APPLICATION OF ALKALI-ACTIVATED CEMENTS FOR IMMOBILIZATION OF DRY LOW-LEVEL RADIOACTIVE WASTE CONTAINING COPPER FERROCYANIDE

Sergii Guzii
Corresponding author
Department of Nuclear and Physical Technologies[1]
sguziy2@gmail.com

Borys Zlobenko[1]

[1]*SI "Institute of Environmental Geochemistry of the National Academy of Sciences of Ukraine"*
34a Palladin ave., Kyiv, Ukraine, 03142

Summary: The possibility of using alkali-activated slag-Portland cement for immobilization of dry radioactive waste containing copper ferrocyanide they been confirmed. Because of optimization, the areas of existence of compositions that provide the criterion requirements for strength have been established. Introduction of magnetite additives in the amount of 14...15 wt. % (factor *X*1), zeolite in the amount of 6.5...7.5 wt. % (factor *X*2) and dry radioactive waste on the basis of copper ferrocyanide in the amount of 10...12 wt. % (factor *X*3) provides criterion requirements for compressive strength. The maximum value of strength – 13.2 MPa on the 28th day of hardening is characteristic for the above-mentioned quantities of additives, and it is 1.32 times higher than the standard level of strength. Introduction of zeolite for 6.5...7.5 wt. % allows to reduce the mass and density (1.07 times), radioactivity (1.09 times) of composites. Because of modelling of compound compositions, especially in the expected reactions, the factor X3 shows a weakening factor contributing to the reduction of values of output parameters. Therefore, the introduction of dry radioactive waste into the alkaline slag-Portland cement matrix containing copper ferrocyanide is limited to no more than 12 wt. %. The processes occurring in the volume of the material explain the reduction of mass, density and radioactivity of the compounds. The energy released during radioactive decay of cesium, strontium and other radionuclides is absorbed by magnetite and converted into heat. Heat promotes the removal of physically bound and partially chemically bound water from the structure of tobermorite-like low-basic calcium hydrosilicates, hydrogranates, alkaline-alkaline-earth zeolite-type hydroaluminosilicates, and copper ferrocyanide hydrate shell. However, the passage of radiolysis does not affect the kinetics of strength gain of the compounds, but contributes to the increase of their compressive strength by 1.87 times compared to the strength of the compounds on 7 days of curing.

Keywords: alkali-activated cements, compound, compressive strength, dry copper ferrocyanide radioactive waste, immobilization, magnetite, radioactivity zeolite.

1. Introduction

An urgent task of environmental safety is to solve problems not only in the removal of residual concentrations of radioactive $^{137}Cs^{+1}$ [1, 2] from low-level aqueous solutions, but also in the utilization of the sorption product. The most common methods of cesium ion extraction are adsorption, ion exchange, chemical precipitation, chemical reduction, membrane technologies, coagulation, extraction, ion flotation [3–6]. Adsorption methods have become the most widely used in liquid radioactive waste decontamination technologies due to a wide range of adsorbents, process efficiency, simple technology and a wide range of applications [7]. The most effective sorbents for cesium extraction are ferrocyanide sorbents (synthetic materials based on iron (III), nickel (II), copper (II) and other metals or their mixtures) [8, 9]. These materials, due to their stability, cost, and sorption parameters, are superior to the known synthetic sorbents based on silica gel and silica. The issue of immobilization of low-level radioactive ferrocyanide complexes arises, namely, the creation of a mineral-like durable matrix in which the complexes be chemically bound.

In our opinion, it is advisable to use alkali-activated cements [10] for immobilization of waste of low and medium specific activity, which they characterized by high strength and water resistance. In case of radionuclides immobilization in them, the latter is incorporated into the cement stone structure as an active chemical component and reliably bound in it. The synthesis of zeolite-like hydrate formations in alkaline cement stone, which have a high sorption capacity, is an additional factor in the physical blocking of radioactive elements. Toxic elements not only form the structure of the artificial stone, but also find themselves locked in the three-dimensional lattice of the zeolite matrix, which has large energy-unsaturated cavities [11, 12].

Alkali-activated cements are products of the chemical interaction of alkali element compounds with an aluminosilicate component. In the case of metallurgical slag, the mineralogical composition of the curing products (slag cements) also includes tobermorite -like low-base calcium hydrosilicates, hydrogranates, and alkaline-alkaline earth hydroalumina of zeolite type [13, 14].

Thus, unlike traditional cementation, when radionuclides fixed only mechanically in the cement stone matrix, cementation with alkaline activated cements allows their long-term fixation due to adsorption and chemical binding.

The aim of the study is to establish the possibility of immobilizing dry low-level radioactive waste containing copper ferrocyanide with alkali-activated cements. To achieve this goal, it to plan to solve the following tasks, namely, to optimize alkali-activated cement by adding magnetite, zeolite and dry radioactive waste based on copper ferrocyanide and determine the main properties of the compound.

2. Materials and Methods

In the study, alkaline slag Portland cement LCEM IV [10] are used, obtained by mixing ground granulated blast furnace slag – slag basicity module 1.09; Blaine specific surface 3000 cm^2/g (ArcelorMittal, Kryvyi Rih, Ukraine) and Portland cement PC I-500 (Dyckerhoff, Ukraine) in a ratio of 80:20. As alkaline activators, a mixture of Na_2CO_3 and $Na_2SiO_3 \cdot 5H_2O$ is used in the amounts regulated by [10], and sodium lignosulfonate "Borresperse Na" (Norway) is used as a plasticizer. Magnetite concentrate (Poltava Mining Plant, Ukraine) and zeolite (Sokyrnytsia Zeolite Plant LLC, Ukraine) were used as additives-modifiers. The dry average composition of real radioactive waste obtained after sorption of cesium ions with complex sorbents based on copper ferrocyanide (*RW* – dry radioactive waste) is used as low-level radioactive waste.

The optimization of the compositions of the compounds was carried out using a three-factor simplex central design of the experiment in the mathematical environment STATISTICA 12 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 factors of variation and the matrix for planning the experiment they given in **Tables 1, 2**.

The following parameters they chosen as the initial parameters: mass, density, compressive strength and activity. The compressive strength of the mixture samples after 7 and 28 days was determined on 3×3×3 cm cubes of alkali-activated cement (*W*/*C*=0.36=const), which was cured at a relative humidity of 65 % at a temperature of 20±2 °C. The activity of the compound samples (ARR) is measured using a FoodLight radiometer (developed by State Institute "Institute of Environmental Geochemistry" of National Academy of Sciences of Ukraine). The technical characteristics of the device are as follows:

- NaI(TI) detector with a crystal ∅63×63 mm;
- lead protection thickness 40 mm;
- energy resolution of the spectrometer is 6.5 %;
- minimum detection activity for $^{137}Cs^{1+}$ 2 Bq/l;
- mode of express measurement 1–5 min;
- standard volume of measuring samples in a Marinelli vessel is 1.00±0.01 l;
- own background is not more than 5 imp/s;
- time for setting the operating mode is not more than 10 min.

The numerical values of the initial parameters they given in **Table 3**. The standard level of assessment of the compressive strength of composites on the 28th day of curing should be at least 10 MPa.

Table 1

Variation factors

Factors, view	Natural	Codes	Varying levels		Interval of variation
			0	1	
Magnetite	%	*X*1	5	15	10
Zeolite	%	*X*2	2.5	7.5	5
RW	%	*X*3	10	25	15

Table 2

Planning matrix experiment

No. point plan	Matrix plan codes			Matrix plan in full size		
	*X*1	*X*2	*X*3	Magnetite	Zeolite	RW
1	0.00	1.00	0.00	5	7.5	10
2	0.33	0.33	0.33	8.3	4.2	15
3	1.00	0.00	0.00	15	2.5	25
4	0.50	0.50	0.00	10	5	10
5	0.00	0.00	1.00	5	2.5	25
6	0.50	0.00	0.50	10	2.5	17.5
7	0.00	0.00	0.50	5	5	17.5

Table 3

Results of experiment

No. point plan	Hardening 7 days				Hardening 28 days			
	m, g	ρ, g/cm³	*Rcs*, MPa	*ARR*, Bq	*m*, g	ρ, g/cm³	*Rcs*, MPa	*ARR*, Bq
1	53.74	1.901	7.8	31.49	52.47	1.871	13.9	29.06
2	53.37	2.016	3.2	14.77	50.09	1.789	6.34	11.45
3	58.22	1.958	3.0	18.22	54.94	1.863	6.1	18.02
4	48.44	1.739	0.68	10.96	44.11	1.58	1.08	10.79
5	47.41	1.601	0.43	10.54	42.75	1.439	0.87	9.07
6	46.97	1.623	0.42	3.68	41.98	1.515	0.86	3.48
7	55.51	1.815	2.75	3.68	53.98	1.761	4.55	3.62

3. Results

Using the three-factor simplex central plan, mathematical models (1), (2) and isoparametric surfaces of response functions (**Fig. 1**) of the influence of the varied factors on changes in the mass of composites after 7 and 28 days of curing were obtained:

$$m^7=58.22x1+53.74x2+47.41x3-30.16x1x2-23.38x1x3+19.74x2x3+108.16x1x2x3, \tag{1}$$

$$m^{28}=54.94x1+52.47x2+42.75x3-38.38x1x2-27.46x1x3+25.48x2x3+122.1x1x2x3. \tag{2}$$

Using the three-factor simplex central plan, mathematical models (3), (4) and isoparametric surfaces of response functions (**Fig. 2**) of the influence of the varied factors on changes in the density of composites after 7 and 28 days of curing:

$$\rho^7=1.95x1+1.9x2+1.6x3-0.76x1x2-0.42x1x3+0.26x2x3+8.1x1x2x3, \tag{3}$$

$$\rho^{28}=1.86x1+1.87x2+1.44x3-1.15x1x2-0.54x1x3+0.43x2x3+5.54x1x2x3. \tag{4}$$

Using a three-factor simplex central plan, mathematical models (5), (6) and isoparametric surfaces of response functions (**Fig. 3**) were obtained for the influence of varying factors on changes in the compressive strength of composites after 7 and 28 days of curing:

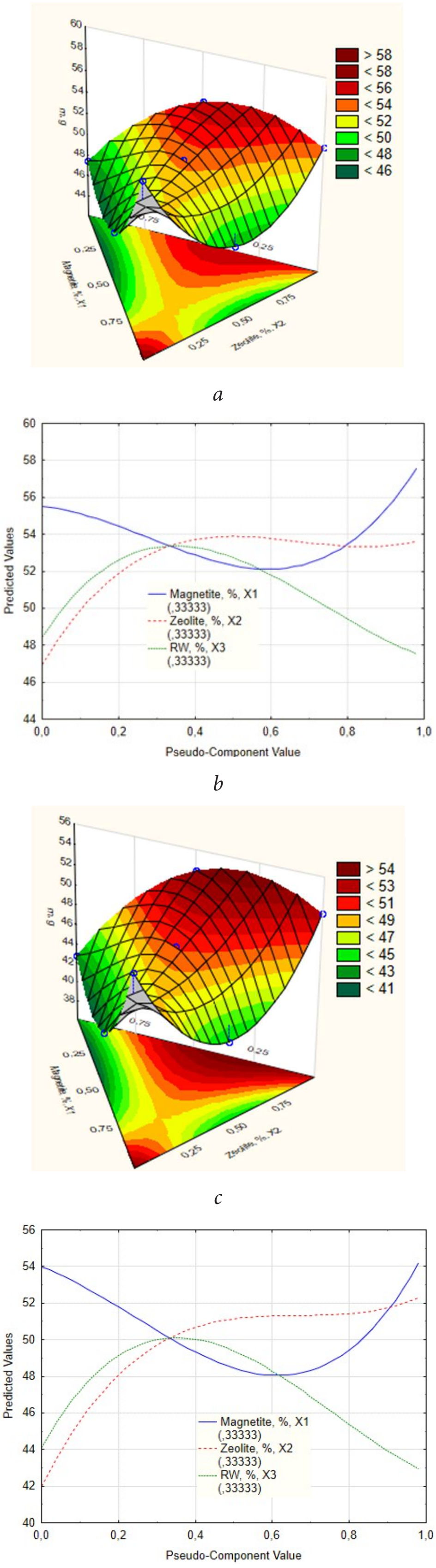
$$R_{cs}^{7}=3x1+7.8x2+0.43x3-18.88x1x2-5.18x1x3-5.46x2x3+73.89x1x2x3, \tag{5}$$

$$R_{cs}^{28}=6.1x1+13.9x2+0.87x3-35.68x1x2-10.5x1x3-11.34x2x3+155.91x1x2x3. \tag{6}$$

Using the three-factor simplex central plan, mathematical models (7), (8) and isoparametric surfaces of response functions (**Fig. 4**) of the influence of the varied factors on changes in the radiation activity of composites after 7 and 28 days of curing:

$$ARR^7=19.9x1+33.26x2+12.31x3-55.58x1x2-42.8x1x3-69.34x2x3+359.7x1x2x3, \tag{7}$$

$$ARR^{28}=19.74x1+30.78x2+10.79x3-51x1x2-40.26x1x3-61.38x2x3+261.7x1x2x3. \tag{8}$$

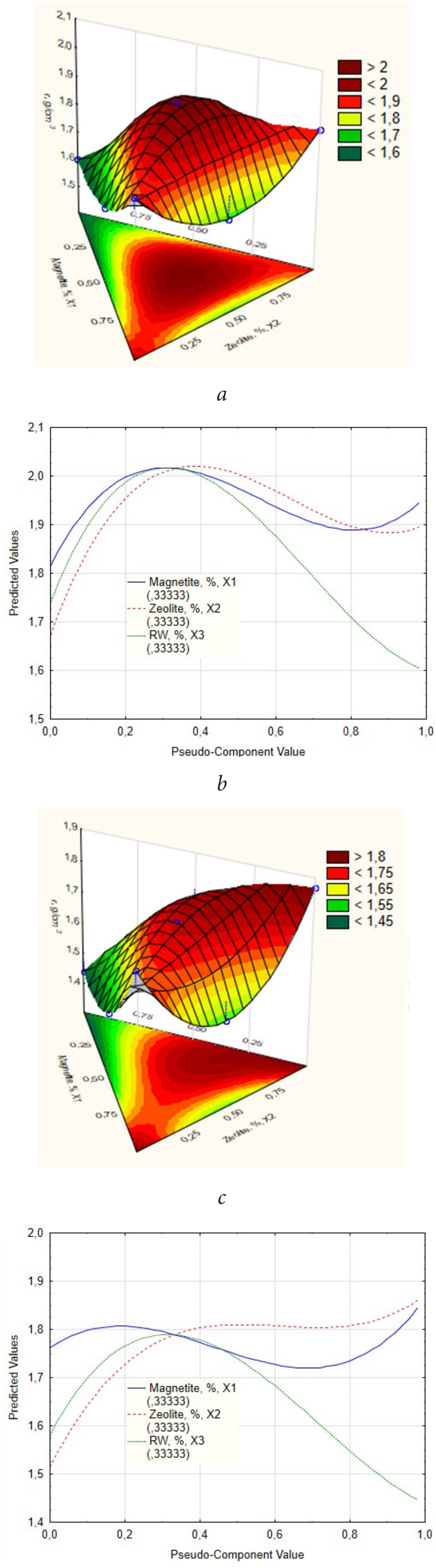


a

b

c

d



a

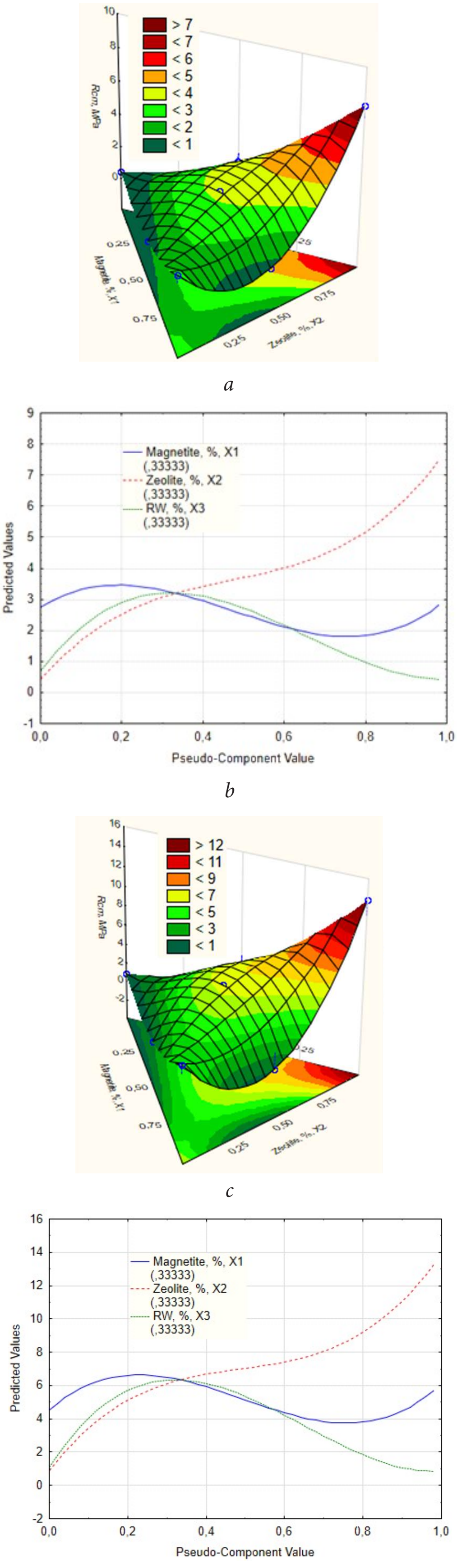
b

c

d

Fig. 1. Influence of variable factors on the change in mass (g) of composites on response surfaces with the expected responses after curing: *a*, *b* – 7 day; *c*, *d* – 28 day

Fig. 2. Influence of variable factors on the change in density (g/cm^3) of composites on response surfaces with the expected responses after curing: *a*, *b* – 7 day; *c*, *d* – 28 day



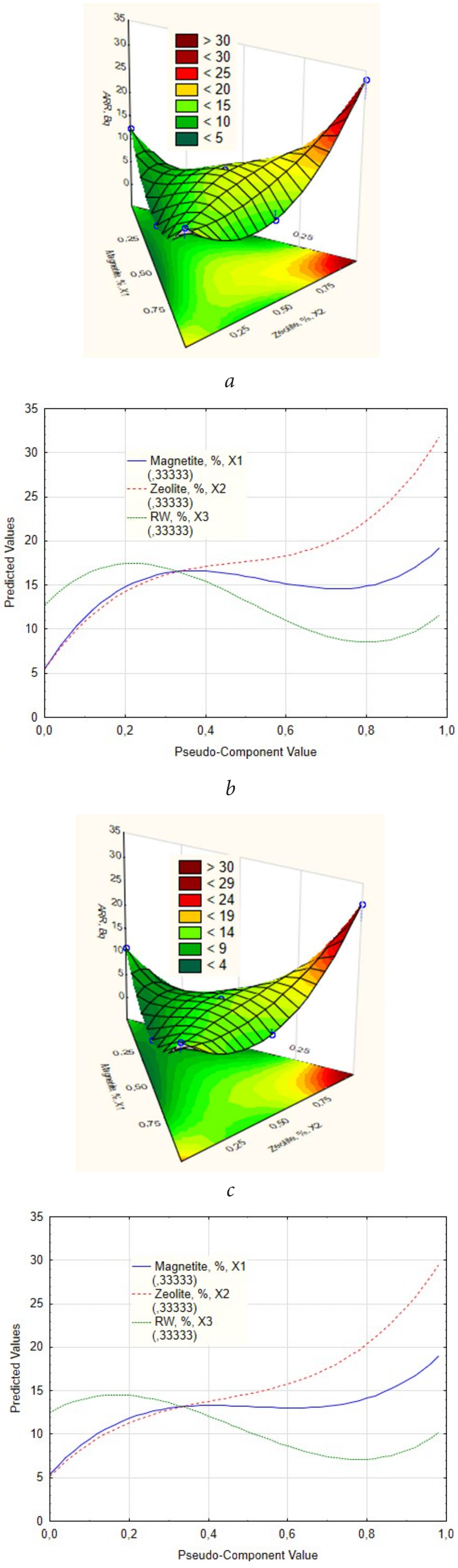
a

b

c

d

Fig. 3. Influence of variable factors on the change in compressive strength (MPa) of composites on response surfaces with expected reactions after curing: *a*, *b* – 7 day; *c, d* – 28 day



a

b

c

d

Fig. 4. Influence of variable factors on the change in radiation activity (*Bq*) of composites on response surfaces with expected reactions after curing: *a*, *b* – 7 day; *c, d* – 28 day

4. Discussion and scope of application

The analysis of regression equations (1), (2) shows that the varied factors are significant for the change in the weight of the compounds both on day 7 of curing and on day 28, with the most significant effect of $x1$ and $x2$, which is confirmed by the expected responses shown in **Fig. 1, *b*, *d***. The isoparametric surfaces are similar but differ in numerical values (**Fig. 1, *a*, *c***). Regardless of the influence of the factors, on average, the weight of the composites on the 28th day of curing decreases by 1.07 times compared to the 7th day (**Table 3**).

The analysis of regression equations (3), (4) shows that the varied factors are significant for changing the density of the compositions both on the 7th day of curing and on the 28th day, with the most significant effect being exerted by $x1$ and $x2$, which is confirmed by the expected responses shown in **Fig. 2, *b*, *d***. The isoparametric surfaces are similar but differ in numerical values (**Fig. 2, *a*, *c***). The maximum density value (2.016 g/cm^3) is characteristic of a compound containing 8.3 wt. % magnetite, 4.2 wt. % zeolite, and 15 wt. % radioactive waste. On the 28th day of solidification, the isolines of the maximum values of the densities of the compositions (1.867 g/cm^3) shift to the region containing 10 wt. % magnetite, 10 wt. % zeolite and 17.5 wt. % radioactive waste. In general, the densities of the compounds decrease by 1.07 times compared to day 7 (**Table 3**).

Analysis of the regression equations (5), (6) shows that the varied factors are significant for the change in compressive strength both on the 7th day of curing and on the 28th day, with the most significant effect being exerted by factor $x2$, which is confirmed by the expected responses shown in **Fig. 3, *b*, *d***. The isoparametric surfaces are similar but differ in numerical values (**Fig. 3, *a*, *c***). The maximum value of compressive strength at 7 days of curing – 7.8 MPa, and at 28 days – 13.2 MPa is characteristic of the compound containing 15 wt. % magnetite, 7.5 wt. % zeolite, and 10 wt. % radioactive waste. In general, the compressive strength of the composites increased by 1.87 times compared to day 7 (**Table 3**).

The analysis of regression equations (7), (8) shows that the varied factors are significant for the change in radiation activity values both on the 7th day of curing and on the 28th day, with the most significant effect being exerted by factor $x2$, which is confirmed by the expected responses shown in **Fig. 4, *b*, *d***. The isoparametric surfaces are similar but differ in numerical values (**Fig. 4, *a*, *b***). The maximum radiation activity values of 31.49 and 29.06 Bq, respectively, are characteristic of a compound containing 15 wt. % magnetite, 7.5 wt. % zeolite, and 10 wt. % of radioactive waste. In general, the values of radiation activity of the compounds decrease by 1.09 times compared to the 7th day (**Table 3**).

The processes occurring in the volume of compounds explain the decrease in mass, density and radiation activity of the compounds. The energy released during the radioactive decay of cesium, strontium and other radionuclides absorbed by magnetite and converted to heat [15]. Heat promotes the removal of both physically bound and partially chemically bound water from the structure of tobermorite-like low-basic calcium hydrosilicates, hydrogranates and alkaline-alkaline-earth zeolite-type hydrous aluminosilicates, as well as from the hydrate shell of copper ferrocyanide. This assumption is confirmed by the data of [16, 17].

5. Conclusions

As a result of optimization of a compound based on alkali-activated slag-portland cement, the areas of existence of compositions containing magnetite in the amount of 14...15 wt. % (factor $X1$), zeolite in the amount of 6.5...7.5 wt. % (factor $x2$) and dry radioactive waste based on copper ferrocyanide in the amount of 10...12 wt. % (factor $x3$), which allow obtaining an artificial stone with a compressive strength of 13.2 MPa on the 28th day of hardening, which meets the requirements of the regulatory level. It has been shown that the priority factor affecting the indicators of changes in mass, compressive strength density and radiation activity of composites is the addition of zeolite, which contributes to the formation of alkaline-alkaline-earth hydroalumina of zeolite-like type in the binder, which, in turn, contribute to a decrease in the intensity of β-radiation from copper ferrocyanide-based waste. The presence of magnetite in the composition of the compound contributes to the scattering of γ-radiation from cesium ions. The presence of hydrosilicate and hydroalumino silicate compounds in alkaline slag Portland cement curing products helps to reduce heat release from radionuclide decay.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

Financing

The work we carried out within the framework of the contractual topic at the State Institution Institute of Environmental Geochemistry of the National Academy of Sciences of Ukraine No. 001/2023-d of 23.03.23 “Scientific support of research using PLASMA-SORB technology for the processing of liquid radioactive waste”.

Data availability

Manuscript has no associated data.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

Acknowledgements

The authors would like to thank PhD Vladimir Burtnyak, Senior Researcher at the State Institute “Institute of Environmental Geochemistry” of National Academy of Sciences of Ukraine, for his assistance in measuring the radiation activity of compound samples.

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Received date 11.09.2023
Accepted date 14.11.2023
Published date 29.11.2023

How to cite: *Guzii, S., Zlobenko, B. (2023). Application of alkali-activated cements for immobilization of dry low-level radioactive waste containing copper ferrocyanide. Technology transfer: fundamental principles and innovative technical solutions, 3–8. doi: https://doi.org/10.21303/2585-6847.2023.003200*