

## CHEMICAL STABILITY AND STRUCTURAL CHARACTERISTICS OF CEMENT COMPOUNDS WITH RADWASTE SIMULATORS AFTER IONIZING RADIATION EXPOSURE

A. A. Zherebtsov,<sup>1</sup> V. V. Kapustin,<sup>2</sup> G. A. Varlakova,<sup>2</sup> A. P. Varlakov,<sup>2</sup>  
V. G. Petrov,<sup>3</sup> I. E. Vlasova,<sup>3</sup> I. D. Kharitonov,<sup>3</sup> and S. N. Kalmykov<sup>3</sup>

UDC 621.039.73

*The chemical and structural properties of cement compounds, containing radwaste simulators, after exposure to  $\gamma$ -radiation and electrons to absorbed dose 100 MGy are examined. It is shown that the phase composition and surface morphology of samples of cement compounds do not change much and the chemical stability remains satisfactory.*

For purposes of disposal, radioactive wastes must be put into a stable form – confined in a matrix. The matrix must possess high mechanical, chemical, and radiation stability and the technical process of obtaining the matrix with wastes must be reliable, simple, and economically acceptable. Of the simulated solidification technologies, cementation meets the indicated requirements.

Comprehensive studies of the mechanical properties, phase composition, and microstructure have shown that cement matrices are capable of maintaining the physicomaterial characteristics for doses up to 100 MGy [1–4]. It has been suggested that the influence of  $\gamma$ -radiation at irradiation dose to 10 GGy on the mechanical properties of a solidified compound can be neglected [5]. However, studies of irradiated samples revealed microcracks caused by  $\gamma$ -radiation up to 100 MGy [6]. As is well-known, cracking makes the matrix less stable in a water medium and increases the yield of radionuclides.

The purpose of the present work is to investigate the effect of different types of ionizing radiation on cement compounds containing a simulator of liquid high-level nitrate-containing wastes. To this end, the phase composition, surface morphology, and chemical stability of cement compounds after exposure to electronic and gamma radiation were studied.

Cement compounds prepared from TsEM I 42,5B Portland cement with or without the addition of PBM-V bentonite clay powder served as the objects of study. The water-to-cement ratio (W/C) was equal to 0.5. The bentonite clay powder was taken into account in the overall mass of the binder in the amount 5 wt.%. Tap water and the simulator of nitrate-containing high-level waste with salt content about 530 g/liter, corresponding to the average composition of the waste from the Mayak Association, was used as the grouting fluid (Table 1) [7].

The cement samples were irradiated in a <sup>60</sup>Co  $\gamma$ -chamber to absorbed doses 1, 10, and 100 MGy and in a UELV-10-10-S-70 linear electron accelerator with the following parameters: energy 8 MeV, pulse width 6  $\mu$ sec, pulse repetition frequency 300 Hz, average beam current  $\leq 800 \mu$ A, sweep width 245 mm, and sweep frequency 1 Hz. The dose rate depending on the passage time of the sample through the electron beam was equal to 1.2 kGy/sec on average.

The chemical stability of the cement compounds was evaluated by determining the leach rate of radionuclides by the standard method under static conditions in a thermostat at 25°C [8]. Deionized water with conductivity 18 M $\Omega$ /cm was used as the leaching medium. To determine the leach rate of plutonium, <sup>239</sup>Pu in the form of a nitric acid solution was introduced into the grouting fluid. To prevent the solution from affecting the pH of the grouting fluid, aliquots of the <sup>239</sup>Pu solution were pre-evaporated to wet salts and diluted with water. A Tri-Carb 2810T (USA) liquid scintillation spectrometer was used

<sup>1</sup> Innovation-Technology Center for Project Breakthrough (ITTsP Proryv), Moscow, Russia.

<sup>2</sup> Bochvar High-Technology Research Institute of Inorganic Materials (VNIINM), Moscow, Russia; e-mail: vitkap1990@gmail.com.

<sup>3</sup> Lomonosov Moscow State University, Moscow, Russia.

TABLE 1. Composition of Cement Compound W/C = 0.5

Composition No.	Binder	Additive	Grouting fluid
1	Portland cement	–	Water
2		Bentonite clay powder	
3		–	Simulator
4		Bentonite clay powder	

Simulator composition, g/liter: NaOH 196.8, NaNO<sub>3</sub> 209.1, NaNO<sub>2</sub> 108.1, NaHCO<sub>3</sub> 17.64, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> 10.82, KCl 1.47, Zn(NO<sub>3</sub>)<sub>2</sub> 0.02, Pb(NO<sub>3</sub>)<sub>2</sub> 0.07, CsCl 0.05, SrCl<sub>2</sub> 0.5.

TABLE 2. Leaching of Radionuclides on the 28th Day from Unirradiated Cement Compounds, g/(cm<sup>2</sup>·day)

Composition No.	<sup>137</sup> Cs	<sup>90</sup> Sr	<sup>239</sup> Pu
1	7.1·10 <sup>-5</sup>	9.7·10 <sup>-6</sup>	3.1·10 <sup>-6</sup>
2	5.6·10 <sup>-5</sup>	8.4·10 <sup>-5</sup>	1.9·10 <sup>-6</sup>
3	2.2·10 <sup>-4</sup>	4.5·10 <sup>-5</sup>	5.8·10 <sup>-6</sup>
4	8.3·10 <sup>-5</sup>	2.7·10 <sup>-5</sup>	4.1·10 <sup>-6</sup>

TABLE 3. Leaching of Radionuclides on the 28th Day from Irradiated Cement Compounds, g/(cm<sup>2</sup>·day)

Composition No.	Irradiation dose, MGy	<sup>137</sup> Cs	<sup>90</sup> Sr	<sup>239</sup> Pu
1	100 (electrons)	4.4·10 <sup>-5</sup>	8.2·10 <sup>-6</sup>	1.2·10 <sup>-6</sup>
	100 (γ)	2.9·10 <sup>-5</sup>	4.3·10 <sup>-6</sup>	8.5·10 <sup>-7</sup>
3	100 (electrons)	7.0·10 <sup>-5</sup>	1.5·10 <sup>-5</sup>	8.6·10 <sup>-6</sup>
	100 (γ)	9.1·10 <sup>-5</sup>	8.3·10 <sup>-6</sup>	1.2·10 <sup>-7</sup>

to measure the content of <sup>239</sup>Pu in the leaching waters; mass-spectrometry with inductively coupled plasma (Agilent 7500, USA) was used to measure the leaching of cesium and strontium. An Ultima-IV diffractometer (Japan) was used to perform x-ray phase analysis. The working regime of the diffractometer was: 40 kV, 40 mA, CuK<sub>α</sub> radiation, nickel filter, 2θ measurement range 2–80° with scan angle step 0.02°. A JSM 6380 LA scanning electron microscope (Japan) was used to study the surface morphology of the samples in secondary electrons, using preparations in the form of a thin section with a gold coating.

The leach rate, equated with the quality criteria [4], was taken to be the value obtained on the 28th day of testing – the yield of radionuclides owing to diffusion and not washing-off of the surface of the samples. It follows from Table 2 that the cement samples 2 and 4 with bentonite clay added are characterized by a lower (to 30%) leach rate of cesium, strontium, and plutonium. The cesium leach rate reduction is especially noticeable.

The primary component of bentonite is montmorillonite, which is a smectic mineral. It possesses a layered structure, in which sodium, calcium, or magnesium cations, located in the interlayer space, can be replaced by cesium or strontium cations by means of ion-exchange. This results in high sorption of metal cations (especially cesium) on bentonites [9, 10]. From the samples 3 and 4 with high-level waste simulator the leachrate of cesium, strontium, and plutonium is higher but does not exceed the quality criteria in terms of cesium 10<sup>-3</sup> g/(cm<sup>2</sup>·day).

We can see in Fig. 1 and Table 3 that the leaching of radionuclides from cement samples corresponds to the following mechanism: on the initial days the elements/radionuclides are washed from the surface of the samples and subsequently removed by diffusion.

The rate of leaching from irradiated samples is lower than from unirradiated samples. An increase of mechanical strength and other properties of cement compounds as a result of radiation strengthening was noted in [11]. It can be supposed that under irradiation the porosity decreases and the structure of the pores changes, which promotes an increase of strength,

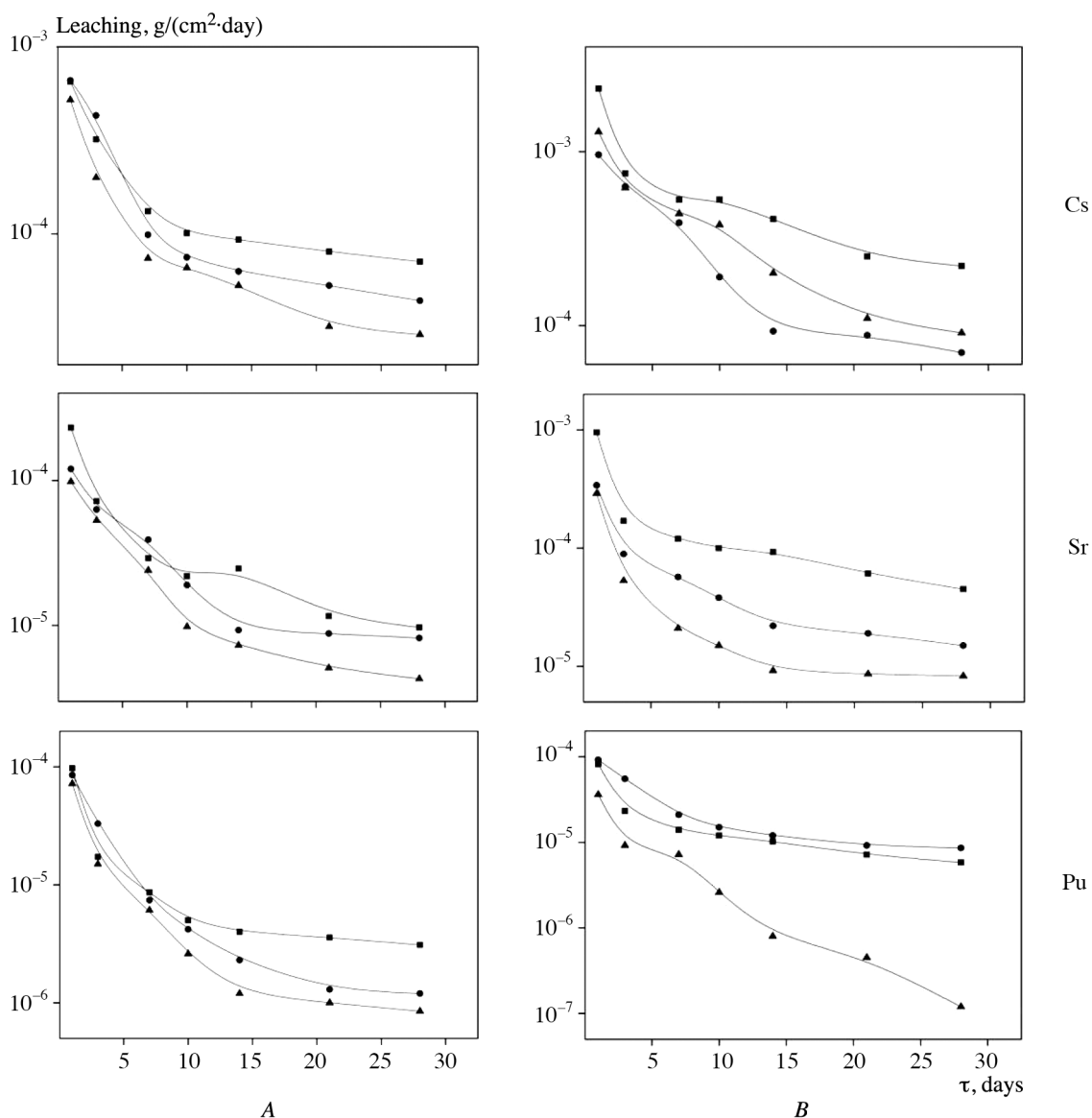


Fig. 1. Leaching of cesium, strontium, and plutonium from samples of cement compounds with composition 1 (A) and 3 (B) before (■) and after irradiation by electrons (●) and  $\gamma$ -rays (▲) to absorbed dose 100 MGy.

reduction of diffusion of radionuclides in cement stone, and escape from the matrix [1, 2]. On the whole, the leach rate does not exceed the normative maximum value for cemented radioactive wastes [4].

The primary phases characteristic of cement stone at the early as well as later hydration times were identified in samples by x-ray phase analysis of cement compounds 1, 3 before and after irradiation up to 100 MGy: alite (tricalcium silicate)  $3\text{CaO}\cdot\text{SiO}_2$ , belite (dicalcium silicate)  $2\text{CaO}\cdot\text{SiO}_2$ ,  $2\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$ , as well as portlandite  $\text{Ca}(\text{OH})_2$ , calcium carbonate  $\text{CaCO}_3$  and different phases of mixed aluminum-calcium silicate, specifically,  $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$  and  $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot 2\text{H}_2\text{O}$ . In sample 3, aside from the primary phases, phases corresponding in terms of composition to nitrate  $\text{NaNO}_3$ , silicate  $\text{Na}_2\text{Si}_2\text{O}_5$ , sodium aluminum silicate  $\text{NaAlSiO}_4$ , and potassium chromate  $\text{K}_2\text{CrO}_4$  were found. Their appearance could be due to the composition of the high-level waste simulator. The x-ray diffraction patterns of samples do not differ from the x-ray diffraction patterns of the honor radiated samples. Probably, the crystallographic phases of the early stages of hydration are capable of withstanding the exposure to ionizing radiation. This corresponds to observations of similar systems in different ages of hardening of the cement stone [11].

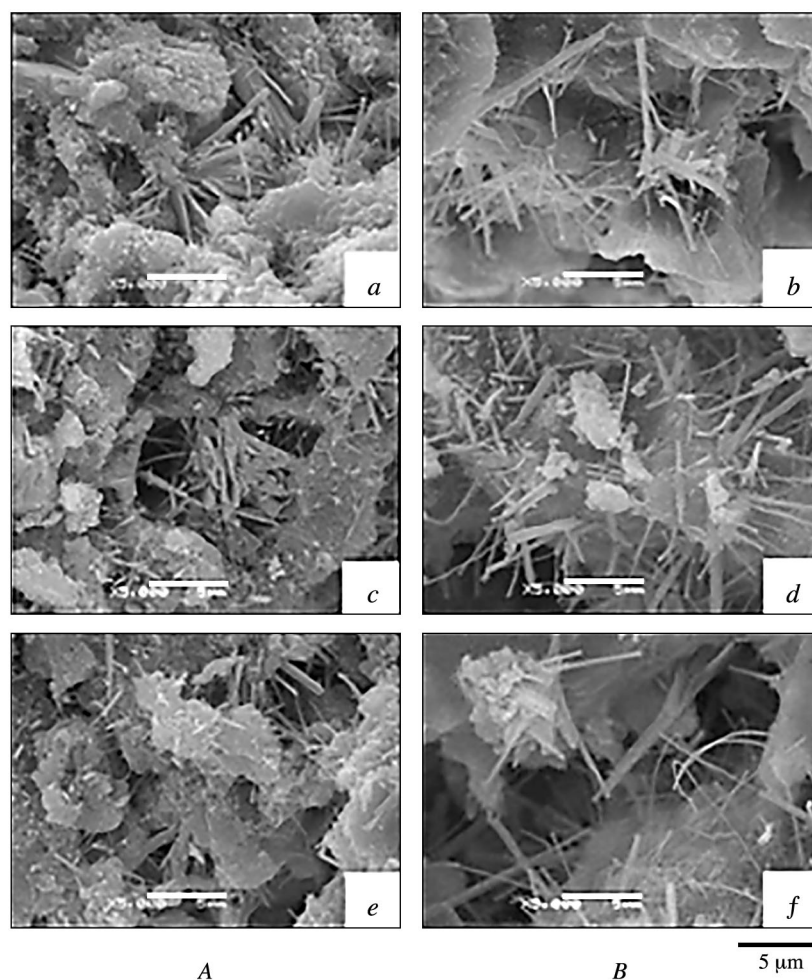


Fig. 2. Scanning electron microscopy of samples of cement compound with composition 1 (A) and 3 (B) before (*a, b*) and after irradiation by electrons (*c, d*) and  $\gamma$ -rays (*e, f*) up to absorbed dose 100 MGy (see Fig. 1) ( $\times 5000$ ).

We can see in Fig. 2 that the microstructure is characterized by alternation of needle crystals approximately 1.5–2  $\mu\text{m}$  in length and large aggregates 5–30  $\mu\text{m}$  in size; individual plate-shaped crystallites are also observed. Pores can be seen between the crystalline formations; the pore size is comparable to 1.5–3  $\mu\text{m}$  needle crystals. The sizes and shapes of the crystals and the sizes and number of pores in unirradiated samples do not differ from irradiated samples. Irradiated samples have no new formations or defects in the form of microcracks and channels. No changes of the microstructure and morphology of samples of cement compounds as a result of exposure to  $\gamma$ -radiation or electrons were observed. Analysis of studies shows a correlation between the rate of leaching radionuclides from cement compounds and their microstructure and phase composition.

In summary, photomicrographs of samples, data from x-ray phase analysis, and leaching of radionuclides do not show structural changes of cement stone at the micro-level. The structure and phase composition do not change under irradiation of cement compounds with high-level waste simulators up to absorbed dose 100 MGy. The addition of bentonite clay promotes reduction of the leaching of radionuclides. The maximum rate of leaching does not exceed  $10^{-4}$  g/(cm<sup>2</sup>·day) for cesium for almost all samples, including irradiated samples, and  $10^{-5}$  g/(cm<sup>2</sup>·day) for strontium and plutonium.

## REFERENCES

1. A. P. Varlakov, V. V. Kapustin, G. A. Varlakova, et al., “Effect of radiation loads characteristic of high-level radwaste on the properties of a cement matrix,” *Radioakt. Otkh.*, No. 1(2), 89–96 (2018).

2. A. P. Varlakov, A. A. Stallions, V. G. Petrov, et al., "The behavior of the cement matrix under radiation loads," *Vopr. Rad. Bezopasn.*, No. 3, 13–20 (2018).
3. A. Varlakov, A. Zherebtsov, V. Kapustin, et al., "Characteristics of cement compounds after irradiation up to doses typical for high level radioactive waste," in: *3rd Int. Symp. on Cement-Based Materials for Nuclear Waste, NUWCEM 2018*, Avignon, France, Oct. 24–26, 2018, p. 103.
4. GOST R 51883-2002, *Cemented Radioactive Wastes: General Technical Requirements*, Izd. Standartov, Moscow (2002).
5. J. Pachner, *Assessment and Management of Ageing of Major Nuclear Power Plant Components Important to Safety: Concrete Containment Buildings*, IAEA-TECDOC-1025, IAEA, Vienna (1998).
6. Y. Kitsutaka and K. Matsuzawa, "The effect of gamma radiation on the fracture properties of concrete," in: *Fracture Mechanics of Concrete and Concrete Structures – Recent Advances in Fracture Mechanics of Concrete*, Korea Concrete Institute, Seoul, May 23–28, 2010, pp. 61–64.
7. S. E. Vinokurov, Yu. M. Kulyako, O. M. Slyuntchev, et al., "Low-temperature immobilization of actinides and other components of high-level waste in magnesium potassium phosphate matrices," *Nucl. Mater.*, **385**, 189–192 (2009).
8. GOST R 52126-2003, *Radioactive Wastes: Determination of the Chemical Stability of Solidified High-Level Waste by Continuous Leaching*, Izd. Standartov, Moscow (2003).
9. M. N. Sabodina, S. N. Kalmykov, Yu. A. Sapozhnikov, et al., "Neptunium, plutonium and <sup>137</sup>Cs sorption by bentonite clays and their speciation in pore waters," *Radioanal. Nucl. Chem.*, **270**, 349–355 (2006).
10. S. A. Khan, "Sorption of the long-lived radionuclides cesium-134, strontium-85 and cobalt-60 on bentonite," *Radioanal. Nucl. Chem.*, **258**, 3–6 (2003).
11. N. Mobasher, S. A. Bernal, H Kinoshita, et al., "Gamma irradiation resistance of an early age slag-based cement matrix for nuclear waste encapsulation," *Mater. Res.*, **30**, No. 9, 1563–1571 (2015).