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THE EFFECT OF ADDITIVES OF REFRACTORY COMPOUNDS AND FIRING TEMPERATURE ON THE GAMMA SCATTERING OF GEOCEMENT COMPOUNDS DURING THE CONDITIONING OF RADIOACTIVE WASTE

ВПЛИВ ДОБАВОК ТУГОПЛАВКИХ СПОЛУК ТА ТЕМПЕРАТУРИ ВИПАЛУ НА ГАММА РОЗСІЮВАННЯ ГЕОЦЕМЕНТНИХ КОМПАУНДІВ ПРИ КОНДИЦІЮВАННІ РАДІОАКТИВНИХ ВІДХОДІВ

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В роботі розглянуто вплив тугоплавких сполук і температури випалу в діапазоні температур 350…950°С на гамма розсіювання геоцементних компаундів для кондиціювання радіоактивних відходів. Відмічено позитивний вплив сплаву вольфраму нікелю та карбіду бору на загальне гамма розсіювання і лінійний коефіцієнт послаблення, а дисиліциду молібдену на теплове розсіювання, що сприяє уповільненню радіолізу при кондиціюванні радіоактивних відходів, зниженню гамма навантаження на металеві барабани та внутрішні поверхні бетонних контейнерів. Цим вимогам відповідає склад компаунду, що містить 2.5–5% WNi, 5% $MoSi_2$ і 2.5–3.5% B_4C. Знання об’ємних деформацій компаундів дозволить оптимально наповнювати металеві барабани радіоактивним розчином по висоті чи об’єму.

The paper considers the influence of refractory compounds and firing temperature in the range of 350–950 °C on the gamma scattering of geocement compounds for conditioning radioactive waste. A positive effect of tungsten-nickel alloy and boron carbide on the total gamma scattering and linear attenuation coefficient is noted, and molybdenum disilicide on thermal scattering, which contributes to the slowdown of radiolysis during radioactive waste conditioning and a reduction in gamma radiation exposure to metal drums and the inner surfaces of concrete containers. These requirements are met by a compound containing 2.5–5% WNi, 5% $MoSi_2$ and 2.5–3.5% B_4C. Knowledge of the volumetric deformations of compounds will allow metal drums to be optimally filled with radioactive solution in terms of height or volume.

Ключові слова:
Геоцемент, кондиціювання, радіоактивні відходи, тугоплавкі сполуки, коефіцієнт поглинання, об’ємні деформації, лінійний коефіцієнт ослаблення, температура випалу.
Geocement, conditioning, radioactive waste, refractory compounds, absorption coefficient, volumetric deformations, linear attenuation coefficient, firing temperature

Introduction. Currently, a wide range of binding agents is used for conditioning low- and medium-level radioactive waste, selected with a view to ensuring the long-term durability of the compounds. Depending on the type of waste and its impact on the radiation resistance of matrices, the surfaces of metal drums and concrete containers, it is most appropriate to use alkaline binding systems, primarily aluminosilicates [1-3]. Their selection, in addition to the reliable adsorption-chemical binding of radionuclides in water-insoluble compounds, is also determined by the accelerated processes of polycondensation of zeolite-like new formation under the intense action of gamma radiation [4]. However, as a result of radiolysis [5, 6], a significant increase in temperature in the range of 700-950°C is recorded in the compounds. In addition to radiation, this increase contributes to a decrease in the structural properties of metal container drums. This is a rather pressing issue that needs to be addressed in order to ensure compliance with the conditions for intermediate and long-term storage of radioactive waste [7-9].

Analysis of recent studies. Materials with higher atomic mass and density are used to protect against gamma radiation and attenuate it: lead (11.34 g/cm^3), tungsten (19.3 g/cm^3), etc. [9, 10]. Lighter materials are often used, but less scarce and cheaper steel, cast iron, copper alloys [11]. Stationary screens that are part of building structures should be made of concrete and barite concrete, and the surfaces of walls and ceilings should be finished with barite mixtures ($BaSO_4$ - 4.48 g/cm^3) [9]. The use of refractory non-metallic materials for gamma attenuation in compounds for the conditioning of radioactive waste is one of the new directions in radiation materials science [12, 13]. The above-mentioned works contain data on the use of anti-radiation additives, such as B_4C, AlB_{12}, TiB_2, SiC, as well as their combinations in polymer coatings and concretes to increase the radiation protection of structures and materials [12, 13]. However, these works focus primarily on external protection rather than on the stability of binding agents during the conditioning of radioactive waste, especially at the moment of radiolysis. Therefore, the aim of the research presented in this scientific paper is to consider the possibility of increasing the radiation resistance of binding agents used in the conditioning, long-term storage and disposal processes.

Materials and methods. The object of the study was compounds based on mordenite-type geocement [1, 14], modified with refractory metallic and non-metallic compounds, the physical properties of which are given in Table 1.

Table 1

Physical properties of refractory non-metallic materials [15-17]

Title	ρ, g/cm^3	λ, W/m·K	Cp, J/g·K	α, 10-6 degrees-1	T, °C, oxidation in air
WNi	18,75	190	0,14	4.0	1700
$MoSi_2$	6,3	0,07	0,45-	4,0	1700
B_4C	2,52	11,0	-	4,5	1000

The selection of refractory additives is based on a combination of their high gamma scattering and low thermal conductivity, which is effective during radiolysis in compounds during their long-term burial and storage.

The optimisation of compound compositions was carried out using a three-factor simplex central design of experiments in the STATISTICA 12 mathematical environment with the implementation of a special cubic model that takes into account the non-linearity of the influence of factors on the properties of the initial parameters. The variation factors and matrix for planning the experiment are given in Table 2 and Table 3.

Table 2

Variation intervals and values of variable factors

Factors, appearance	Natural	Coded	Levels of variation		Variation interval
			0	1	
WNi	%	X1	2,5	7,5	5
$MoSi_2$	%	X2	5	15	10
B_4C	%	X3	1,5	3,5	2

Table 3

Experiment planning matrix

Plan points	Matrix plan in codes			Full-size matrix plan		
	X1	X2	X3	WNi, %	$MoSi_2$, %	B_4C, %
1	0,00	1,00	0,00	2,5	15	1,5
2	0,33	0,33	0,33	4,17	8,33	2,17
3	1,00	0,00	0,00	7,5	5	1,5
4	0,50	0,50	0,00	5	10	1,5
5	0,00	0,00	1,00	2,5	5	3,5
6	0,50	0,00	0,50	5	5	2,5
7	0,00	0,00	0,50	2,5	10	2,5

Regression equations and response surfaces from the influence of refractory additives are not presented in this work. Physical properties (density, porosity and volume shrinkage coefficient) and special properties (gamma absorption and attenuation coefficients – total and linear) were determined on samples measuring 3x3x3 cm depending on the processing temperatures – 80, 350, 650 and 950°C.

The absorption coefficient α γ-quanta and linear attenuation coefficient μ were determined using the formulas [18]:

$$\alpha = \frac{N_0 - N_i}{N_0} \cdot 100\%,$$

$$\mu = \frac{ln(N_0/N_i)}{h},$$

where N_0 is the number of pulses (cps) of the gamma radiation source; N_i is the number of pulses (cps) recorded by the detector after passing through a material with a thickness of h, cm.

The number of gamma pulses radiation pulses (cps) during the time interval τ (s) before and after the tests was determined using a FoodLight spectrometer with TeeChart pro v2012.06.120613 software (developed by the State Institution ‘Institute of Environmental Geochemistry’ of the National Academy of Sciences of Ukraine). Co-60 - K-3A 097 81 was used as the source of gamma radiation.

Research results. The research results are shown in Figs. 1–4. In Fig. 1 shows data on changes in the porosity of compounds, described by a parabolic dependence. The maximum porosity values for all compound samples are characteristic when they are processed at 350°C – the lowest value of 19.44% is characteristic for a compound with a composition of 2.5% WNi, 15% MoSi2 and 1.5% B4C. As the firing temperature increases, the porosity values decrease to 0.6–1.9% due to the compaction of glass-like structures.

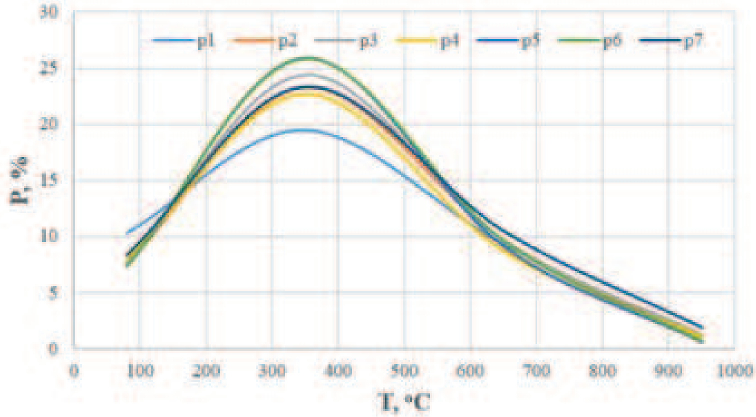

Fig. 1. Kinetics of changes in the porosity of compounds depending on the firing temperature P=f(T). Designations p1...p7 correspond to the points in the plan, Table 3.

The firing temperature has a significant impact on changes in the volumetric shrinkage of compounds (Fig. 2). The nature of the changes in the shrinkage deformation curves is the same for compounds p1...p7. The highest shrinkage values are observed when samples are fired at a temperature of 650°C (from 3 to 18%). Increasing the firing temperature to 950°C leads to a quantitative decrease in shrinkage, and for compositions p2, p3, p5, p6 and p7, this decrease ranges from 3 to 11%, while for composition p4, which contains 5% WNi, 10% $MoSi_2$ and 1.5% B_4C, an expansion of the sample volume of up to 2% is observed.

The composition of the compound containing 2.5% WNi, 15% $MoSi_2$ and 1.5% B_4C is characterized by an abnormal nature of shrinkage change depending on temperature. This composition is characterized by an increase in volume to 11% of the initial volume, with molybdenum disilicide playing an important role in this. Incidentally, this compound composition, in the temperature range of 80...950°C, is also characterized by minimum values of the total gamma attenuation (scattering) coefficient – on average, 21% (Fig. 3).

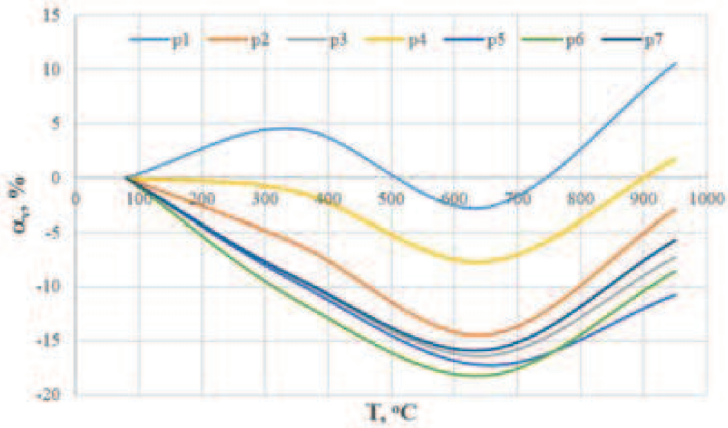

Fig. 2. Kinetics of changes in the volumetric shrinkage coefficient of compounds depending on the firing temperature αv=f(T)

The best scattering coefficient values, ranging from 23 to 26% of gamma radiation intensity in the considered temperature range, are characterized by a compound containing 2.5% WNi, 5% $MoSi_2$ and 3.5% B_4C. The presence of the maximum content of boron carbide contributes to an increase in this indicator (Fig. 3, Table 3). For other compound compositions, the value of $\alpha\gamma$ is within the range of 21–23%.

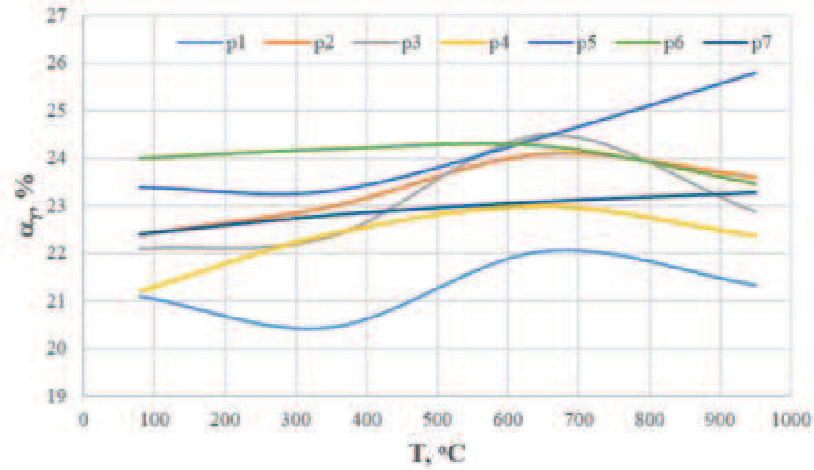

Fig. 3. Kinetics of change in the total gamma attenuation coefficient of compounds depending on the firing temperature $\alpha\gamma=f(T)$

As for changes in the values of the linear attenuation coefficient, the firing temperature affects its increase. The average value of μ in the temperature range of 350...950°C for a compound containing 5% WNi, 5% $MoSi_2$ and 2.5% B_4C is 0.47 cm^{-1}, which is 1.1 times higher than in other compounds (Fig. 4).

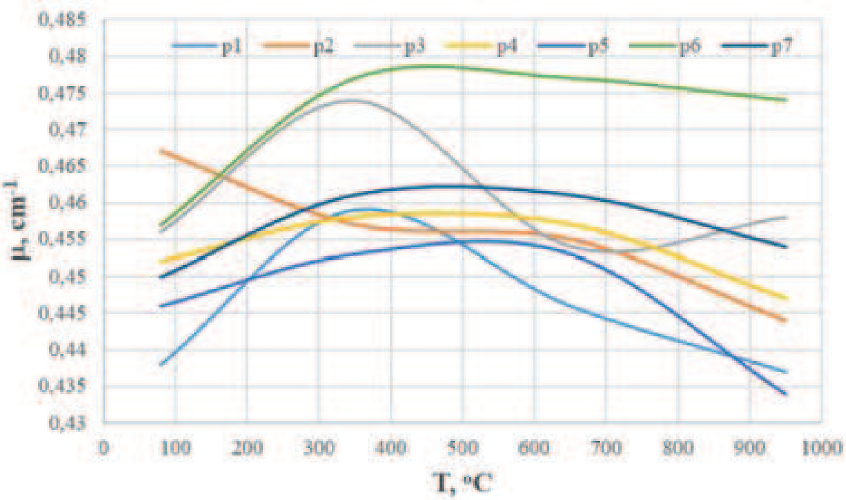

Fig. 4. Kinetics of change in the linear attenuation coefficient of compounds depending on the firing temperature $\mu=f(T)$

Summarising the data obtained, it can be said that in order to obtain an effective binding reagent for conditioning low- and medium-level radioactive waste, it is most expedient to add refractory substances to the composition of mordenite-type geocement in the following quantities: 2.5–5% WNi, 5% $MoSi_2$ and 2.5–3.5% B_4C. This will result in an artificial stone that is resistant to radioactive loads in the event of radiolysis during long-term storage of condensed radioactive waste.

Conclusions. A positive effect of WNi, MoSi2 and B_4C additives in the temperature range of 350-950°C on gamma scattering and linear attenuation coefficient of mordenite-type geocement-based compounds intended for conditioning radioactive waste for long-term storage and disposal has been established. It has been shown that the addition of these additives in amounts of 2.5–5%, 5% and 2.5–3.5%, respectively, contributes to an overall gamma attenuation (scattering) of up to 26% an increase in the attenuation coefficient to 0.47 cm^{-1}, which is 8.7 times higher than the linear scattering coefficient of unmodified mordenite-type geocement [1]. The alloy of tungsten with nickel and boron carbide contributes to gamma scattering, and molybdenum disilicide contributes to thermal scattering, which is important during radiolysis in the temperature range of 700-950°C. The indicators of volumetric shrinkage deformations of the specified compound composition will allow for effective calculation of the filling volume of metal drums of cemented radioactive waste.

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1. Guzii S. γ- weakening properties of aluminosilicate binders of analcimo-geylandite-mordenite composition. XXI international conference on physics of radiation phenomena and radiation material science, 23-25 September, 2024, Kharkiv, Ukraine, pp. 67-68.

2. Guzii S. Immobilisation of treatment products of chemically and radiation contaminated water with alkaline binder compounds. Book of abstracts. Workshop on Methods of water Pollution Control, 3-4 December 2024, Institute of Geotechnics SAS, Kosice, Slovakia, p. 40-41.

3. Guzii S.G. Alkaline binding systems for conditioning radioactive waste. XIII Scientific Conference 'Scientific Results of 2024'. Collection of scientific works, Kharkiv, Technological Centre, 2024, p. 86.

4. Chen X., Qiu M., et al. (2020). Gamma-Ray Irradiation to Accelerate Crystallization of Mesoporous Zeolites. Angewandte Chemie. 59, 28, 2020, pp. 11325-11329.

5. Guzii S., Zlobenko, B. Application of alkali-activated cements for immobilization of dry low-level radioactive waste containing copper ferrocyanide. Proceedings of the 7th annual conference Technology transfer: fundamental principles and innovative technical solutions, (2023), pp. 3–8.

6. Martynov B.V. Radioactive Waste Management. Kyiv: Tekhnika, 1993, 106 p.

7. Radiation Safety Standards of Ukraine; supplement: Radiation Protection from Sources of Potential Exposure (NRBU-97/D-2000).

8. Radiation Protection and Safety of Radiation Sources: International Basic Safety Standards. IAEA, Vienna, 2011, 329 p.

9. Khristich O. V., Deineka V. V., Shabanova G. M. Special-purpose materials for protection against ionising radiation: lecture notes. Kharkiv: NUCSU, 2023. 75 p.

10. Tungsten alloys // Ukrainian Soviet Encyclopedia: in 12 volumes / chief editor M.P. Bazhan; editorial board: O.K. Antonov et al. - 2nd edition. Kyiv: Main Editorial Office of the URE, 1974–1985.

11. Concrete with enhanced radiation protection properties: monograph / V. R. Serdyuk, O. V. Khristich, M. S. Lemeshev. Vinnytsia: VNTU, 2020, 82 p.

12. Guzii S., Prysiazhna O., Barvitskyi P. Research on boride compounds for gamma radiation attenuation in structural materials. International Scientific and Practical Conference "Modern Challenges in Science, Education, and Society: A Global Context": Conference Proceedings (Stanford, USA, September 6, 2025). Stanford, USA: Golden Quill Publishing, 2025. Pp 109-113.

13. Guzii S., Kurska T., Prysiazhna O. The influence of refractory nitrides on the gamma scattering of materials. International Scientific and Practical Conference "Global Challenges and Strategic Development of Science, Education, Economy, and State": Conference Proceedings (Boston, USA, September 12, 2025). Boston, USA: Golden Quill Publishing, 2025. pp. 52-55.

14. DSTU B V.2.7-181:2009 Building materials. Alkali cements. Technical conditions. Kyiv, Ministry of Regional Development and Construction of Ukraine, 2009.

15. Properties of refractory compounds (brief reference tables) / edited by G.V. Samsonov. Kyiv: IPM NASU, 1972, 31 p.

16. Yevdokimenko Yu.I., et al. Thermophysical characteristics and thermoerosion resistance of ceramic material based on boron carbide. Aviation and Space Technology, 2020, No. 8(168), pp. 136-145.

17. Voytovich R.F., Pugach E.A. Oxidation of refractory compounds. Reference book. Moscow: Metallurgy, 1978, 112 p.

18. Guzii S., et al. (2024). Removal of residual concentrations of cesium ions from low-level radioactive solutions. Problems of Atomic Science and Technology. 4(152), p. 84-93.