

Radionuclides in Irradiated Graphite of Uranium–Graphite Reactors: Decontamination of Sleeves Using Liquid Reagents

A. G. Volkova^a, E. V. Zakharova^a, A. O. Pavlyuk^b, and A. A. Shiryayev^{*a}

^a *Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninskii pr. 31, korp. 4, Moscow, 119071 Russia*

^b *Experimental and Demonstration Center for Decommissioning of Uranium–Graphite Reactors, P.O. Box 654, Seversk, Tomsk oblast, 636000 Russia*

**e-mail: shiryayev@phyche.ac.ru, a_shiryayev@mail.ru*

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Abstract—To examine the possibility of disposal of irradiated graphite in ground near-surface repositories, the concentration and spatial distribution of radionuclides in the volume of irradiated graphite sleeves of industrial uranium–graphite reactors was studied, and the efficiency of decontamination using liquid reagent treatment methods was evaluated. The radionuclide distribution in the graphite volume is extremely heterogeneous on the 10–100 μm scale. The degree of decontamination using solutions with high acid concentrations and fluoride ions added does not exceed 16–25% for ¹⁴C and 15–19% for ³⁶Cl. Under these treatment conditions, no structural changes occur in graphite, and ¹⁴C bound with the graphite surface via sorption is removed. Significant differences in the efficiency of the reagent decontamination of irradiated graphite from various producers were revealed.

Keywords: uranium–graphite reactors, irradiated graphite, decontamination

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The problem of irradiated graphite management becomes more and more acute in the Russian Federation and other countries because of large volumes accumulated (more than 250 000 t throughout the world) and need for decommissioning the operating uranium–graphite reactors in the foreseeable future. The ways to solve this problem depend on the level of contamination of the graphite stack parts and on the strength of radionuclide fixation in graphite.

Graphite stack parts are subdivided into nonremovable (blocks, operation time more than 30 years) and removable. In industrial uranium–graphite reactors (IUGRs), the removable parts are sleeves, which were usually replaced every 2–3 years and delivered into near-reactor repositories of various types. However, in some cells of the graphite stack the sleeves functioned in the reactor for 10 years and more. These sleeves functioned for a long time in the final periods of the reactor operation and were not removed after the IUGR decommissioning. The graphite weight in sleeves is high; for example, for three IUGRs it is comparable with the graphite stack weight in one reac-

tor. Bushuev et al. [1] estimated the mean specific activity of radionuclides in spent IUGR graphite sleeves transferred into near-reactor repositories and in the sleeves remaining in the stack of shutdown reactors. The content of neutron activation products, ¹⁴C and ⁶⁰Co, in the sleeve graphite stored in a repository is lower, which is caused by different operation times. Incidents in the course of reactor operation led to contamination of block and sleeve graphite with fission products and actinides [2–5]; the contamination level depends on the character of the accidents.

Various approaches to irradiated graphite management are considered today: incineration, ¹²C/¹⁴C isotope separation and subsequent commercial use of ¹⁴C or immobilization in a carbonate phase, reuse of the irradiated graphite in the nuclear field, and near-surface or deep disposal [6–9]. In accordance with the activity level classification valid in Russia, irradiated block graphite belongs to class 2, with ¹⁴C making the major contribution to its activity (10⁵–10⁶ Bq g⁻¹) [2]. The waste of such activity level should be disposed of in deep repositories. Because the content of ¹⁴C in the

bulk of sleeve graphite is lower, it is interesting to examine the possibility of decreasing its activity to the level corresponding to class 3. Such waste can be disposed of in ground near-surface repositories, which is considerably cheaper. Available data [10, 11] demonstrate the possibility of recovering fission and activation products from irradiated graphite from various European reactors by treatment with solutions of various compositions (alkaline, acidic, containing oxidants). However, the set of radionuclides examined in these studies (^3H , ^{14}C , ^{55}Fe , ^{60}Co , ^{137}Cs , ^{154}Eu) did not include long-lived ^{36}Cl and actinides.

It should be taken into account that the properties of irradiated graphite and primarily the contamination mechanisms depend on the production technology and conditions of operation in a reactor. Therefore, it is very interesting to compare the efficiency of decontamination of irradiated graphite from different producers under the same conditions. In this work, we studied the radionuclide distribution in the volume of graphite sleeves from decommissioned Russian IUGRs and estimated the efficiency of decontamination of irradiated graphite using liquid reagent treatment methods suggested for European types of graphite reactors.

EXPERIMENTAL

Irradiated graphite samples were taken in 2014–2015 from sleeves stored in near-reactor repositories after 2-year operation in the reactor. These samples were located in the graphite stack both in the zones affected by incidents and beyond these zones. The samples were drillcores 8 mm in diameter, covering the whole cross section of the sleeve from the fuel channel to the external part. To determine the radionuclide content and distribution, the drillcore was cut into 2-mm-thick pellets. The spatial distribution of radionuclides in drillcore samples was studied by digital autoradiography using a Cyclon Plus scanner (Perkin Elmer) and imaging plates allowing the spatial distribution of radiation sources (α , β , γ) to be determined with 42 μm resolution (see, e.g., [12]).

To perform decontamination experiments, the drillcores were milled and the sample was averaged. Solutions containing acids, alkali, oxidant, and mixtures of acids with fluoride ions were used for decontamination. Some of the experiments performed allow comparison of the decontamination efficiency for sleeve graphite from IUGR and a number of European reac-

tors [10]. In the next step, we used more aggressive solutions traditionally used in the practice of liquid decontamination [13, 14]. The experiment time was 30 days at $22 \pm 5^\circ\text{C}$ and 12 h at $95 \pm 3^\circ\text{C}$. To estimate the degree of decontamination, we used data on the radionuclide content in an averaged sample (Bq g^{-1}): ^{137}Cs 1.5×10^2 , ^{60}Co 2.4×10^3 , ^{241}Am 17.6, ^{239}Pu 51.8, ^{238}U 5.85, ^{90}Sr 3.3, ^{14}C 4.4×10^4 , and ^{36}Cl 1.5×10^2 .

The reactor operation and the stack dismantling in the course of decommissioning are often accompanied by mechanical disintegration of graphite blocks (cracking, powdering, etc.), leading to the formation of large volumes of finely dispersed graphite. It was interesting to evaluate the behavior of such graphite in the course of decontamination. Therefore, all the decontamination experiments were also performed with milled graphite (particle size smaller than 0.2 mm), which also allows evaluation of the influence exerted by the area of contact of the contaminated surface with the solution.

The content of ^{14}C , ^{36}Cl , and ^{90}Sr was determined by liquid scintillation spectrometry (Tri-Carb-3180 TR/SL). We determined the actinide content using preconcentration, separation, and measurement with an Alpha-Aria low-background α -ray spectrometer (AMETEK). The content of γ -emitting radionuclides was determined with a γ -ray spectrometer with a high-purity germanium detector (Packard, Ortec).

RESULTS AND DISCUSSION

Prior to decontamination experiments, we estimated the volume distribution and activity concentration of radionuclides in sleeve graphite samples (Table 1, Fig. 1) from cells affected and not affected by incidents. As expected, the activity concentrations of ^{60}Co , ^{137}Cs ,

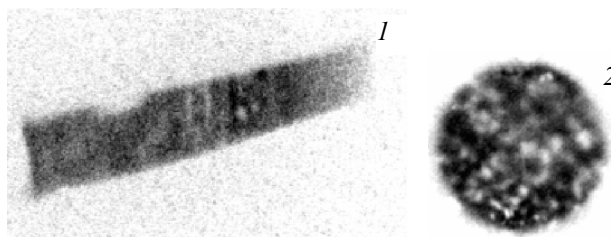


Fig. 1. Autoradiographic images of sleeve graphite samples. Activity distribution (1) along and (2) and across the drillcore is shown. Drillcore length 5 cm, cylinder diameter 8 mm. The blackening intensity is proportional to the integral activity.

Table 1. Radionuclide activity distribution (Bq g⁻¹) in sleeve graphite samples along the drillcore

Cell	Sample position relative to the channel	Radionuclide									
		¹⁴ C (× 10 ⁻⁴)	³⁶ Cl (× 10 ⁻³)	⁶⁰ Co (× 10 ⁻²)	¹³⁷ Cs (× 10 ⁻²)	⁹⁰ Sr	²³⁷ Np	ΣPu	ΣU	²⁴¹ Am	²⁴⁴ Cm
Normal	Inner	6.8 ± 0.8	1.8 ± 0.2	1.1 ± 0.07	0.19 ± 0.02	5.2 ± 0.6	1.1 ± 0.2	12.4 ± 1.3	4.6 ± 0.7	6.2 ± 0.9	0.8 ± 0.1
	Middle	3.1 ± 0.4	1.9 ± 0.2	0.65 ± 0.06	0.12 ± 0.01	<0.01	1.2 ± 0.2	11.3 ± 1.2	0.9 ± 0.1	<0.01	<0.01
	Outer	6.5 ± 0.7	2.4 ± 0.3	0.76 ± 0.07	0.21 ± 0.02	1.2 ± 0.2	1.9 ± 0.2	14.7 ± 1.6	3.6 ± 0.5	5.5 ± 0.8	0.9 ± 0.1
Emergency	Inner	8.5 ± 0.9	2.1 ± 0.3	54.0 ± 2.2	3.1 ± 0.2	3.8 ± 0.4	4.3 ± 0.5	57 ± 6	6.3 ± 0.9	25.4 ± 2.7	1.2 ± 0.2
	Middle	6.2 ± 0.7	1.6 ± 0.2	3.8 ± 0.2	0.87 ± 0.05	<0.01	6.1 ± 0.7	45 ± 5	6.7 ± 0.9	11.8 ± 1.4	0.8 ± 0.1
	Outer	7.5 ± 0.8	2.5 ± 0.3	23.2 ± 1.1	1.3 ± 0.1	4.1 ± 0.5	6.9 ± 0.7	59 ± 7	7.8 ± 1.0	18.9 ± 2.2	0.9 ± 0.1

Table 2. Degree of decontamination of irradiated graphite (%) in relation to processing conditions

Solution	Experiment conditions	Radionuclide						
		¹³⁷ Cs	⁶⁰ Co	²⁴¹ Am	²³⁹ Pu	²³⁸ U	³⁶ Cl	¹⁴ C
6 M HCl + 0.06–0.2 M (NH ₄) ₂ F ₂	30 days, 22 ± 3°C	22.9–35.5	53.8–78.2	71.8–80.2	2.1–12.4	1.0–10.2	15.6–18.5	16.3–20.2
	12 h, 95 ± 3°C	34.7–49.5	65.0–72.2	61.9–79.2	29.7–38.9	8.5–13.3	17.5–19.1	19.4–25.8
7.5 M HNO ₃ + 0.06–0.2 M (NH ₄) ₂ F ₂	30 days, 22 ± 3°C	26.4–40.1	58.7–68.2	74.5–83.1	2.5–6.3	1.2–12.4	16.3–19.1	16.7–18.6
	12 h, 95 ± 3°C	36.8–41.5	55.6–80.2	66.7–76.3	41.8–50.1	10.6–15.1	16.4–18.6	20.1–24.2

²⁴¹Am, and Pu isotopes are somewhat higher in graphite from the incident zone. The content of ¹⁴C and ³⁶Cl varies along the drillcore insignificantly. The content of fission products and actinides in some cases is lower in samples from the middle part of the drillcore, but no statistical relationships can be revealed.

Data of digital autoradiography of the drillcores from sleeve graphite confirm the bulk contamination. On the other hand, autoradiography reveals significant heterogeneities in the spatial distribution of radionuclides on the scale of hundreds of micrometers: Chaotic alternation of domains with significantly different (by a factor of 4–10) activity is observed (Fig. 1). Such behavior of characteristic of all the studied samples of block and sleeve graphite, irrespective of their total activity, reactor from which they were taken, and position in the stack in the course of operation. The results agree with those published previously for graphite from European reactors (see, e.g., [15]).

In the first step of the studies, the conditions for treatment of irradiated graphite were close to those given in [10]: 2.5 M H₂O₂, 5 M NaOH, and 1–2 M acid (H₃PO₄, HCl, HNO₃) solutions at 22 ± 3°C were used. The efficiency of the decontamination of sleeve graphite samples is minimal in solutions of H₂O₂ and alkali, is somewhat higher in acid solutions, but, on the whole, does not exceed 10%, including decontamina-

tion from ³⁶Cl and ¹⁴C. An increase in the HCl and HNO₃ concentrations and addition of fluoride ions lead to an increase in the degree of decontamination from ¹³⁷Cs, ⁶⁰Co, and ²⁴¹Am by nearly an order of magnitude, but no such effect is observed for ²³⁹Pu, ²³⁸U, and ⁹⁰Sr (Table 2). As compared to dilute solutions of the corresponding acids, the degree of removal of ³⁶Cl and ¹⁴C increases. An increase in the temperature only slightly influences this process, but the degree of removal of ²³⁹Pu and ²³⁸U somewhat increases, and the reaction time becomes shorter. An increase in the decontamination time at elevated temperature does not noticeably influence the efficiency of the ³⁶Cl and ¹⁴C removal. With finely dispersed graphite (particle size ~0.07 mm), no significant increase in the process efficiency was observed, but the statistics is limited in this case.

Figure 2 allows us to compare the performance of various solutions in removal of dose-producing long-lived (5730 and 3.01 × 10⁵ years, respectively) ¹⁴C and ³⁶Cl radionuclides mobile in natural systems. The difference between the IUGR graphite that we studied and graphite from Wilfa and BEPO reactors (the United Kingdom) in the liquid decontamination efficiency is worth noting. According to [10], up to 27% of ¹⁴C is removed by keeping finely divided Wilfa graphite at 23°C in 1 M H₃PO₄ (the leaching curve in [10] very rapidly flattened out), whereas no more than

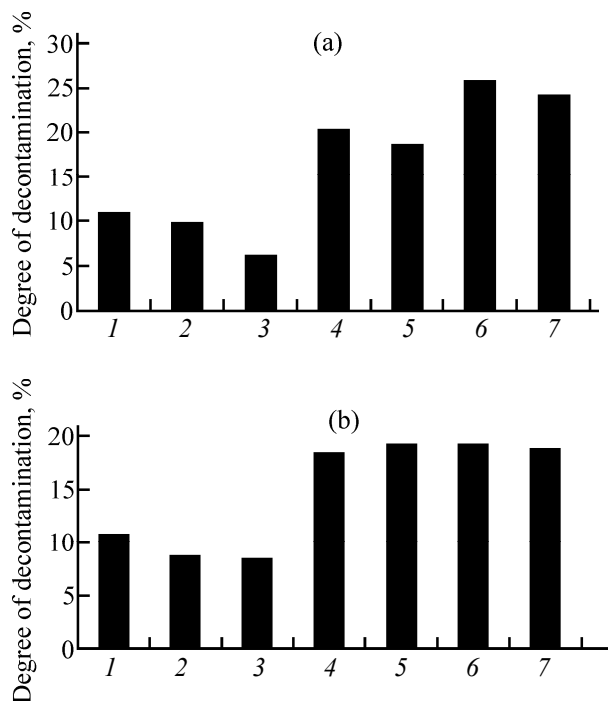


Fig. 2. Degree of decontamination of irradiated sleeve graphite from (a) ^{14}C and (b) ^{36}Cl as a function of the solution composition and treatment conditions: (1) 1 M HCl, (2) 1 M H_3PO_4 , (3) 2.5 M H_2O_2 , (4) 6 M HCl + $(\text{NH}_4)_2\text{F}_2$ at 22°C, (5) 7.5 M HNO_3 + $(\text{NH}_4)_2\text{F}_2$ at 22°C, (6) 6 M HCl + $(\text{NH}_4)_2\text{F}_2$ at 95°C, and (7) 7.5 M HNO_3 + $(\text{NH}_4)_2\text{F}_2$ at 95°C.

10% of ^{14}C was removed from IUGR graphite. Similar results were obtained when keeping the samples in concentrated (2.5 M) H_2O_2 : ~15% of ^{14}C was removed from BEPO graphite and only ~6%, from IUGR graphite. Such a significant difference is probably caused by differences in the microstructure and composition of carbon precursors (filler, binder) of graphites from different producers. Therefore, it is of crucial importance to study in detail different grades of graphite to obtain representative data significant for practice.

When using solutions with high acid concentrations and solutions containing F^- ions, the degree of decontamination from ^{14}C varies within 16–25%. An increase in the content of F^- ions somewhat intensifies the process. For ^{36}Cl , the degree of decontamination is lower (15–19%) and is mainly determined by the relative content of ^{36}Cl in graphite in the inorganic form, which is considerably lower compared to the organic form [16]. The kinetics of radionuclide removal with concentrated acid solutions containing F^- ions does not noticeably vary with time, which was also noted for Wilfa and BEPO graphites [10].

The treatment under our conditions does not involve structural changes in graphite and, correspondingly, does not lead to the removal of ^{14}C formed by activation of ^{13}C present in the natural isotope mixture, $^{13}\text{C}(n,\gamma)^{14}\text{C}$. One more source of ^{14}C is neutron activation of molecular nitrogen adsorbed on the pore surface from the purging gas in the course of reactor operation. The ^{14}C produced by this mechanism can be present in different forms, which is determined by the time of the gas–graphite interaction and by the possibility of nitrogen diffusion into graphite surface layers. Most probably, the decontamination methods that we used ensure predominant removal of surface-adsorbed ^{14}C . For all the sleeve graphite samples, its fraction is in the range 16–25%.

Thus, liquid reagent decontamination of sleeve graphite does not ensure the reduction of the activity of dose-determining ^{14}C to the level corresponding to class 3 and allowing near-surface disposal. However, taking into account individual properties of different irradiated graphite samples, it is necessary to evaluate the possibility of using this approach for reducing the activity of nonremovable and removable RBMK (high-power channel reactor) graphite parts in disassembling of the stack and near-reactor repositories and to obtain representative data significant for practice.

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