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DESIGN OF PROTECTIVE SOLUTIONS BASED ON A NANOMODIFIED GYPSUM ALUMINA CEMENT SYSTEM AND INVESTIGATION OF THEIR PROPERTIES

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The object of this study is the structuring processes and the physical-mechanical properties of nanomodified ion-protective coatings based on the gypsum-alumina cement system. Under the influence of ionizing radiation, defects are formed in the calcium hydroxide crystalline lattice causing radiation shrinkage. As a result of the shape anisotropy and aggregate deformations, uneven deformations are transferred to the concrete skeleton. Therefore, the effective use of gypsum alumina binders for creating ion-protective coatings for biological shielding against radioactive radiation is a pressing issue being solved. The sulfate and sulfoaluminate phases solution modification by carbon nanotubes (CNTs) leads to a decrease in the linear expansion coefficient and an increase in the gamma-ray scattering coefficient by 30–40 % due to the high specific surface area. The results are explained by the ettringite phase formation leading to the 15 % increase in the chemically bound moisture content in the optimal composition. At the same time, arithmetic mean value of the chemically bound moisture content improves the linear attenuation coefficient of ionizing radiation by 0.0088–0.009 cm^{-1}. Under such conditions, the total coefficient could reach up to 0.354 cm^{-1} making it possible to reduce the radiation-protective layer equivalent thickness (14.6 cm^{-1}) by 1–1.5 mm. A special feature of the result, which made it possible to reach the purpose of the study, is the maximum 46 % ettringite content in the most complete water binding contributing to the effective ionizing radiation absorption in the protective coating. The application of research findings is solutions for ion-shielding coatings for X-ray rooms

Keywords: composite binder, mortar, ettringite, ettringite stabilization, aluminate cements, sulfoaluminate cements

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1. Introduction

Reconstruction of buildings and structures destroyed as a result of the war in Ukraine, as well as accelerated construction and reconstruction of X-ray rooms require designing new semiconductor and X-ray protective materials.

In Ukraine, many sectors widely use various sources of ionizing radiation. At the same time, around modern sources of ionizing radiation, radiation levels are so significant that as a result of their influence, there is a loss of operational qualities of devices and a loss of qualitative characteristics of the material of structures [1].

It is very important when designing building structures that operate under the influence of ionizing radiation to know how materials would change their dielectric, physical, technical, and thermophysical properties as a result of irradiation. Radiation resistance is an important parameter that characterizes the ability of a material to retain its properties after irradiation.

Whereas radiation resistance of materials that were used to construct nuclear facilities had been studied since the construction of nuclear facilities, the radiation resistance of building materials has not been given due attention. The latter prevents designing materials that would have high operational properties.

Therefore, research into the design of new X-ray-protective and radiation-resistant building materials is relevant. Given the growing need to restore destroyed infrastructure, ensure the safety of X-ray rooms and other facilities with increased levels of ionizing radiation, design of materials that could effectively resist its effects is an important task of modern science and the construction industry. This would not only increase the durability of structures but also reduce risks to human health and the environment.

2. Literature review and problem statement

Paper [1] reports the results of research into the mechanism of designing a cement composite with enhanced hydrophysical and radiation-protective properties. It is shown that the modification of the cement binder with chemical additives contributes to the synthesis of crystal hydrates with a high water content, which improves its hydrophysical characteristics. Additionally, polydisperse systems in the form of ferruginous quartzites were introduced into the composition, in which micron particles of iron are evenly distributed in the composite, which contributes to increased radiation protection. However, there are still unresolved problems associated with the uniform distribution of ultrafine particles in the material, which significantly affects its protective functions. The main factors are the objective difficulties associated with the agglomeration of microparticles during the mixing process, as well as the fundamental impossibility of achieving ideal dispersion without the use of special technological methods. In addition, the economic factor plays a significant role, since the production of such composites requires additional costs for modified additives and control over hydration processes, which can make their industrial application less profitable. A possible way to solve these difficulties may be to devise technologies for ultrasonic or electromagnetic dispersion of particles during mixing, as well as the use of additional stabilizers that prevent their sticking. All this allows me to argue that it is advisable to conduct further research on optimizing the composition and production technology of nanomodified concretes with improved radiation-protective properties.

In [2], the results of studies on the influence of various wastes from the metallurgical industry on the radiation shielding ability of concrete materials are described. It was shown that the addition of iron waste in an amount of 30 wt. % significantly increases the linear radiation attenuation coefficient compared to concrete samples containing steel balls or slag. The study also confirmed that a uniform distribution of metal waste particles in the concrete matrix is a critical factor for improving radiation protection. However, there are open questions related to the optimal ratio between concrete density, porosity, and distribution of metal particles, which affects the shielding efficiency. This can be explained by objective obstacles associated with the heterogeneity of the material and the influence of different types of metal fillers, as well as the fundamental impossibility of ensuring ideal particle dispersion in the concrete matrix during large-scale production. In addition, the cost aspect should be taken into account since additional technological processes are required for cleaning and grinding of metal waste, which makes the study economically unprofitable at an industrial scale. A possible solution to these difficulties may be the application of new methods of concrete mix modification, such as the use of nano admixtures or alternative cementing materials that make it possible to optimize the structure and uniform distribution of fillers. All this gives grounds to argue that it is advisable to conduct further research on the development of optimal formulations of nanomodified concrete materials for radiation protection, taking into account technological compatibility and durability of the resulting materials.

Paper [3] reports the results of studies on the influence of ultrafine mineral additives and superplasticizers on the properties of low-carbon high-performance concretes. It is shown that the use of a polycarboxylate superplasticizer together with mechanically activated ultrafine mineral additives makes it possible to obtain concrete mixtures with increased mobility and homogeneity, as well as concretes with high early and final strength, improved deformation properties, density, increased frost resistance and durability. An important factor is the reduction of the clinker factor, which contributes to the reduction of CO_2 emissions, and therefore, the reduction of the environmental load. At the same time, certain unresolved issues remain related to the optimal ratio between different types of mineral additives and their influence on the structure formation of the cement matrix. The main factors in this may be objective difficulties associated with the variability of the granulometric composition of additives and the need for their additional mechanical activation. The fundamental impossibility of achieving uniform distribution of ultrafine particles without special technologies is also an important factor affecting the final properties of the material. In addition, the cost aspect should be taken into account since the use of modern superplasticizers and ultrafine additives increases the cost of the material, which can make it less competitive in mass construction. A possible solution to the relevant difficulties may be to devise methods for activating mineral additives, for example, the use of ultrasonic dispersion or electromagnetic influence for uniform distribution of particles in the concrete matrix. All this allows me to conclude that it is advisable to conduct further research on optimizing the composition of low-carbon high-performance concretes and improving the methods for dispersing active additives.

Paper [4] reports the results of research on the development of fast-hardening ultra-strong cement composites using super zeolite and alkaline nanomodifier N-C-S-H-PCE. It is shown that the use of super zeolite in combination with nanomodifiers makes it possible to significantly improve the early strength of cement stones. In particular, after 12 and 24 hours of hardening, the strength reaches 16.9 and 30.5 MPa, respectively, and after 28 days – 104.1 MPa. The use of such an approach contributes not only to the acceleration of the processes of structure formation but also to the increase in the heat resistance of cement stones at temperatures up to 400 °C. The introduction of super zeolite contributes to the "self-autoclaving" of the cement material, which improves its operational properties under thermal stress. At the same time, some aspects related to the uniformity of the distribution of nanomodifiers in the cement matrix and the control of their agglomeration remained unresolved. This can be explained by objective difficulties associated with the technological complexity of introducing nanomodifiers into the cement mortar. The fundamental impossibility of ensuring ideal particle uniformity without the use of additional dispersion methods also remains a problem. In addition, the cost part is also significant since the synthesis and introduction of nanomodifiers at an industrial scale require high costs, which can make the widespread use of these technologies economically unprofitable. One of the approaches to overcoming the relevant difficulties may be the introduction of new technologies for dispersing nanomodifiers, such as the use of ultrasonic treatment or electromagnetic methods for uniform distribution of particles in the cement material. All this allows me to conclude that it is advisable to conduct further research on improving the methods of introducing nanomodifiers into cement systems, increasing the efficiency of structure formation to ensure high strength and durability of cement materials.

In [5, 6] the results of studies of nanomodified Portland cement compositions with high early strength are given. It is shown that the use of ultra-dispersed mineral additives, polycarboxylate superplasticizer, and calcium hydro silicate nanoparticles contributes to the intensive development of early strength of cement. However, the issues related to the uniform distribution of nanomaterials in the cement matrix remain unresolved. The reason for this may be objective difficulties associated with the heterogeneity of particles and their surface activity. An option for overcoming the relevant difficulties may be the use of nanoparticle synthesis technology directly in the cement production process. All this allows me to state that it is advisable to conduct a study on improving the methods of uniform distribution of nanoparticles in cement compositions to increase their early strength.

In work [7], the results of studies on the influence of nanomodified basalt fiber (NBF) and bottom ash (BA) on the properties and durability of cement concrete are reported. It is shown that the combination of NBF and BA significantly increases the compressive strength (up to 59.2 MPa) and bending strength (up to 17.8 MPa) and also improves frost resistance and water resistance. However, open questions remain related to the mechanisms of interaction between components with increasing ash and fiber content, as well as the optimal ratios of their concentrations. The unresolved problems are associated with the complexity of controlling the material structure and the heterogeneity of fiber distribution. This problem can be solved by devising new methods for activating components and improving mixing processes. From all of the above, I can conclude that it is advisable to conduct a study on optimizing the composition of cement composites using nanomodified basalt fiber and bottom ash to improve their physical, mechanical, and operational characteristics.

In [8], the results of studies on the influence of hardening conditions on the structure and properties of nanomodified concrete are described. It is shown that under favorable conditions in the early stages of hardening, concrete gains high strength and reduces porosity. However, a number of issues remain debatable, related to the influence of low temperatures on structural changes in concrete, especially during freezing in the early stages. Difficulties are associated with plastic shrinkage and mass transfer processes, which lead to loss of frost resistance and water resistance. Overcoming these problems is possible by ensuring critical strength before freezing and temperature control in the early stages of hardening. The specified approach was applied in [7]; however, additional studies on the long-term effect of low temperatures are necessary to fully solve the problem. All this allows me to state that it is advisable to conduct a study on increasing the frost resistance of nanomodified cement composites.

In [9], the results of studies on physicochemical methods for modifying polymer composites are reported. It has been shown that improving the interfacial interaction of components is a key factor for increasing the reliability of polymer composites. However, not all aspects have been finally resolved, related to the uniform distribution of nanoparticles in a liquid medium. A possible factor is the difficulty in achieving a uniform distribution of nanofillers due to their aggregation, which complicates the formation of composites. An option for solving these problems may be the use of ultrasonic treatment to achieve deagglomeration and uniform distribution of nanoparticles. This method was introduced in [8] but requires further research to optimize the processing parameters. Therefore, it is advisable to conduct a study on improving the methods of ultrasonic modification of polymer composites.

Papers [10, 11] report the results of studies on the influence of the biochar nanomodified concrete additive on its strength and deformation characteristics. It is shown that the introduction of a biochar component obtained from rice straw waste makes it possible to increase the compressive and tensile strength of concrete, improve the elastic modulus, and reduce deformation indicators. The issues related to the optimization of the amount of additive and its uniform distribution in concrete remain unresolved. A possible factor is the limitation in achieving a homogeneous mixture due to the complexity of its processing technology. An option for solving the problem is the further development of methods for processing concrete mixtures using electromagnetic activation. All this allows me to state that it is advisable to conduct a study on improving the technologies for strengthening concrete with biochar nanomodifiers.

Existing techniques for preparing protective coatings involve the mandatory use of expensive dry concrete mixtures and special mixers [11, 12], which have low productivity. The problems of the lack of clear and tested in practice recommendations on the technology of preparation and ion-protective coatings, without the use of dry mixes and special mixers, which significantly limits their application, remain unresolved. In this regard, the technologies for preparing and laying the mortar mixture when arranging coatings require improvement and testing under construction site conditions.

There are many technologies that allow for effective work on the arrangement and repair of ion-shielding coatings. The choice of the scheme is made taking into account specific objects. However, there are unresolved issues related to the fact that increased technological and operational requirements are imposed on most coatings. Ion-shielding coatings arranged using standard technologies with the use of solutions, characterized by high compressive strength, have always had the same problem – low resistance to tearing and the formation of shrinkage cracks during hardening. And with further operation, such disadvantages as low frost resistance, low impact resistance, susceptibility to abrasion, high degree of penetration of water and chemicals are revealed. Solving these problems under these conditions and designing a competitive material, as shown by the results of many studies, is possible by making fiber-reinforced concrete [11, 12], in particular, concrete reinforced with dispersed fibers from polymeric materials. Disperse reinforcement technology makes it possible to reduce labor costs, increase chemical inertness and adhesion to the old base [11, 12]. It can also be used to design a binder that helps improve the basic technological and physical-mechanical properties.

Papers [12, 13] report the results of studies into foam concrete modified with micro silica and reinforced with polypropylene fibers. It is shown that the addition of micro silica (10 %) and polypropylene fibers (2 %) makes it possible to increase the compressive strength by 44 %, the bending strength by 73 %, and to reduce the thermal conductivity coefficient by 9 %. Unsolved problems are related to the optimization of the mixture to achieve the best distribution of fibers and filler, the solution of which is possible by devising new methods for mixing and activating materials. All of the above confirms that it is advisable to conduct research on improving the methods for producing foam concrete with nanomodified additives.

In [14, 15], the results of studies on the influence of nanomodifiers on high-temperature and low-temperature properties of asphalt concrete are described. It is shown that the effectiveness of such additives depends on the type of base asphalt, the type of nanomodifier, its dosage, particle size, and preparation method. Among the unsolved problems is the difficulty of selecting optimal parameters due to the incompatibility of materials and high production costs, which sometimes makes research impractical for different operating conditions. Solving these problems is possible by systematically studying the mechanisms of interaction of nanomodifiers with different types of asphalt. This is the approach used in [16]; however, the studies do not cover all possible influences of different operating conditions. All this allows me to state that it is advisable to conduct further studies on optimizing the composition and methods for preparing nanomodified solutions and concretes.

3. The aim and objectives of the study

The aim of this study is to design building (specialized) solutions for ion-shielding coatings based on mineral composite substances of the CaO-Al_2O_3-SO_3-H_2O system. This could make it possible to make X-ray protective coatings with high resistance to ionizing radiation and increased physical and mechanical properties.

To achieve the goal, the following tasks were set:

– to design the composition of an ion-shielding coating based on mineral composite substances, taking into account the influence of modifiers on the structure and properties of the material;

– to investigate the physical and mechanical properties of ion-shielding coatings, in particular their resistance to radiation and mechanical characteristics.

4. The study materials and methods

The object of this study is the processes of structure formation, physical-mechanical, and protective properties of plasters for X-ray rooms based on nanomodified gypsum-alumina compositions.

The hypothesis of the study assumes that increasing the attenuation of ionizing radiation and the physical-mechanical properties of composites is possible by introducing barium concentrate into the gypsum-alumina cement system in combination with nanomodifiers.

The assumptions accepted are that the ability to bind water contained in the hardened cement stone of gypsum-alumina cement in combination with the modification of the gypsum-alumina cement system could make it possible to obtain coatings with improved protective and physical-mechanical properties.

The simplifications adopted are that the introduction of plasticizers and carbon nanotubes improves adhesion to the base and ensures a uniform distribution of components in the structure of the material.

The composition of the X-ray protective plaster was devised based on a composite mixture of gypsum+alumina cement and barite concentrate. Molecular weight – 233.4 g/mol; ρ=4500 kg/m^3. Attenuation of ɣ-rays of barite concentrate – 4.15 cm^{-1}.

To reduce water consumption and regulate the rheological properties of nanomodified alumina compositions, additives based on surfactants of the plasticizing group were used.

The Sika plasticizer was added in an amount of 0.4 % of the weight of the binder.

For studying alumina cements, polyfractional standard sands were also used, which meet the basic requirements [17]. The sieve analysis of the sand revealed a high content of fractions less than 0.63 mm. The sand corresponds to [17] in terms of granulometric composition and can be used for the manufacture of heavy concrete.

Current procedures and regulatory documents were used when determining the construction, technical, and physical-mechanical properties of X-ray protective plasters.

To assess the influence of the ratio of the initial components on the properties of nanomodified alumina compositions, a mathematical planning of the experiment was carried out. The method of statistical treatment of results was used – simplex-gradient experimental design.

Determination of the adhesion strength of these X-ray protective solutions to the bases [18] was carried out using a testing machine. According to the procedure, the stamp was glued to the surface of the test surface. Then, using the testing machine, a tensile load was generated. The latter is transmitted through the stamp parallel to the test surface without jerks and with the same speed.

To determine the total amount of water in the X-ray protective coating, the thermogravimetric method (TGA) was used. For this purpose, the sample was placed in a thermogravimetric analyzer. During the heating of the sample, the change in mass with increasing temperature was determined. The total amount of water in the coating corresponds to the mass of water lost during heating.

A thermogravimetric analyzer was used to determine the content of chemically bound water. The procedure involved preliminary removal of adsorbed moisture by drying in a drying oven and subsequent heating in a TGA analyzer according to the program from 30 to 1100 °C with a heating rate of 10 °C/min. Depending on the temperature, the mass of the sample was recorded, and the percentage of chemically bound water was calculated.

To determine the linear ion density attenuation coefficient (μ), homogeneous conditions were created in order to minimize the effects. The study was carried out under a vacuum mode. At different distances (x) detectors were installed along the trajectory of the ion flow. During the study, the zero point is registered. Then, the ion density is measured in accordance with the direction of the ion flow.

The calculation of the linear attenuation coefficient of the ion density (μ), cm^{-1}, was carried out at a neuron energy of $1^{<}E^{>}5$ MeV (1):

$$\mu_n = N_a\left(\frac{Pn}{Am}\cdot\sigma_n+\frac{Pc}{Ac}\cdot\sigma_c+\frac{Pti}{Ati}\cdot\sigma_{ti}\right), \tag{1}$$

where N_a is the scaling factor;

Pn, Pc, Pti are the mass fractions of the components in the system;

Am, Ac, Ati are the molar and atomic masses of the components in the system;

σ_n, σ_c, σ_{ti} – effective interaction parameters – the characteristics of the quantity that lead to attenuation.

5. Results of designing solutions for ion-protective coatings based on the CaO-Al_2O_3-SO_3-H_2O system

5. 1. Devising the composition of the ion-protective coating

During the study, the composition of the ion-protective coating based on mineral composite substances was designed, taking into account the influence of modifiers on the structure and properties of the material. The basis of the composition is a solution based on alumina cement (GC-40), building gypsum (G5), and barium concentrate (BC-3). The optimal content of nanotubes and Sika plasticizer was determined in previous studies and is 0.18 % and 0.8 %, respectively [19].

For statistical treatment of the results, the method used was simplex-gradient experimental design. The second-order model was described by a third-power polynomial.

When constructing the "composition – compressive strength" diagram, the influence coefficients for the compressive strength for a raw material mixture based on alumina cement, gypsum, barium concentrate + (Sika+BNT) were found:

$b_1=R_1=2.98$; $b_2=R_2=2.56$; $b_3=R_3=3.24$;

$b_{12}=4R_{12}-2R_1-2R_2=4\times3.88-2\times2.98-2\times2.56=4.44$;

$b_{13}=4R_{13}-2R_1-2R_3=4\times3.64-2\times2.98-2\times3.24=2.12$;

$b_{23}=4R_{23}-2R_2-2R_3=4\times2.93-2\times2.56-2\times3.24=0.12$;

$b_{123}=27R_{123}-12(R_{12}+R_{13}+R_{23})+3(R_1+R_2+R_3)=$
$=27\times2.22-12(4.44+2.12+0.12)+$
$+3(2.98+2.56+3.34)=-39.12$.

The variables of the planning matrix (Table 1) are: alumina cement (X_1), gypsum (X_2), and BC-3+(Sika+BNT) (X_3). According to the input data (Table 1), the change in the state diagrams was determined. The compressive strength is the output variable (Table 1, Fig. 1, 2). The ranges of variation of the input variables are 5 %.

Table 1

Planning matrix

Plan point	Encoded scale component content			Natural content of components, % by weight					Compressive strength (R_{comp}), MPa
	X_1	X_2	X_3	A	B	C			
				AC	G	BC-3	Sika	CNTs	
1	1	0	0	70.97	26.85	1.2	0.8	0.18	2.98
2	0	1	0	65.97	31.85	1.2	0.8	0.18	2.56
3	0	0	1	65.97	26.85	6.2	0.8	0.18	3.24
4	0.5	0.5	0	68.47	29.35	1.2	0.8	0.18	3.88
5	0.5	0	0.5	68.47	26.85	3.7	0.8	0.18	3.64
6	0	0.5	0.5	65.97	29.35	3.7	0.8	0.18	2.93
7	0.333	0.333	0.333	67.64	28.52	2.86	0.8	0.18	2.22

Based on the results of planning and conducting the experiment, a mathematical model (2) was built, which adequately estimates the dependence of compressive strength on change in composition:

$$R_{comp}=2.98X_1+2.56X_2+3.24X_3+4.44X_1X_2+ +2.12X_1X_3+0.12X_2X_3-39.12X_1X_2X_3. \quad (2)$$

At the test point, in the center of the simplex, six parallel experiments were implemented to check the adequacy of the model. Using the Student's test (r) at the points, the adequacy of the received responses was checked. The critical value of the test at $\alpha=0.05$ and $p=5$; $m=n-1=4$ is 0.5441. Thus, $G_{calc.}<G_{crit.}$; the hypothesis of homogeneity of the dispersion of measurement errors is confirmed with a probability of 95 %.

All obtained experimental data for correlation analysis were processed using the software tools Statistica SPSS V 7.0 and StatGraphics V 2.1. (Fig. 1, 2).

Using the mathematical model, the calculation was carried out and the diagram "composition-compressive strength limit" was constructed, which is shown in Fig. 1.

The content of components of the optimal region of compositions in the coded scale:

$X_1=0.34\div0.75$; $X_2=0.25\div0.66$; $X_3=0\div0.19$.

Calculation of composites in percentages of the optimal composition range, calculated using formulas (3):

$$A=(A_{max}-A_{min})\cdot X_1+A_{min},$$
$$B=(B_{max}-B_{min})\cdot X_1+B_{min}, \quad (3)$$
$$C=(C_{max}-C_{min})\cdot X_1+C_{min}.$$

Alumina cement=67.67÷69.72,

Gypsum=28.1÷30.15,

Barium concentrate (Sika+CNTs)=1.2÷2.15 (0.8+0.18).

With an increase in the content of barium concentrate and gypsum, the strength indicators decrease. The isoline of the response surface in Fig. 1, 2 has a value of 3.88 MPa in dark red with coordinates ($X_1=0.34-0.75$; $X_2=0.25-0.66$; $X_3=0-0.19$). The values converted to natural form (Table 1): $X_1=67.67-69.72$ %; $X_2=28.1-30.15$ %; $X_3=1.2-2.15$ %.

During the tests, the influence of different ratios of components on the physical-mechanical characteristics of the material was determined. In particular, studies have shown that increasing the content of alumina cement increases the strength of the material, while increasing the amount of gypsum contributes to better formation of the coating structure. Barium concentrate significantly improves the radiation-protective properties of the solution.

The study of the material structure using electron microscopy showed the formation of a microporous structure, which improves the material's ability to absorb radiation. It was found that the inclusion of nanomodifiers makes it possible to reduce porosity and increase adhesion between components.

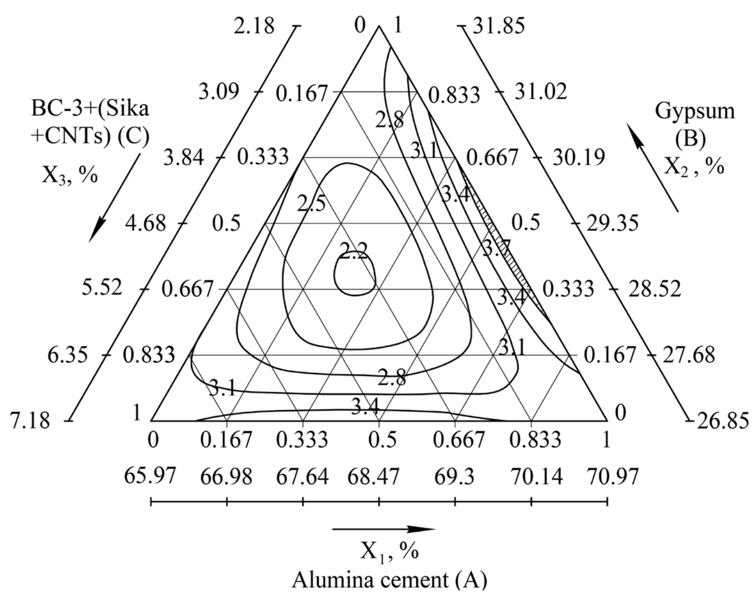

Fig. 1. Composition-compressive strength state diagram for an X-ray protective coating containing alumina cement, gypsum, and barium concentrate (plasticizer+carbon nanotubes)

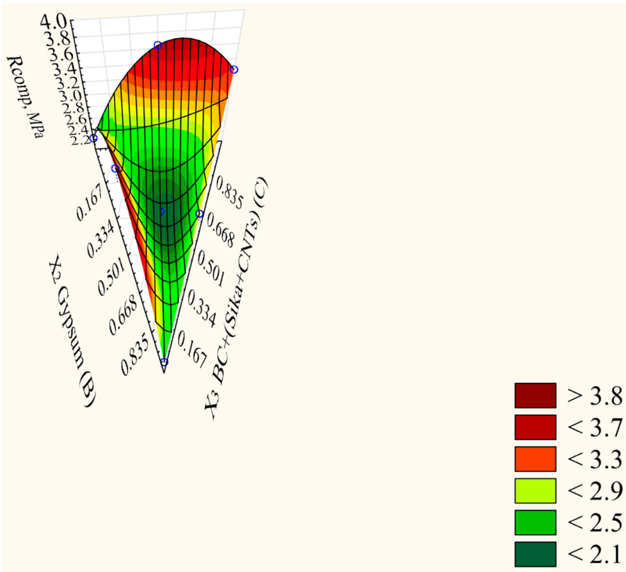

Fig. 2. Three-dimensional projection of the diagram of the influence of an X-ray protective coating of the composition: alumina cement, gypsum, and barium concentrate (plasticizer+carbon nanotubes)

5. 2. Investigating the physical-mechanical properties of ion-shielding coatings

The research of physical-mechanical properties of ion-shielding coatings was carried out by assessing their strength, density, resistance to mechanical loads, and ability to attenuate ionizing radiation. It was determined that coatings using alumina cement and barium concentrate demonstrate improved properties compared to conventional cement mortars.

To assess the characteristics of the material, a series of laboratory tests were conducted, which included determination of the ultimate strength in compression and bending, assessment of the density of the material, analysis of the influence of nanomodifiers on the general physical-mechanical characteristics.

The characteristics of the protective properties of the optimal composition of the X-ray shielding coating when changing the water-hardness ratio are given in Table 2.

When justifying the use of gypsum-alumina cement and barium concentrate to make ion-shielding coatings, the absence of radiation shrinkage and the ability to retain a large amount of chemically non-bonded water in the closed pores of the structure were taken into account. During operation, water will be retained in the coating for a long time.

Fig. 3 shows the dependence of the ion density attenuation coefficient of the X-ray protective coating containing alumina cement, gypsum, and barium concentrate (plasticizer+carbon nanotubes) on the change in neuron energy.

The dependence $\mu(E)$ was obtained by experimental measurement of gamma-ray attenuation at different energies. The data show an exponential decay of the attenuation coefficient with increasing energy, which is consistent with the physical laws of radiation permeability. The least squares approximation gave the equation $\mu=2.860\cdot\exp(-1.019\cdot E)$ with high accuracy ($R^2=0.9734$). The resulting model reliably describes the experimental data and can be used to predict radiation attenuation.

The results confirm that the material has high resistance to mechanical loads and retains its characteristics even after prolonged exposure to radiation. The linear attenuation coefficient of ionizing radiation at neuron energy (E) up to 1 MeV is 0.88–0.9 cm^{-1}. When the neuron energy (E) increases to 5 MeV, the attenuation coefficient of ionizing radiation is 0.088–0.09 cm^{-1}, which makes it possible to reduce the required thickness of the protective layer to 14.6 mm.

The main physical-mechanical properties of the designed X-ray protective coating composition: compressive strength – 3.88 MPa, bending strength – 1.85 MPa, and grafting strength with a concrete surface – 2.31 MPa.

During experimental studies, it was found that the optimal amount of chemically bound water ensures uniformity of the coating structure, and the introduction of carbon nanotubes improves the cohesive properties of the material. The use of barium concentrate contributes to an increase in the level of neutron radiation absorption.

Industrial tests of the material were also conducted, which confirmed its effectiveness under real operating conditions. The coating demonstrated high adhesion to concrete and metal surfaces, which allows it to be used to protect critically important objects, such as medical institutions, nuclear power plants, and military facilities.

In general, the results of the studies indicate the feasibility of using the designed materials in the field of radiation protection. Increased strength and effective absorption of ionizing radiation can significantly improve the safety level of structures exposed to radiation.

Table 2

Characterization of protective properties for an X-ray protective coating containing alumina cement, gypsum, and barium concentrate (plasticizer+carbon nanotubes)

Property	W/C		
	0.25	0.3	0.33
Specific gravity of X-ray protective coating, kg/m^3	2310	2256	2186
Total amount of water in X-ray protective coating, kg/m^3	772	734	756
Content of chemically bound water after 28 days of curing, kg/m^3	492	478	437
Compressive strength after 28 days of curing, MPa	3.88	3.55	2.76

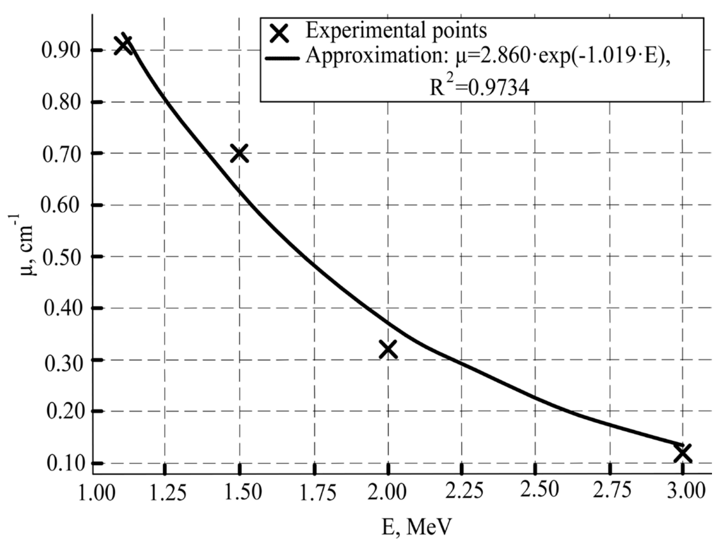

Fig. 3. Dependence of the ion density attenuation coefficient of the X-ray protective coating GC-40:G5:BC-3 concentrate:plasticizer:CNT on the change in neuron energy

6. Discussion of results based on the design of building (specialized) solutions for ion-shielding coatings

The results of designing the composition of the ion-shielding coating can be explained by the fact that the used solution matrix (gypsum-alumina cement system) has the ability to contain an increased amount of chemically bound water (up to 42 %) due to the ettringite content. In contrast to [14, 15], in which nanomodifiers were used to increase the density of the cement stone structure, the result of designing a binder with a stable ettringite phase makes it possible to increase the radiation-shielding properties of the X-ray shielding coating. The latter is associated with the formation of ettringite and the development of an optimal composition using carbon nanotubes (CNTs, Fs=80–120 m^2/g) (Table 1, Fig. 1, 2). The optimal composition of the nanomodified solution of the X-ray protective coating, which provides a compressive strength of 3.88 MPa:GC-40:G5:BC-3 concentrate:plasticizer:CNT – 68.47:29.35:1.2:0.8:0.18 % (Table 1, Fig. 1, 2).

The results related to the properties of ion-shielding coatings (Tables 1, 2, Fig. 3) can be explained by the fact that by using modern techniques for obtaining a binder – by modifying calcium sulfoaluminates, the problem of stability of the ettringite phase is solved. This will make it possible to purposefully regulate the rate of hydration and coordinate the process of structure formation in time. Unlike [14, 15], in which the attention is focused on the analysis of mechanical properties, the result of studying the structure of a binder based on gypsum-alumina cement makes it possible to obtain a fine-pore structure with stable properties (Tables 1, 2, Fig. 3). This becomes possible due to the use of nanomodifiers and new techniques for obtaining compositions for the production of a binder, which are effective in technical terms.

The obtained indicators regarding the results of the study of the physical-mechanical properties of protective coatings (Tables 1, 2) are due to the fact that the binder does not contain factors of instability of the ettringite phase – $Ca(OH)_2$ and highly basic hydroaluminates. Thus, during hydration reactions, ettringite will not lose stability due to the absence of the formation of new formations that can lead to gypsum corrosion. Unlike [9], in which the attention is focused on the development of a composite binder without solving the problem of the stability of the ettringite phase, the results of this study confirm the increase in protective properties (Table 2). This is possible due to the selection and calculation of the ratio of components that, during the hydration process, will have a sufficient amount of low-basic hydroaluminates and $Al(OH)_3$ gel to ensure the stability of ettringite. Thus, the optimal water-hardness ratio for making ion-protective coatings is 0.25. As it increases, the total amount of water in the X-ray protective coating decreases (Table 2).

The reported solutions completely resolve the task through the improvement of stability of the ettringite phase made on the basis of gypsum-alumina mineral binders (Table 2, Fig. 3). They are of great importance for the production of biological protection by making ion-shielding coatings. This is explained by the increase in the efficiency of ion-shielding coatings (Table 2, Fig. 3), ensuring their resistance to radiation exposure and optimizing their production for practical use in the construction industry.

The binder designed, with improved technological, physical-mechanical, and operational properties, can be used for ion-shielding coatings at X-ray rooms.

The results have limitations and are adequate under the condition of using ultrasonic treatment to evenly distribute nanotubes in water with a plasticizer for the preparation of the solution. The limits of variation of the variables are 5 %. After 4.5 minutes of ultrasonic treatment, the colloidal system is mixed with gypsum-alumina cement and barium concentrate. Taking into account the limitations, practical and theoretical expectations will be met.

The disadvantages of the study are that the technology for preparing the mortar mixture when installing ion-shielding coatings requires verification under the conditions of a construction site.

This study may be advanced in the future by investigating the influence of radioactive factors on the structure, analyzing the technological and economic advantages of using gypsum-alumina cements for the manufacture of ion-shielding coatings. New effective compositions based on gypsum-alumina cement and production waste are quite effective in technical and economic terms.

7. Conclusions

1. A composition of an ion-shielding coating based on mineral composite substances has been designed, which includes alumina cement (GC-40), building gypsum (G5), and barium concentrate (BC-3). The optimal proportions of the components that provide a balance between strength, radiation-shielding properties, and structural stability of the material are GC-40:G5:BC-3 concentrate:plasticizer:CNT – 68.47:29.35:1.2:0.8:0.18 %. A feature of the designed composition is the increased amount of chemically bound water – up to 50 %, which contributes to the effective absorption of ionizing radiation.

2. The study of physical-mechanical characteristics showed that the designed coatings have increased strength – 3.88 MPa, and the ability to effectively attenuate ionizing radiation – at a neutron energy of up to 1 MeV, the attenuation coefficient of ionizing radiation is 0.9 cm^{-1}. It was determined that the use of barium concentrate significantly improves radiation protection, and the introduction of carbon nanotubes increases the adhesive properties of the material – 2.31 MPa. The linear attenuation coefficient of radiation is 0.009 cm^{-1}, which makes it possible to reduce the required thickness of the protective layer to 14.6 mm. Experimental studies confirmed the high resistance of the material to mechanical loads, which ensures its effective use under conditions of increased radiation hazard.

Conflicts of interest

The author declares that she has no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study, as well as the results reported in this paper.

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Data availability

The manuscript has associated data in the data warehouse.

Use of artificial intelligence

The author confirms that she did not use artificial intelligence technologies when creating the current work.

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