 (KIPT). It is shown that the material of the obtained glass matrices retains its integrity and amorphous structure after irradiation with X rays up to an absorbed dose of 10 KGy and 100KGy. According to IR spectrometry, as a result of irradiation of samples of glass matrices to an absorbed dose of 10 kGy, there is an insignificant decrease in the degree of bonding of the silicon–oxygen framework of the glass. When the dose is increased to 100 kGy, no significant changes occur.

The resulting lead-borosilicate glass matrix, which is characterized by high radiation resistance and includes the maximum amount of radioactive waste simulator - up to 45 wt.%, can be used for effective fixation of bottom residues of NPP LRW.

Table 4. Assignment of bands in the spectra of glass matrix samples SK45-Pb10

Before exposure	Irradiation D=10 kGy	Irradiation D=100 kGy	Band assignment [8, 9]
470	480	470	Deformation vibrations of the Si-O-Si bond in tetrahedra SiO_4^{4-}
700	-	-	Symmetric stretching vibrations of Si-O-Si bridges
980, 1020	960	850, 1000	Stretching vibrations of the Si-O-Si bond in tetrahedra SiO_4^{4-}
1590	-	-	Bending vibrations of the OH bond in water molecules
3400, 3450	-	3360	Stretching vibrations of the OH bond in water molecules

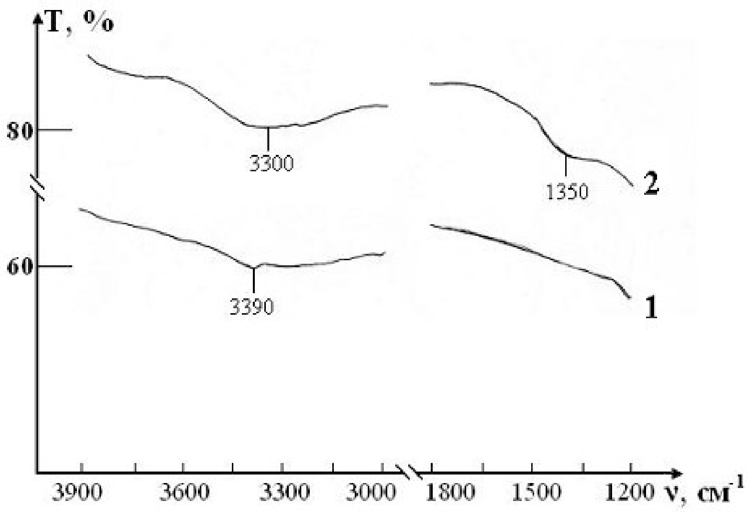


Figure 9. IR absorption spectra of SK45-CF10 glass samples in the range 1200-4000 cm^{-1}
1 – before irradiation, 2 – Irradiation (10 kGy).

Table 5. Assignment of bands in the spectra of glass matrix samples SK45-Pb10

Before exposure	**Irradiation D=10 kGy**	**Band assignment [8, 9]**
470	485	Deformation vibrations of the Si- O-Si bond in tetrahedra SiO_4^{4-}
700	-	Symmetric stretching vibrations of Si-O-Si bridges
980	940, 1000	Stretching vibrations of the Si-O- Si bond in tetrahedra SiO_4^{4-}
–	1350	Boron in triple coordination in groups BO_3
3390	3300	Stretching vibrations of the OH bond in water molecules

A code was developed for calculating absorbed doses over 300 years in lead-borosilicate glass (chemical composition is given in Table 3) for isotopes ^{137}Cs, ^{134}Cs, ^{60}Co for the GEANT4 software package. The calculated absorbed dose received by 200-liter cylinder of lead-borosilicate glass is equal to 627.9 Gy. Main absorbed dose in the sample accumulates over the first 150 years.

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РОЗРАХУНОК ПОГЛИНЕНОЇ ДОЗИ МАТРИЦЕЮ БОРОСИЛІКАТНОГО СКЛА ТА ЇЇ МОДЕЛЬНЕ ОПРОМІНЮВАННЯ

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Стан поводження з рідкими радіоактивними відходами (РРВ) на АЕС України характеризується відсутністю завершеного технологічного циклу від переробки до отримання кінцевого продукту, придатного для подальшого тривалого зберігання або захоронення. В результаті резервуари для донного залишку (ДЗ) заповнені на 65-75% (Запорізька та Південно-Українська АЕС), а ресурс розміщення соляного розплаву на Запорізькій АЕС (92,7%) близький до вичерпання. Тому розробка технологій і матеріалів для затвердіння РРВ АЕС є актуальною і спрямована на забезпечення переробки РРВ до твердого стану, який відповідатиме критеріям прийнятності для захоронення в централізованих сховищах. Одним із ефективних методів затвердіння РРВ є їх осклування. Основна перевага вітрифікації полягає в тому, що під час процесу вітрифікації об'єм відходів зменшується в кілька разів, що економить дороге місце для зберігання. Метою цієї роботи є розрахунок поглиненої дози, яку накопичують матриці з боросилікатного скла з доданим донним залишком протягом 300 років зберігання, а також дослідження впливу імітованого рентгенівського опромінення на їхні фізико-механічні властивості.

Ключові слова: рідинні радіоактивні відходи, кубовий залишок, матриця з боросилікатного скла, поглинена доза, чисельне моделювання.