Investigations of the influence of tungsten carbide and tungsten oxide nanopowders on the radiation protection properties of cement matrix-based composite materials

V Gavrish¹, N Cherkashina² and T Chayka¹

¹Scientific and educational center "Advanced technologies and materials", Sevastopol State University, 33 Universitetskaya Str., 299053, Sevastopol, Russian Federation
²Department of Chemistry and chemical technologies, Sevastopol State University, 33 Universitetskaya Str., 299053, Sevastopol, Russian Federation

E-mail: vmgavrish@sevsu.ru

Abstract. The influence of tungsten carbide and tungsten oxide nanopowders on radiation-protective properties of a composite material based on a cement matrix has been studied. These powders are obtained from carbide scrap production. In the radiation energy range of 0.06...1.408 MeV the gamma radiation attenuation coefficients at various concentrations of nanopowders WC and WO₃ (3.6%, 6.4%, 9.6% of the material mass) have been considered. The mass attenuation coefficient and the multiple of attenuation of radiation of investigated materials are calculated. It is shown that nanomodified composite material has high radiation protection characteristics and can find wide application as a radio protection material.

1. Introduction

The need for radiation protection materials arises in various industries and human activities: nuclear power, medicine, space technologies [1]. Active use of ionizing radiation sources requires development of modern effective materials for protection against radiation [2]. The solution of these problems is expressed in creation of radiation-protective materials providing safety.

At present special binding cements (barium [3], lead-barium, iron-lead-barium) and others [1,4] have been developed, but portland cement is usually used for construction works and manufacturing of protective materials and products. For improvement of operational and radiation-protective properties of building materials it is recommended to enter into their structure special additives-modificators [5].

For today introduction of nanotechnologies is rather perspective as their application opens new technological decisions in the plan of creation of the materials possessing unique properties, including radio-protective. Studies carried out by scientists from different countries [5-12] have shown that the use of nanoparticles as new materials in the field of radiation protection has led to significant progress. Currently, the nanoparticles most frequently used to modify cement composites are PbO₂, H₄B [6], WO₃ [7] SiO₂ [8], Fe₂O₃, [9] Fe₃O₅, ZnO [10], Bi₂O₃ [11], PbO, PbTiO [12] and others. However, despite the positive effect of nanoparticles on the increase in the radio-protective properties of materials, their large-scale use is constrained by the impossibility of large-scale production of nanopowders and their high cost.

The solution to this problem is the use of nanopowders of metals and their compounds from carbide scrap, proposed by the authors [13]. This method of obtaining nanopowders, which has no analogues in
the world, makes it possible to obtain various nanopowders at low cost and the possibility of producing powders in large volumes.

Research carried out earlier by the authors [14] on the influence of tungsten carbide nanopowders and tungsten oxide nanopowders on the strength characteristics of concrete has shown an increase in the strength of concrete samples by more than 50% when using a nanomodifier WC at its concentration in a mixture of 0.36%, more than 36% when using tungsten oxide (WO₃) at its concentration in a mixture of 0.6%. And if we consider that tungsten is a heavy element with potentially high radioprotective properties, then studying the influence of tungsten oxide nanopowders and tungsten carbide on the radioprotective properties of materials based on portland cement is very promising.

2. Experimental part

To obtain nanomodified composite materials, the following were used: portland cement from the manufacturer NOVOROSCEMENT PTs 500 D-0, sea gray sand in a ratio of 1:4.6, with a water-cement ratio of V/C 0.6 and additives of nanopowders (3.2%, 6.4%, 9.6% of the mass of the material).

Nanopowders derived from tungsten carbide (WC) and tungsten oxide (WO₃) from tungsten carbide cobalt waste [13] have been used as modifiers. Tungsten oxide nanopowder was obtained by gradual heating of tungsten carbide nanopowder in a Bossert muffle furnace at temperature up to 750 °C [15].

As it has been established in previous studies [16], tungsten carbide nanopowders WC and tungsten oxide WO₃ are nanobjects of nanoplate size less than 100 nm. Tungsten carbide nanopowder consists of one phase – tungsten carbide WC hexagonal crystal structure, the main phase of tungsten oxide nanopowder is triclinic oxide.

Samples in the form of 50×50×6 mm plates were used for the study. The tests were carried out on gamma-spectrometric equipment and a set of sample gamma-ray sources (GMS) with isotopes ²⁴¹Am and ¹⁵²Eu (figure 1). The source is a flat aluminium ring 3 mm thick and 25 mm in diameter. The active part is sealed between two polyimide films with a total thickness of 100±10 µm and a diameter not exceeding 3 mm. Radionuclide ²⁴¹Am is a source of soft γ-radiation with an energy of 59.5 MeV for the most part and radionuclide of photon radiation ¹⁵²Eu (Table 1). The scheme of investigation of radiation-protective properties of the material is shown on figure 2.

![Figure 1. Source of gamma radiation with isotopes ²⁴¹Am and ¹⁵²Eu: 1 – flat aluminium ring; 2 – sealed active part.](image1)

![Figure 2. Study scheme of radiation-protective properties of the material: 1 – source of ionizing radiation, 2 – case around the source with radiation protection, 3 – sample under study, 4 – stand.](image2)
Table 1. Radiation and physical characteristics of gamma–ray source radionuclides.

| Radionuclide | Half-decay period (years) | $E_\gamma$, keV (percentage of energy, %) | Nominal activity $\mu$Ci/kBq | Equivalent dose H, $\mu$Sv/h |
|--------------|---------------------------|------------------------------------------|-----------------------------|----------------------------|
| Europium-152 | 13.516                    | 121.78 $\div$ 1408.0 (0.027 $\div$ 27)/(1 $\div$ 1000) | $\leq$2.0                   |                            |
| Americium-241 | 432.6                     | 6.3 (2.4%) $\div$ 59.5 (35.8%) (0.027 $\div$ 27)/(1 $\div$ 1000) | $\leq$0.04                 |                            |

3. Analysis of results obtained

The values of linear coefficients of gamma radiation absorption of investigated composite materials on the basis of cement matrix modified with tungsten carbide and tungsten oxide nanopowders at their different contents in the material in the energy range of 0.06...1.408 MeV are given on figure 3. This range of energies and type of radionuclides is characterized by photon radiation, therefore, in the calculation of the value of the full linear coefficient of attenuation of the compton effect and the effect of pair formation can be neglected.

![Figure 3](image_url)

Figure 3. The values of the linear attenuation coefficient for gamma radiation of composite materials based on a cement matrix modified with tungsten oxide (a) and tungsten carbide (b) nanopowders.

Analysis of the results shows that the studied composites can significantly weaken the fluxes of gamma rays with energies up to 0.3 MeV, with further increase in gamma radiation energy the linear attenuation coefficient decreases.

Gamma attenuation efficiency depends on operating conditions, so at $E_\gamma = 0.245$ MeV application of nanosize additive of tungsten carbide allows to increase efficiency of attenuation of gamma radiation in more than 2.2–2.7 in comparison with a cement sample without addition of nanopowder, at application of tungsten oxide nanopowder decrease is observed in 1.5–2.4 times in a range of considered concentrations of nanopowder. However, the increase of radiation energy in the range from $E_\gamma = 1.0$ MeV requires separate experimental studies, because for the studied values from 1 MeV to 1.5 MeV values of coefficients have not changed.

The results of comparative analysis of mass attenuation coefficient for investigated composite materials on the basis of cement matrix with addition of tungsten carbide and tungsten oxide nanopowders (concentration of nanopowder is 9.6%) and without addition, depending on energy of photon radiation is presented in table 2.

Comparing the results of the data (table 2), it can be seen that the mass absorption coefficients for a material based on a cement matrix with the addition of tungsten carbide nanopowder and tungsten oxide in the energy range under consideration significantly outperforms the sample without the addition of nanopowder, the best results for a sample with the addition of WC, this can be explained by the difference in density of these materials. In the energy range from 0.3 to 1.0 MeV, the mass absorption coefficient of the material under study with the addition of tungsten oxide nanopowder is on average...
19 times higher, while a sample with tungsten carbide nanopowder is more than 26 times higher than a sample without the addition of nanopowder.

**Table 2.** Mass attenuation coefficient for cement and materials under study as a function of photon energy (sample thickness 0.6 cm).

| E, MeV | Mass attenuation coefficient µ, cm²/g |
|--------|--------------------------------------|
|        | Cement-matrix-based composite material |
|        | With the addition of nanopowder | With the addition of nanopowder | Without adding nanopowder |
|        | WO₃ (9.6%) | WC (9.6%) | |
| 0.122 | 2.4248 | 3.4488 | 0.0345 |
| 0.245 | 1.8592 | 2.592 | 0.0289 |
| 0.344 | 0.7056 | 0.9648 | 0.0295 |
| 0.778 | 0.6048 | 0.828 | 0.0282 |
| 0.964 | 0.336 | 0.4644 | 0.0279 |
| 1.112 | 0.3304 | 0.414 | 0.0271 |
| 1.408 | 0.2744 | 0.3348 | 0.0254 |

The attenuation rate for the studied composite materials at different thicknesses (0.6 and 1.2 cm) in the energy range from 0.06 to 1.408 MeV in comparison with the widely used radio protective materials – iron and lead is presented in table 3.

**Table 3.** Frequency of attenuation of composite materials based on a cement matrix with the addition of tungsten carbide nanopowder (9.6%), tungsten oxide (9.6%) and without the addition of nanopowder at different thicknesses (0.6 and 1.2 cm) in comparison with radio protective materials – iron and lead [17].

| Cement-matrix-based composite material |
|---------------------------------------|
| With the addition of nanopowder | With the addition of nanopowder | Without adding nanopowder |
| WO₃ (9.6%) | WC (9.6%) | |
| 2.8 g/cm³ | 3.6 g/cm³ | 2.3 g/cm³ |
| Iron | Lead |
| 7.86 g/cm³ | 11.34 g/cm³ |


| h/E, MeV | Frequency of attenuation |
|---------|--------------------------|
|        | 0.6 cm | 1.2 cm | 0.6 cm | 1.2 cm | 0.6 cm | 1.2 cm | 0.6 cm | 1.2 cm |
| 0.06   | 1.73 | 2.8 | 1.88 | 3.2 | 1.21 | 8.8 | 79.1 | _a_ | _a_ |
| 0.122  | 1.51 | 2.2 | 1.6 | 2.37 | 1.17 | 2.03 | 4.12 | _a_ | _a_ |
| 0.245  | 1.17 | 1.36 | 1.18 | 1.49 | 1.13 | 1.18 | 1.40 | 23.33 | 54.45 |
| 0.344  | 1.14 | 1.3 | 1.16 | 1.34 | 1.10 | 1.16 | 1.35 | 3.94 | 15.52 |
| 0.778  | 1.07 | 1.16 | 1.08 | 1.17 | 1.06 | 1.14 | 1.29 | 1.40 | 1.96 |
| 0.964  | 1.07 | 1.15 | 1.07 | 1.18 | 1.06 | 1.13 | 1.28 | 1.3 | 1.69 |
| 1.112  | 1.06 | 1.13 | 1.06 | 1.15 | 1.05 | 1.12 | 1.27 | 1.27 | 1.61 |
| 1.408  | 1.06 | 1.11 | 1.06 | 1.13 | 1.05 | 1.12 | 1.25 | 1.21 | 1.47 |

* _a_ lead protection is not used at low energy [17].

As can be seen from their presented research results in the entire dipasone of the studied energies, the reduction factor for nanomodified samples is greater than that for a sample without the addition of nanopowder. Maximal values are obtained in the range of energies from 0.06 MeV to 0.3 MeV, in the range from 0.3 ... 1.4 MeV values practically do not change.

Comparing the attenuation multiples of a cement matrix-based composite material with the lead values, it can be seen that in the energy range from 0.2 to 0.4 MeV the attenuation multiples for lead are significantly greater. In the range of energies of radiation 0.4 ... 1.408 MeV values of multiple of lead
attenuation at thickness 0.6 cm is more than 30% of the nanomodified sample, thus density of the investigated composite material is less than in 3 times.

As can be seen from the obtained results (table 3) in the low energy range from 0.2 to 1.408 MeV the values of multiple of attenuation of the nanomodified sample differ from the values of iron at the thickness of 0.6 cm material not more than 6.5 %, and at the thickness of 1.2 cm material not more than 12%. In the energy range of 0.2 ... 0.408 MeV the values of multiple attenuation of radiation for iron and for tungsten nanomodified carbide based material on cement matrix are the same, while the density of the investigated composite material is more than 2 times less.

Thus, as a result of research it is visible, that the offered nanomodified composite material on the basis of a cement matrix is an effective radio protective material, thus in comparison with such radio protective materials, as iron and lead more than in 2–3 times is easier. It will allow to create less overall and lightweight contrasts in situations when the weight and size of the protective material is one of the important indicators (in the manufacture of containers, mobile protective devices, protective screens, partitions, coatings, insulation materials, etc.).

4. Conclusions

On the basis of the conducted research on the influence of tungsten carbide and tungsten oxide nanopowders obtained from carbide scrap production on the radiation protection properties of a composite material based on a cement matrix, the following conclusions can be drawn:

– the nanomodified composite material has high radiation-protection characteristics in comparison with the sample without addition of nanopowder: gamma radiation attenuation coefficient in the range of considered concentrations of nanopowder (3.6%, 6.4%, 9.6% of the material mass) increases more than 2.2–2.7 times when tungsten carbide nanopowder is used, when tungsten oxide nanopowder is used 1.5–2.4 times at radiation energy 0.245 MeV. Values obtained by increasing radiation energy in the range from Eγ = 1.0 MeV and above require separate experimental studies;

– mass absorption coefficient of composite material based on cement matrix with addition of tungsten oxide nanopowder is on average 19 times higher, with addition of tungsten carbide nanopowder more than 26 times higher than that of material without addition of nanopowder in the energy range from 0.3 to 1.0 MeV.

– radiation attenuation factor, in the whole diphasone of the investigated energies, is higher for nanomodified samples than for a sample without addition of nanopowder. In the range of energies from 0.06 to 0.2 MeV the attenuation multiplicity for a composite material based on a cement matrix with the addition of tungsten carbide nanopowder is more than 42% more than with the addition of tungsten carbide by more than 55%. In comparison with iron in the energy range of 0.2 ... 1.408 MeV the values of multiple attenuation of radiation for iron and for tungsten carbide nanomodified material based on cement matrix are the same, while the density of the studied composite material is more than 2 times less.

Thus, the proposed composite material based on a cement matrix with the addition of nanopowders of tungsten carbide and tungsten oxide derived from carbide waste can find a wide range of applications as a radio protective material, for example, for the production of construction concrete, plaster and masonry mortars used in construction and finishing works to reduce the level of radiation generated by both external and internal sources.

Further research is required to investigate cement matrix-based composite nanomodified materials in the high energy range.

Acknowledgements

This work was performed with the assistance of Russian Fund for Basic Research (18-43-920001\19).

References

[1] Amirabadi E, Salimi M, Ghal-Eh N, Etaati G and Asadi H 2013 Study of Neutron and Gamma Radiation Protective Shield J. Innovation and Applied Studie 4 1079–85
[2] Radiation protection and safety in industrial radiography 1999 (Vienna: International Atomic Energy Energy) p 24

[3] Korolev E, Grishina A and Satyukov A 2014 Radiation-Protective Composite Binder Extended With Barium Hydrosilicates J. Advanced Materials Research [1040] 351–5

[4] Lyubomirskiy N, Bakhtin A and Bakhtina T Alternative approach to the organization of hardening of dolomite binding materials 2018 IOP Conf. Series: Materials Science and Engineering (MSE) [365] 32032. DOI: 10.1088/1757-899X/365/3/032032

[5] Inozemtcev S and Korolev E 2013 Development of nanomodifiers and research into their influence on the properties of bituminous binders Vestnik MGSU 131–9

[6] Mesbahi A and Ghiasi H 2018 Shielding properties of the ordinary concrete loaded with micro- and nano-particles against neutron and gamma radiations J. Applied Radiation and Isotopes 136 27–31

[7] Tekin H O, Sayyed M, Altunsoy E, Manici T 2017 Shielding properties and effects of WO3 and PbO on mass attenuation coefficients by using MCNPX code. Digest J. Nanomaterials and Biоструктуры 12 (3) 861–7

[8] Zaghoul Ya and Elwan S 2017 Characterization of Nano-Silica Concrete for Nuclear Uses J. Current Engineering and Technology 7 (1)

[9] Lesbayev A, Elouadi B, Borbotko T, Manakov S, Smagulova G, Boiprav O and Prikhodko N 2017 Influence of Magnetite Nanoparticles on Mechanical and Shielding Properties of Concrete J. Eurasian Chemico-Technological 19 223–9

[10] Abo-El-Enein S A, El-Hosiny F I, El-Gamal S M A, Amin M S, Ramadan M 2018 Gamma radiation shielding, fire resistance and physicochemical characteristics of Portland cement pastes modified with synthesized Fe2O3 and ZnO nanoparticles J. Construction and Building Materials 173 687–706

[11] Tekin H O, Sayyed M I and Issa S 2018 Gamma radiation shielding properties of the hematite-serpentine concrete blended with WO3 and Bi2O3 micro and nano particles using MCNPX code. J. Radiation Physics and Chemistry 150 95–100

[12] Hassan H, Badran H, Abdulkadir A and Sharshar T 2015 Studying the effect of nano lead compounds additives on the concrete shielding properties for γ-rays Nuclear Instruments and Methods in Physics Research Section B Beam Interactions with Materials and Atoms 360 81–9

[13] Gavrish V, Gavrish M, Baranov G, Chayka T and Derbasova N 2014 Pat UA 91420 U

[14] Gavrish V, Chayka T, Baranov G, Fedorova S and Gavrish O 2019 Effect of additives being WC, TiC, TaC nanopowder mixtures on strength property of concrete Materials today: proc. 19 (5) 1961–64

[15] Gavrish M, Baranov G and Chayka T 2019 On the issue of the techniques to produce mass and low-price tungsten oxide nanopowder J. Procedia Manufacturing 37 306–10

[16] Gavrish V, Chayka T and Baranov G 2019 The study on agglomerates of WC, TiC, TaC nanopowder mixtures obtained from hard-alloy waste products J. Phys.: Conf. Ser. 1410 012010

[17] Mashkovich V and Kudryavcev A 1995 Protection from ionizing radiation: Handbook (Moscow: Energoatomizdat) p 496