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Investigation of the Influence of Gamma Radiation on Structural Transformations in Portlandcement Stone

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The radiation resistance of concrete under the influence of large doses of gamma radiation was investigated. To study the behavior of concrete under the influence of gamma radiation, two series of samples were taken: one was the reference sample, and the other was exposed to gamma radiation. The temperature of the irradiated samples during testing did not exceed 40 °C, the reference temperature was also accepted to be 40 °C. The dose of gamma radiation was 10^9 rad. Its value corresponds to the dose that concrete can receive when it comes into contact with high-level radioactive waste from the Shelter over 300 years. Characteristics of an industrial gamma radiation equipment are: radiation energy is 1.25 MeV and dose rate is 2 Mrad/h. The use of such equipment allows reaching a dose of 10^9 rad in less than a month, and 10^8 rad - in 4-5 days. Concretes that were 28 days old and stored under normal conditions were exposed to gamma radiation.

Keywords: radiation, gamma rays, radiation protective, radiation-resistant, composite.

Introduction

The quality of radiation-shielding concretes is determined not only by their high ability to absorb ionizing radiation, but also by their high radiation resistance in the radiation field.

γ-rays, which are electromagnetic waves of high energies and frequencies, have a high penetrating power. As they pass through a substance, they are absorbed. At a certain thickness of the substance, γ-rays can be completely absorbed. The passage of γ-radiation through the matter is accompanied by formation of electrons, which, moving at a high velocity, ionize the environment. This leads to local changes (radiation defects) in the crystal lattice or microstructure of the material (cracks and voids).

Radiation resistance is the ability of a material to retain its properties after irradiation [1], [2]. It is known that concretes based on both Portland cement and slag-alkaline cement during long-term exposure to γ-rays have a sufficiently high radiation resistance compared to reference samples [1]-[5].

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БЕЗПЕКИ

The impact of γ-radiation on the properties, and as a consequence, on the radiation resistance of slag-alkaline concretes, is described in [6]. Under its influence, the content of plagioclases, zeolite-like phases, and low basic calcium hydrosilicates in the hydration products increases, which leads to an increase in the strength of the stone in comparison with the unirradiated one. The authors pointed out a similar nature of γ-radiation influence also on compositions based on Portland cement.

The radiation resistance of the investigated non-shrinking composites, which contain a significant amount of highly basic calcium hydrosulfoferites under prolonged exposure to γ-radiation, is not known [7], [8]. Therefore, special studies were carried out to study the behavior of these composites under the radiation impact. It is known that gamma radiation leads to a profound change in the crystal, molecular and nano-structure of a material, which is accompanied by a change in all its properties.

If during the long-term impact of ionizing radiation the structure of the material does not change, and its strength, deformability, density and thermo-physical properties remain stable, then this material can be referred to materials with high radiation resistance.

Investigate the structure of the modified binder and composites based on it at the macro and micro levels after prolonged exposure to gamma radiation 10^9 rad and evaluate the radiation resistance and durability of these materials.

Materials and research methods

The study of the effect of prolonged exposure to γ-radiation on the properties of the material was carried out using composites, the compositions of which are shown in Table 1. Two groups of concrete samples were used: concrete samples that were not exposed to γ-radiation and concrete samples that were exposed to long-term γ-radiation exposure. The samples were taken based on the Portland cement M400 (produced by the Zdolbuniv Cement Plant), modified with a complex multifunctional additive and dispersed iron powder. The additive consists of mechanically activated iron oxides, iron salts and amorphous microsilica.

To assess the radiation resistance of composites, the samples were exposed to gamma radiation at the Bilgorod-Dniester enterprise JSC "Hemoplast" with an industrial certified γ-device for sterilizing products with a radiation energy of 1.25 MeV and a dose rate of 2 Mrad/h.

During the testing, the temperature of the samples under study did not exceed 40 C. The control temperature was also up to 40 C. The radiation dose from the concrete received from the gamma emitter was 10^9 rad. The radiation resistance of composites was evaluated by the loss of tensile strength in bending and compressive strength on samples-beams with dimensions of 40x40x160 mm, as well as using a set of physic-chemical research methods.

X-ray phase analysis was carried out using the DRON-3 device by the method of ionization registration of X-ray intensities, equipped with a rotation angle counter from $2\theta = 10^0$ to $2\theta = 60^0$. X-ray diffraction patterns were deciphered by comparing with natural and artificial minerals described in the literature [9]-[11]. Thermo-gravimetric and differential thermo-gravimetric analyses were carried out using a derivatograph Q1500D at a heating rate of 10 °C. The new formations were identified by comparison with natural minerals or artificial formations known in the literature [9]-[11].

The influence of gamma radiation on the nature of cracking of cement stone of various compositions and on the nature of the crystalline phase on its cleavage was studied using an electron microscopic research method.

Research results

To study the behavior of concrete under the gamma radiation impact, two series of sampling were performed. One was the reference sample, and the other one was exposed to gamma radiation. The temperature of the irradiated samples during testing did not exceed 40 °C, the reference temperature was also accepted to be 40 °C. The dose of gamma radiation was 10^9 rad. Its value corresponds to the dose that concrete can receive when it comes into contact with high-level radioactive waste from the Shelter over 300 years. Characteristics of an industrial gamma radiation device are: radiation energy is 1.25 MeV and dose rate is 2 Mrad/h. The use of such a device makes it possible to achieve a dose of 10^9 rad in less than a month, and 10^8 rad - in 4-5 days. Concretes that were 28 days old and stored under normal conditions were exposed to gamma radiation. The compositions of the composites are shown in Table 1.

To study the effect of gamma radiation on the structural transformations of the binder, a complex of physical-chemical studies of Portland cement with the proposed additive before and after radiation was carried out. The complex of physical-chemical studies included X-ray phase, thermo-gravimetric and electron microscopic analyzes.

The results of X-ray phase analysis are shown in Figures 1, 2. Analyzing the results obtained, it can be noted that after the gamma radiation impact with a power of 10^8 and 10^9 rad, the structure of the material changes, its amorphization is observed.

Table 1 – Average density and composition of radiation-shielding concretes

№	Composition of the composite, wt %	B:A*	Density, kg/m^3
1	Modified binder – 75 Dispersed iron (0.08–0.16mm) – 25	3:1	2350
2	Modified binder – 65 Dispersed iron (0.08–0.16mm) – 35	2:1	2520
3	Modified binder – 50 Dispersed iron (0.08–0.16mm) – 50	1:1	2860
4	Modified binder – 35 Dispersed iron (0.08–0.16mm) – 65	1:2	3640
5	Modified binder – 35 Dispersed iron (0.08–0.16mm) – 65	1:3	3900
6	Modified binder – 25 Dispersed iron (0.08 –0.16mm) – 75	1:3	5130

*- ratio «binder : aggregate

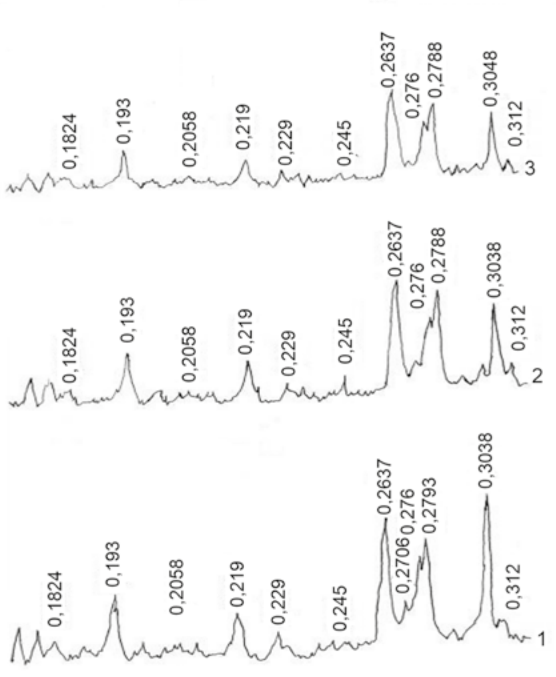

Figure 1 – Radiographs of Portland cement stone without additive: 1 – reference sample; 2 – after exposure to γ-radiation with a dose of 10^8 rad; 3 – after exposure to γ-radiation with a dose of 10^9 rad

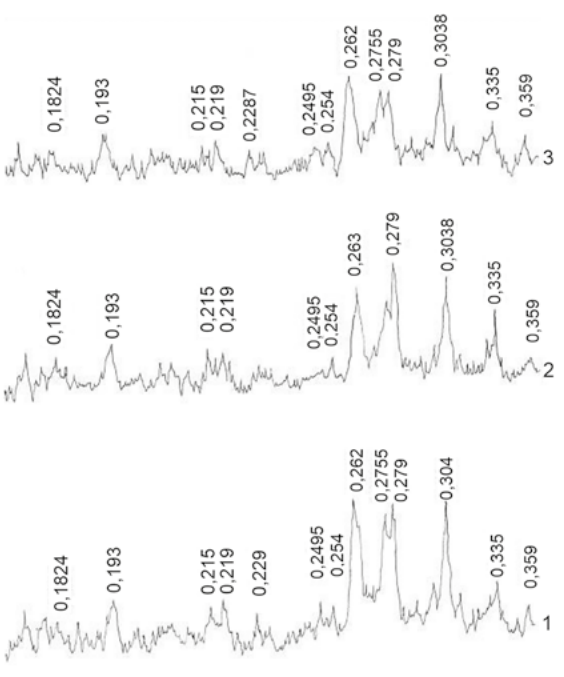

Figure 2 – Radiographs of a cement stone with a multifunctional complex additive: 1 – reference sample; 2 – after exposure to γ-radiation with a dose of 10^8 rad; 3 – after exposure to γ-radiation with a dose of 10^9 rad

This is confirmed by decreasing diffraction maxima peaks in the X-ray diffraction patterns of irradiated samples as compared to non-irradiated ones, especially for hydrated compounds. The weakly crystallized compounds of the tobermorite group are most affected by the gamma radiation impact. Thus, there is a significant decrease in the intensity of the peaks with d = 0.3038; 0.278; 0.245; 0.229; 0.215; 0.182 nm, which belong to low-basic hydrosilicates of the tobermorite group C-S-H (Figures 1, 2, curves 1, 3), the peaks corresponding to hydration phases also decrease (d = 0.359; 0.335; 0.304; 0.254; 0.249; 0.193 nm) (Figures 1, 2, curves 2, 3). At the same time, peaks with d = 0.359; 0.298; 0.254; 0.249; 0.219 nm (Figure 2, curves 2, 3), which can be attributed to highly basic calcium hydrosulfoferites and mixed highly basic calcium hydrosulfoaluminates and calcium hydrosulfoferrites after treatment of the binder with gamma radiation, decreased not so much. This confirms the advisability of introducing iron oxide into Portland cement and the formation of highly basic calcium hydrosulfoferrites on its basis.

Thus, the results obtained indicate the amorphization of the hydrated phase of the hardening cement and, as a consequence, the formation of self-organizing structures [12]-[13]. The degree of this amorphization depends on the type of bound water. In addition, such amorphization of the binder leads to an increase in the strength of the material in compression, which is confirmed by our data (see Table 2) and known data on the role of poorly crystallized substances [12]-[14].

To study the behavior of different forms of water bonding (mechanically, physic-mechanically, physic-chemically and chemically bound) during cement irradiation, studies were carried out using thermo-gravimetric and differential thermo-gravimetric (TG and DTG) analyses (Figures 3, 4).

The analysis of the data of the differential thermo-gravimetric study demonstrated that as a result of gamma radiation the nature of endothermic effects changes. This is due to removal of part of the bound water from hydrates as a result of the impact of γ-radiation on the binder.

For a more detailed study of this process, we analyzed the loss of water during heating of samples irradiated with doses of 10^8 and 10^9 rad (Figures 3, 4). Analysis of these data showed that, as a result of irradiation, the nature of water loss depends on the composition of the binder and the intensity of the radiation dose received. So, in the samples of Portland cement after gamma irradiation with a dose of 10^8 rad, a significant decrease in the content of water (10.5 %), which is removed when heated at temperatures of 130…150 °C, is observed.

This indicates the release from hydrates during their irradiation, first of all, water, which is mechanically and physically and mechanically bound in a cement stone [9]-[11]. For a cement stone based on modified Portland cement with the proposed additive, loss of such water after irradiation did not exceed 8.5 %. The same tendency persists for hydrated water, which is removed in the temperature range up to 250 °C in samples on Portland cement – 16 %, on a modified binder – 13 %. This is the evidence of the greater resistance of the proposed binder against the impact of gamma radiation 10^8 rad.

Table 2 – Changes in the compressive and bending strength of composites after prolonged exposure to gamma radiation

№*	Composite tensile strength, MPa							
	compressive *strength*				bending *strength*			
	control at the age, days		absorbed the dose, rad		control at the age, days		absorbed the dose, rad	
	28	56	10^8	10^9	28	56	10^8	10^9
1	55	55	55	56	1,9	2,0	1,5	2,0
2	51	52	51	52	1,9	2,1	2,0	2,4
3	51	51	52	52	1,6	1,85	1,85	2,3
4	53	54	54	55	1,2	1,3	1,3	1,4
5	48	49	48	49	1,2	1,2	1,2	1,2
6	64	66	67	70	0,93	0,94	1,00	0,76
*- Composition of the composite according to table 1								

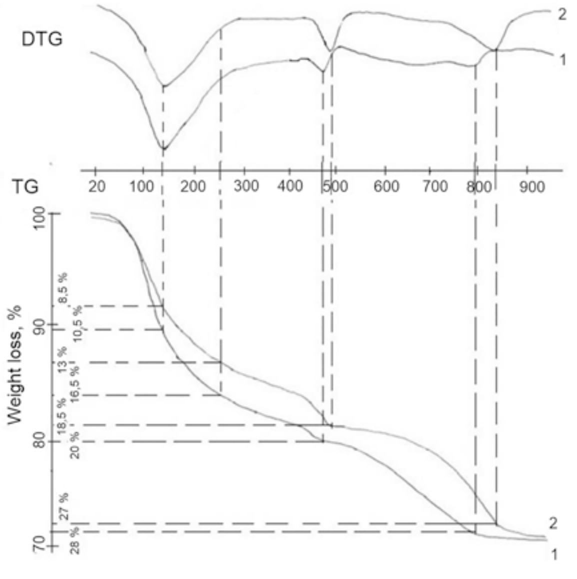

Figure 3 – Derivatograms of cement stone after exposure to γ-radiation with a dose of 10^8 rad: 1 – based on Portland cement; 2 – based on a modified binder.

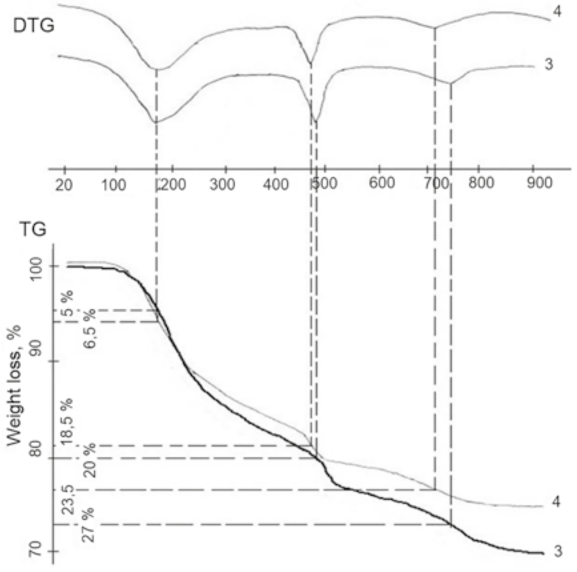

Figure 4 – Derivatograms of cement stone after exposure to γ-radiation with a dose of 10^9 rad: 3 - based on Portland cement; 4 - based on a modified binder.

In the temperature range of 200…500 °C, the nature of the removal of chemically bound water from hydrates, based on Portland cement and a modified binder, remains. So, after irradiation of Portland cement samples in a temperature range of up to 500 °C, weight loss of up to 20 % is observed, while in the samples on a modified binder – 18.5 %. This result confirms the advantages of the proposed binder in comparison with Portland cement, since this temperature range corresponds to the dehydration of portlandite. In the proposed binder, portlandite, which is formed during the hydration of cement, is bound into hydrated compounds. Therefore, during irradiation, this process is accelerated with formation of the corresponding silicate, sulfoferite and carbonate phases. This leads to a decrease in the content of free lime after irradiation of a cement stone based on a modified binder. Obtaining a stone with low content of free lime should lead to an increase in the resistance of the material during the aggressive action of chemical compounds and the gamma radiation impact. Therefore, for samples on ordinary cement, a decrease in the bending strength of the stone after irradiation is characteristic, and for a binder with the proposed additive, on the contrary, an increase in strength is observed. The amount of chemically bound water in hydrates, which is removed at higher temperatures (500…700 °C), depends slightly on the type of cement. After irradiation of the samples with a dose of gamma radiation with a power of 10^9 rad, three endothermic effects were recorded on the thermal curves (TG-DTG) (Figure4). The first effect in the temperature range 30…370 °C with a maximum at 170 °C refers to the process of dehydration of hydrosulfoaluminates and calcium hydrosulfoferrites. The second dehydration effect in the range 400…550 °C with a maximum at 470 °C indicates the presence of portlandite, the third transformation interval of 550…830 °C with a maximum at 720…760 °C can be attributed to the endothermic effect of decarbonization of calcite formed during hydration and hardening, which generally indicates the absence of serious destructive processes in the cement stone. For the identified intervals, the weight loss values were also determined from the curves of thermo-gravimetric and differential thermo-gravimetric (TG-DTG) analyzes, for the studied samples irradiated with a dose of 10^9 rad (Figure 4). When considering samples of cement stone of various composition, the presence of ongoing hydration processes is confirmed by the corresponding weight loss in all considered intervals of transformations.

The effect of gamma radiation on the crack formation character of cement stone of various compositions and on the character of the crystalline phase on its cleavage was studied using electron microscopy according to the research methodology given in [14]. The data of electronic microscopic studies confirm and supplement the results of X-ray phase and thermo-gravimetric analyses. The results of electron microscopic studies are shown in Figures 5-7. Analyzing the data obtained, it can be noted that unirradiated samples of Portland cement (Figure 5) have significant cracks, while in the samples based on the modified binder (Figure 6), such cracks were not found. Thus, the crack width for the first samples was 0.3…0.6 μm and the length was 40…70 μm, while for cement stone samples based on the modified binder, the width was 0.15…0.3 μm, and the length was 10...20 μm. This is explained both by the shrinkage of the Portland cement stone, in contrast to the modified Portland cement, and by the presence of microsilica in the latter case, which acts as a damping additive that stops the development of cracks [16]. After irradiation, the nature of the cracks changes. Cracks in samples based on Portland cement have a through character (Figure 7), while cracks based on modified binder are grouped around metal inclusions that are part of the additive (Figure 8).

The character of crack formation [15]-[18] explains why specimens based on modified binder have higher bending strength after irradiation than specimens based on conventional Portland cement. As you can see from the pictures, gamma radiation changes the structure of new formation.

On the one hand, they amorphize, and on the other, conditions for their accelerated crystallization are created. So, in the images of Portland cement stone (Figure 7), you can see fibers and plates, which, according to [9]-[11], can be respectively attributed to the compounds of the tobermorite group and portlandite. In the images of a stone based on a modified binder (Figure 8), prismatic, needle-like crystals are visible along with fibers. Irradiation changes the appearance of the crystals: after irradiation of Portland cement samples, in their images one can see large well-crystallized crystals of portlandite and their germination together with the amorphized surface.

At the same time, the images of samples based on the modified binder (Figure 8) demonstrate amorphized crystals, which can also be attributed to portlandite [9]-[11].

The results obtained can be explained by the phenomenon that irradiation intensifies the hydration processes. For ordinary Portland cement this leads to the formation of a significant amount of "fresh" well-crystallized lime. At the same time, for a stone based on a modified binder, it is characteristic that as a result of irradiation, the processes of binding free lime into calcium hydrosilicates and highly basic calcium hydrosulfofferites are accelerated. Therefore, these images contain a destructed crystal of "old" lime and prismatic crystals of highly basic calcium hydrosulfofferite.

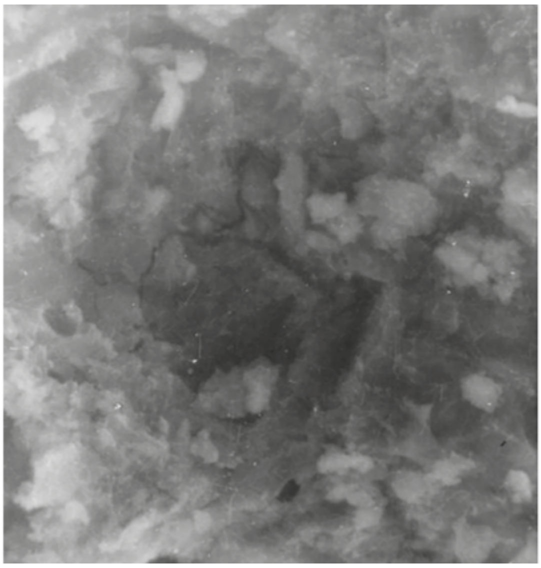

Figure 5 – Micrographs of cement stone based on Portland cement (control)

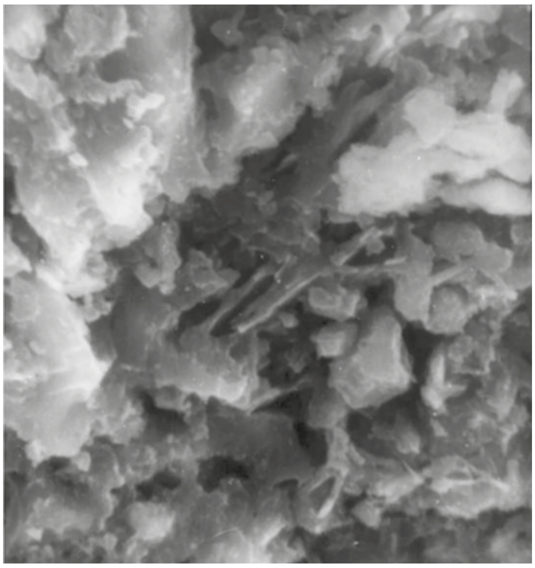

Figure 6 – Micrographs of a cement stone based on a modified binder

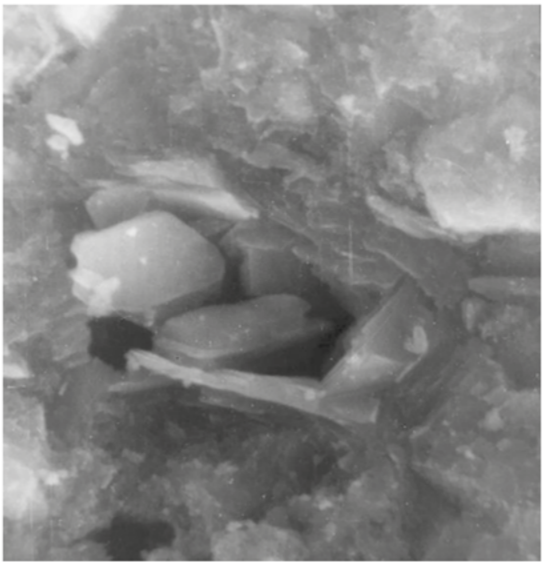

Figure 7 – Micrographs of cement stone based on Portland cement after the action γ-radiation with a dose of 10^9 rad

Figure 8 – Micrographs of a cement stone based on a modified binder after exposure to γ-radiation with a dose of 10^9 rad

Conclusions and prospects for further research

Thus, the studies carried out have demonstrated that the developed binders and concretes based on them are radiation-resistant and effective radiation-shielding materials. They are able to gain compressive strength after irradiation with a dose of 10^9 Rad.

The positive results obtained make it possible to proceed to the study of the corrosion resistance of these composites and structures based on them in various corrosive environments.

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Дослідження впливу гамма-випромінювання на структурні перетворення в портландцементному камені

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У статті наведено дослідження структури модифікованого в'яжучого і композитів на його основі на макро- і мікрорівні після тривалого впливу гамма-випромінювання 10^9 рад, а також наведено оцінку радіаційної стійкості і довговічності цих матеріалів. Для дослідження змін структури бетонів під дією гамма-випромінювання були виготовлені дві серії зразків. Одна – контрольна, а друга – що підпадає під дію гамма-випромінювання. Температура зразків, що підпадали під дію гамма-випромінювання, під час випробувань не перевищувала 40°C, температура контрольних зразків була прийнята також 40°C. Доза гамма-випромінювання становила 10^9 рад та відповідає дозі, яку може отримати бетон під час його контакту з високоактивними радіоактивними відходами об'єкта «Укриття» за 300 років. Характеристика промислової установки гамма-випромінювання – енергія випромінювання 1,25 МеВ і потужність дози 2 Мрад/ч. Використання такої установки дозволяє досягти дози 10^9 рад менше ніж за місяць, а 10^8 рад – за 4-5 діб. Під дію гамма-випромінювання підпадали бетони, які досягли віку 28 діб і зберігалися в нормальних умовах. Вплив гамма-випромінювання на характер тріщиноутворення цементного каменю різного складу і на характер кристалічної фази вивчався за допомогою електронно-мікроскопічного методу досліджень. У результаті зауважимо, що після опромінення тріщини в зразках на основі портландцементу мають наскрізний характер, тоді як тріщини на основі модифікованого в'яжучого групуються навколо металевих включень, які входять до складу добавки. Цим пояснюється більш висока міцність у зразків на основі модифікованого в'яжучого після дії гамма-випромінювання. Отже, проведені дослідження показали, що розроблені в'яжучі та бетони на їх основі є радіаційно стійкими і є ефективними радіаційно захисними матеріалами. Вони здатні набирати міцність після опромінення дозою 10^9 рад.

Ключові слова: радіація, гамма-випромінювання, радіаційно-захисний, радіаційно-стійкий, композит.

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