METHODS OF IRRADIATED GRAPHITE TREATMENT – CHARACTERISTIC PROPERTIES OF IRRADIATED GRAPHITE

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Abstract

The results of investigations of irradiated graphite waste treatment and decontamination processes are presented in this report. As the treatment methods – incineration of graphite in air flux and molten salt oxidation were studied; as the decontamination methods – molten salt oxidation, oxidation in air flux at different temperatures and oxidation in water vapor flux were studied. Experiments of graphite waste incineration in air flux were aimed at more precise definition of physical and chemical parameters of graphite incineration process and the off-gases composition. The process of graphite waste molten salt oxidation was investigated from the point of view of the prospective technology with many advantages such as its universality and possibility of receiving a solid durable final product suitable for the following conditioning. The decontamination processes were studied for estimation of a possibility of specific activity reduction in graphite waste for satisfaction of waste acceptance criteria for waste types intended for their disposal in near-surface disposal facilities.

1. INTRODUCTION

Uranium-graphite reactors (UGR) were used both for electric power production and for research purposes and as well as in military purposes – for plutonium production. During the period of 1948-1956, thirteen industrial UGR were built and commissioned in USSR and a part of them was for weapon-grade plutonium production and one intended for plutonium production along with the production of heat and electric power for industrial and household needs [1]. Later, for electric power production, RBMK (LWGR) type reactors were actively used. Altogether in the countries of the world there are more than a hundred nuclear reactors where graphite is used for moderating or reflecting of neutrons. In the Russian Federation today, most of the UGR reactors are shut down and subjected to decommissioning. However, some continue in operation (TABLE 1). By the time when all such reactors are stopped in 2030-2035, about 60 thousand tonnes of spent irradiated reactor graphite will have been accumulated in Russia and about 250 thousand tonnes in the world [2].

TABLE 1. UGR REACTORS SHUT DOWN AND IN OPERATION IN THE RUSSIAN FEDERATION

Site	No of reactors	Type	Status
FSUE IS «Mayak»	5	Industrial (A, AI, AB)	Shut down
JSC «SHK»	5	Industrial (I, EI, ADE)	Shut down
FSUE «GHK»	3	Industrial (AD, ADE)	Shut down
Beloyarsk NPP	2	Energetic(AMB)	Shut down
Bilibinsk NPP	4	Energetic (EGP)	In operation
Kursk NPP	4	Energetic (RBMK)	In operation
Leningrad NPP	4	Energetic (RBMK)	In operation
Smolensk NPP	3	Energetic (RBMK)	In operation

According to the Industrial Conception of State Corporation "Rosatom" for decommissioning of nuclear- and radiation dangerous objects the following basic options for decommissioning are possible for UGR reactors:

1) **Liquidation of UGR** (with a sub-option of interim storage during 50-100 years on site): dismantling of graphite stack, graphite packaging, interim storage, conditioning and disposal (the most acceptable for the reactors of NPPs JSC "Rosenergoatom sites";

2) **Disposal of UGR** (retention as isolated intact reactor on site): without dismantling of graphite stacks but with retrieval of graphite contaminated with nuclear fuel (this variant is being considered now for industrial UGR) [2].

JSC "ODC UGR" (Pilot Demonstration Center of UGR-type nuclear reactors decommissioning) was established in February 2011 to design and demonstrate these decommissioning options. This center was created on the basis of Reactor Plant JSC "Siberian Chemical Plant" ("SHK") with the purpose of providing serial decommissioning of UGR-type reactors based on technologies suitable for replication at other plants and for export [3]. So far, specialists from this organization together with the specialists from JSC "N.A. Dollezhal NIKIET" have developed the conceptions of decommissioning for units I-1 and EI-2 at JSC "SHK" (Siberian Chemical Plant) according to the option of safety disposal on site. It was also proved by them that this option of decommissioning is preferable for such type of reactors. The technology of creation of protective clay barriers preventing from spreading of radionuclides from a reactor cavity to the environment which is being developed by JSC "SHK" specialists seems to be very promising. It can help to reduce expenses significantly (more than in ten times) in comparison with the liquidation option [4].

According to the presented options, it is necessary to ensure the nuclear- and radiation-safe condition of significant volumes of radioactive graphite. Options for radioactive waste (RW) management are presented below as well as the problems connected with each option:

I. Disposal of graphite stacks "on site" without dismantling with creation of engineering barriers.

Problems:

- It is difficult to prove nuclear and radiation safety of engineering barriers for a long-term period of time;
- It is necessary to change regulatory framework because of the existing limitations for near-surface disposal;

II. Disposal of graphite stacks in containers in deep geological disposal facilities.

Problems:

- Significant financial expenses;
- Absence of a disposal facility in deep geological formations;

III. Treatment of graphite waste by its oxidation and separation from radioactivity.

Problems:

- Political and regulatory eliminations because of CO_2 discharges;
- Absence of an industrial technology of carbon isotope separation;

IV. Near-surface disposal after graphite waste decontamination.

Problems:

- High initial expenses for R&D;
- Absence of an industrial technology for graphite waste decontamination.

Besides graphite stack waste there is also a significant number of graphite sleeves and a small amount of higher activity graphite waste which is formed by high-level graphite in the form of spent fuel assemblies. However, the amount of this type of graphite waste will not increase in future because the industrial UGRs, the source of such waste, are all already shut down (Figure1).

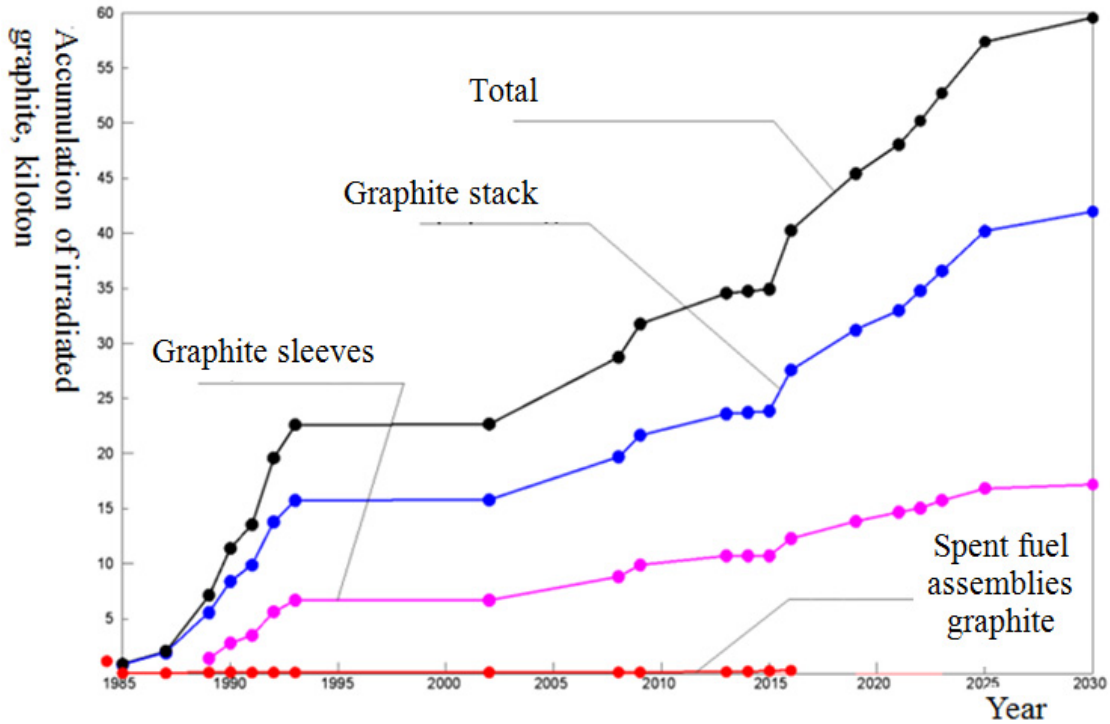


FIG. 1. – The Dynamics of Irradiated Reactor Graphite Accumulation in the Russian Federation

As a result of different technical operations and incidents in the reactor core during long-term operation of UGR-type reactors, there are so-called "spills" – fuel assemblies reactor graphite waste with inclusions of nuclear fuel. During their long-term presence in the reactor core, transuranics – plutonium, americium and curium – and other radionuclides such as ^{14}C, ^{137}Cs, ^{90}Sr, ^{144}Ce, ^{106}Ru, ^{54}Mn, ^{55}Fe, ^{60}Co etc. were accumulated. According to specialists' estimations, more than one hundred tonnes of graphite waste is the result of such "spills". All types of graphite waste contain long-lived ^{14}C isotope (with a half-life of 5730 years), the concentration of which in irradiated reactor graphite can reach an amount of 10 grams per tonne. The content of ^{14}C in graphite sleeves is about 10 times lower [5].

The specialists of FSUE "RADON" together with JSC "N.A. Dollezhal NIKIET" and "Academician A.A Bochvar VNIINM" carried out research of graphite waste treatment processes such as graphite incineration in air flux and oxidation in molten salts and decontamination processes such as thermal treatment in air flux, in water-vapour flux and in salt melt.

2. TEST TREATMENT OF GRAPHITE WASTE

2.1. Incineration of graphite waste in an air flux

Open (flaming) incineration is widely used for treatment of solid combustible RW, in particular low- and intermediate-level waste. However the use of this method for treatment of solid radioactive waste (SRW) has several disadvantages. Ash containing about 90 % of the initial activity is the final product of incineration and it is not suitable for disposal. Therefore, it is necessary to immobilise the ash into some matrix. The gaseous medium of the incineration shaft and offtake pipes contains fine particles of unburnt organic compounds and incombustible materials as well as fumes of volatile metals which form aerosols precipitating on the surfaces of equipment. This complicates the purification of off-gases and decreases the life of the purification equipment. Spent filters are subjected to treatment as secondary RW.

Nevertheless RW incineration is economically feasible because it provides significant volume reduction (up to 99%) and thus helps to reduce expenses for further processing.

For volume reduction of low level waste of graphite sleeves and rings with low specific activity of ^{14}C, the incineration method is quite promising [6].

Information about the physical and chemical aspects of graphite incineration process is quite rare. Graphite incineration includes three stages: first - the reactant gas absorbs onto the outer surface of graphite, second - chemical reaction products are absorbed on the graphite surfaces and third - product gases are desorbed from the graphite surface. At a temperature less than 600°C there is a kinetic mode of oxidation reaction on the surface, above 600°C – diffused gaseous mode when the speed of oxidation depends only on air supply speed [7]. At 700-800°C the reaction produces both CO and CO_2 and can be determined as an oxidation reaction, at 800-850°C the reaction produces only CO and can be regarded as an incineration reaction [8].

If oxygen content in air exceeds 21% then the degree of incineration of graphite (GR-280) at 1000°C during one hour approaches to 100 %, if the oxygen content is about 11 % then the degree of incineration at the same other conditions decreases to 80 %, and if the oxygen content is about 5% then the degree of incineration does not exceed 30%. The speeds of graphite interaction with air presented in literature are 0.3×10^{-2} $kg.m^{-2}.s^{-1}$) at 1200 K and 0.8×10^{-2} $kg.m^{-2}.s^{-1}$) at 2000 K.

In order to optimise the parameters of the graphite incineration process the following work has been done:

- Measured weight loss by thermogravimetric analysis of the graphite oxidation process in an air flux;
- Determined incineration speeds for ground graphite and graphite samples;
- Determined composition of off-gases producing during graphite incineration.

For these investigations, graphite blocks 10x10 mm with lengths of 10, 20 and 40 mm, and ground graphite (particles < 1mm) made of reactor graphite (GR-108 RBMK type) were used.

Thermogravimetric analysis (Figure 2) shows that incineration process and mass loss of powdered graphite in air both begins at ≈570°C. When the temperature increases from 570 to 750ºC graphite incineration speed, determining by derived curve of a mass loss, increases from 0.06 to 2.0 % per minute. When the temperature increases further graphite incineration occurs with a constant speed.

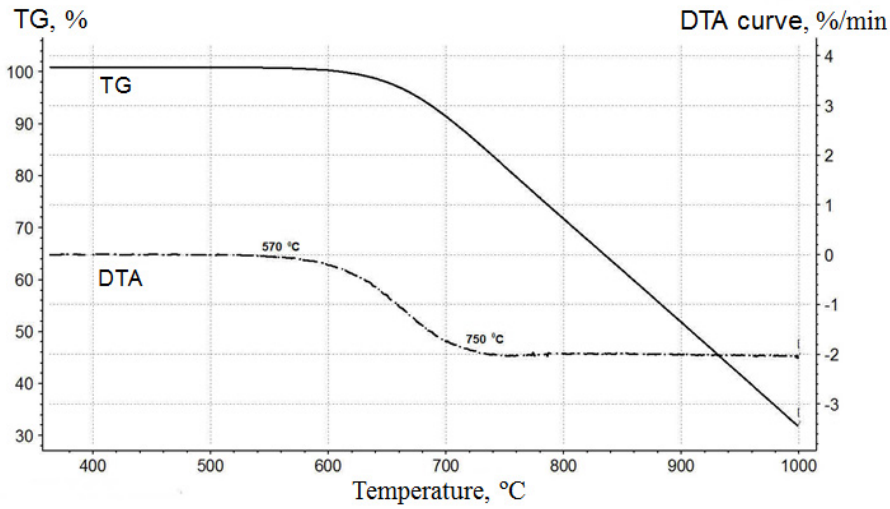


FIG. 2. – *Thermogram of powdered graphite heating in air*

The results of graphite incineration at different modes are presented in Tables 2-4.

TABLE 2. INCINERATION OF GRAPHITE SAMPLES (BLOCKS) *

Temperature, ° C	**Air flow rate, $l.h^{-1}$**	**Time, h**	**Mass loss**		**Graphite incineration speed, $kg.m^{-2}.s^{-1}$**
			g	**%**	
1000	-	5	8,79	32	$0,8\times10^{-4}$
1100	-	5	11,05	40	$0,96\times10^{-4}$
1100	300	1	21,6	80	$1,0\times10^{-3}$
1100	300	2	27,1	100	$>2,3\times10^{-3}$

*Graphite block – 27.2 ± 0,1 g., initial surface area of a samples ≈ $5,8\cdot10^{-3}$ m^2.

TABLE 3 – INCINERATION OF POWDERED GRAPHITE AT DIFFERENT TEMPERATURES DURING ONE HOUR

Graphite mass, g	Temperature, °C	Mass loss, %
2,7	600	7
2,8	600	9
2,5	700	62
2,6	700	60
2,8	700	72
2,3	800	92
2,6	800	99

TABLE 4 – INCINERATION OF GRAPHITE SAMPLES WITH DIFFERENT SURFACE AREA AT 900 °C

Sample dimensions, mm	Surface area, mm^2	Initial mass, g	Mass loss		Air flow rate, l/h	Oxidation speed, $(kg/m^2 \cdot s) \cdot 10^3$
			g	%		
10×10×10	600	1,50	1,21	80,6	60	0,67
10×10×10	600	1,52	1,25	82,1	60	0,69
10×10×10	600	1,45	1,31	90,8	120	0,72
10×10×10	600	1,42	1,18	83,7	120	0,65
10×10×20	1000	2,90	2,26	77,8	60	0,75
10×10×20	1000	3,03	2,32	76,7	60	0,77
10×10×20	1000	3,10	2,20	71	120	0,73
10×10×20	1000	3,04	1,90	62,5	120	0,63
10×10×40	1800	6,53	4,99	76,5	60	0,91
10×10×40	1800	5,62	4,42	78,6	60	0,81
10×10×40	1800	5,81	4,38	75,4	120	0,81
10×10×40	1800	5,69	3,94	69,3	120	0,72

The results from Tables 2-4 are presented in Figure 3 as a linear dependence of speed logarithm lgV and inverse temperature 1/T. The experimental points for the temperatures 600, 900 and 1100°C satisfactorily make a linear dependence and this linear dependence corresponds to the point 1200 °C from reference **Error! Reference source not found.**.

Graphite incineration is accompanied with formation of carbon oxides. The curve characterizing CO_2 formation during incineration of the two graphite samples (10x10 mm) is presented in a diagram (Fig. 4). The reference points of the curves correspond to the moments of achieving the temperature of 900°C and they do not coincide with reference axis because formation of CO_2 starts before 900 °C. The presence of CO was detected only in the beginning of heating and its concentration in the off-gases was insignificant [9].

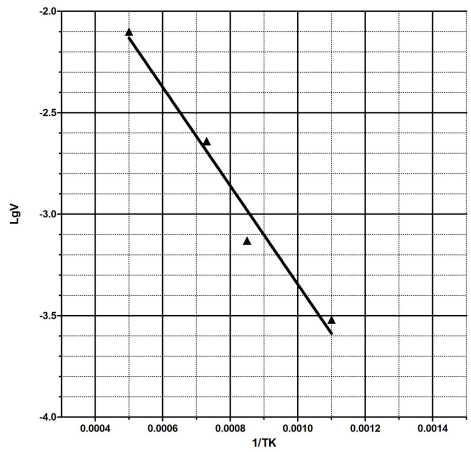


FIG. 3. *Dependence of graphite incineration speed logarithm on reverse temperature*

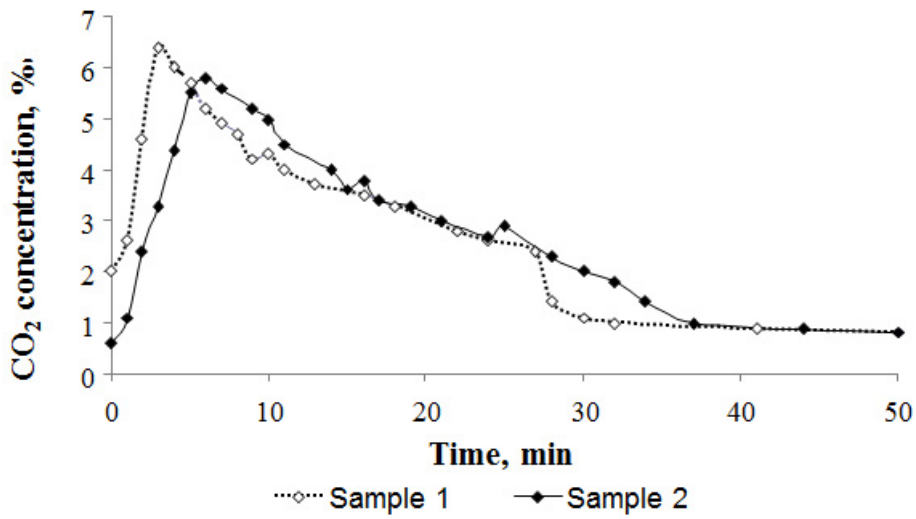


FIG. 4. *Concentration of CO_2 in off-gases during incineration of a graphite sample at 900 °C*

2.2. Graphite molten salt oxidation

Flameless molten salt oxidation (MSO) is one of the prospective methods of treatment for combustible radioactive waste in particular graphite waste and waste containing organic compounds.

Salt melt provides dilution and close contact of the reagents, helps to accelerate chemical processes of destruction and oxidation of waste and formation of accompanying nonvolatile compounds and also provides stability of thermal processes under external effects.

The relatively low working temperature (750-950°C) provides a decrease of radioactive substances carry-over because of volatilization, a reduction of toxic carbon and nitrogen oxide formation, and also helps to prolong life of constructive materials of the equipment.

Most radionuclides and heavy metals are retained in the melt because of their dissolution and formation of nonvolatile compounds. For example, Co Mn, Ni remain in salt melt as metals,

radioactive iodine forms NaI, metal U and also Pu and Sr form oxides UO_2, U_3O_8 and PuO, or carbonates $SrCO_3$. Besides, salt melt can retain ash residue and non-combustible materials.

Salt melt based on alkali metal carbonates is the most effective media. This composition retains most of the radionuclides, including SNF "spills". Moreover acidic gases, forming in the melt volume, are captured and neutralized forming NaCl, NaI, NaBr, NaF, Na_2SO_4, Na_3PO_4, $NaAsO_2$, Na_3AsO_4 etc. Thus the possibility of corrosion of the purification system's equipment is reduced. (Figure 5) [6].

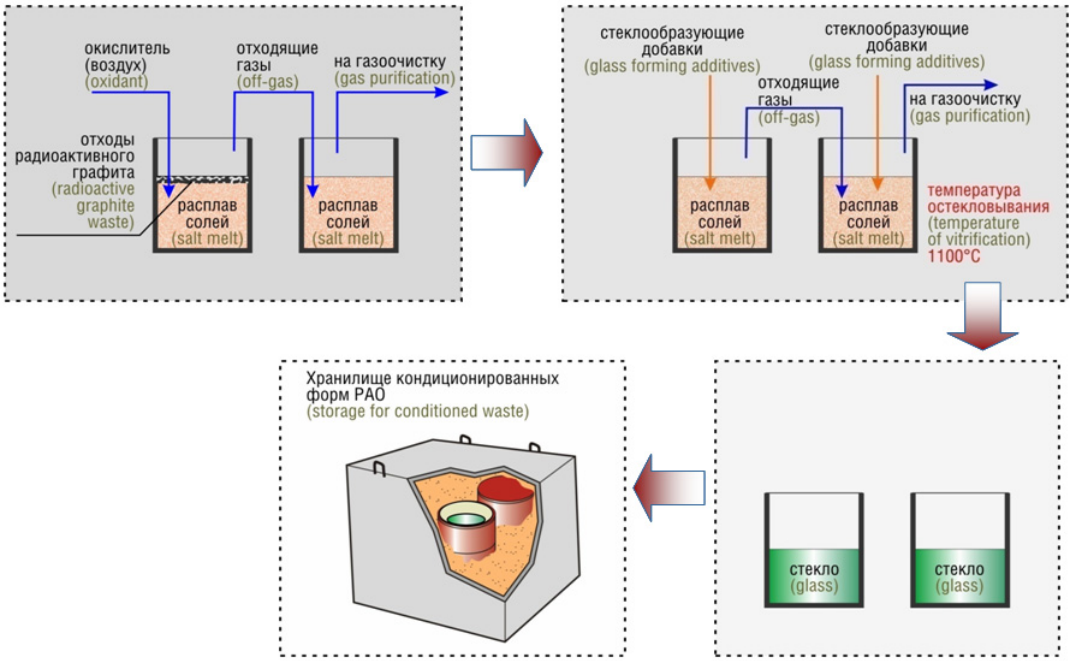


FIG. 5. *Molten salt oxidation of graphite waste*

Thermodynamic assessment with the help of the "TERRA" computer program has been used for estimation of graphite molten salt oxidation effectiveness [10]. Equilibrium compositions of melt and off-gas at various graphite contents were calculated as temperature functions.

The calculations were carried out for the process of graphite oxidation with sodium sulphate or potassium chromate as oxidizing additive at temperatures from 1100-1500K in an inert atmosphere with the following salt composition (mass.%):

Na_2CO_3 (56), K_2CO_3 (44), Na_2SO_4 (25), C(0.1–10).

It has been determined that, under these conditions, salt melt consists of Na_2CO_3, K_2CO_3, K_2SO_4 and K_2S.

Thermodynamic modelling has shown that potassium chromate (K_2CrO_4) has catalytic properties similar to sodium sulphate. Its melting temperature is almost a hundred degrees higher than sodium sulphate. Hence its decomposition with oxygen release occurs at higher temperatures to assist carbon oxidation. Moreover decomposition products do not contain acidic products like sulphur oxides [13].

Investigations of molten salt graphite oxidation were carried out in laboratory conditions and with the help of a pilot installation, shown in Fig 6a and 6b. The results are: pilot installation capacity of about 1 kg/hour by graphite, proved possibility of molten salt vitrification upon completion of the process. The final glasslike products of the process (Fig. 7) with specific activity of about 7.0×10^5 Bq.kg^{-1} by ^{137}Cs have a leaching rate of ^{137}Cs in distilled water not exceeding 10^{-5} g.cm^{-2}.d^{-1}.

During the tests of the installation its several constructive drawbacks were determined which were analyzed and eliminated. Additional experiments at this installation are planned to be carried out in 2014.

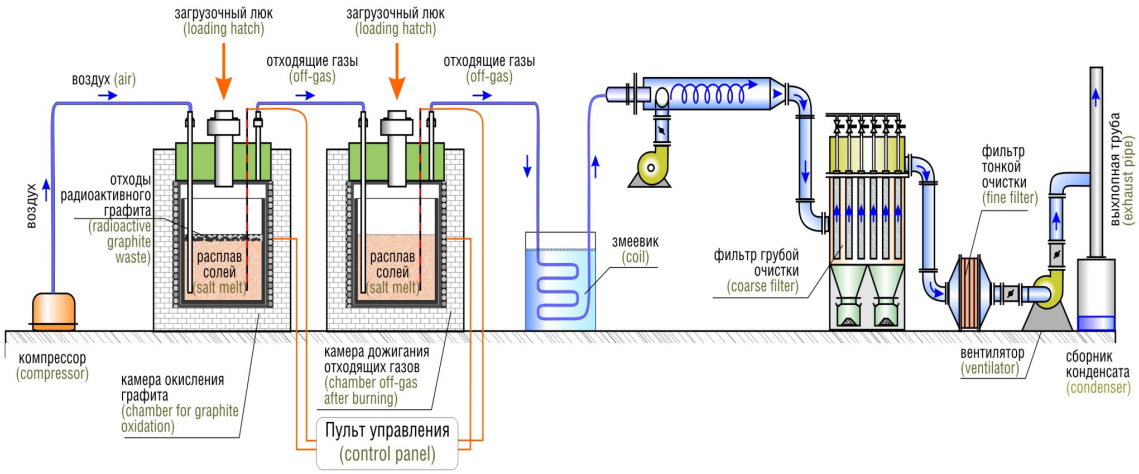


FIG. 6. *Scheme (upper) and outward appearance (lower) of installation for molten salt oxidation*

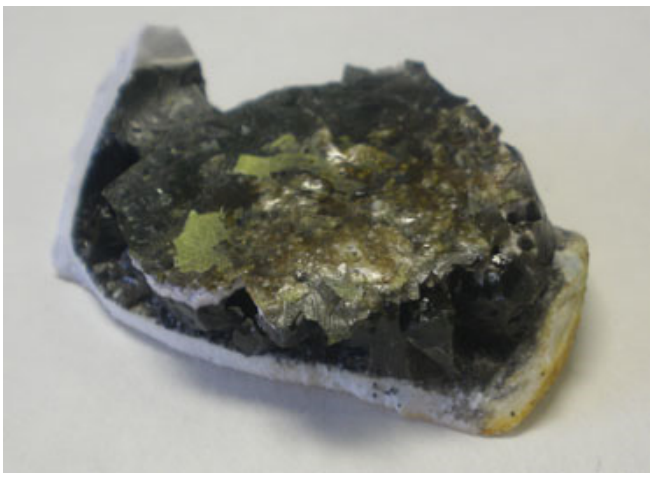


FIG. 7. *Glasslike final product of graphite molten salt oxidation*

3. DECONTAMINATION OF IRRADIATED GRAPHITE WASTE

Specific activity of radionuclides in irradiated graphite waste intended for disposal in near surface disposal facilities must not exceed the following values:

- 10^7-10^8 Bq.g^{-1} – for tritium containing waste;
- 10^3-10^4 Bq.g^{-1} – for radioactive waste containing beta-emitting radionuclides (with the exception of tritium);
- 10^2-10^3 Bq.g^{-1} – for radioactive waste containing alpha-emitting radionuclides (with the exception of transuranic radionuclides);
- 10^1-10^2 Bq.g^{-1} – for radioactive waste containing transuranic radionuclides [14].

For example averaged specific activity of irradiated graphite waste from RBMK (LRWG) reactor is 10^6 Bq.g^{-1} and it exceeds the regulatory value. Because of that there is limitation for such waste disposal in near surface disposal facilities. Because of that, in order to satisfy the waste acceptance criteria for such disposal, it is necessary to decrease specific activity of graphite waste to regulatory values.

Analysis of works devoted to radionuclide composition and radionuclides distribution within graphite waste shows the following:

- Fission products and actinides (outer contamination of graphite) are distributed mainly in the surface layers of graphite waste and the depth of this contamination does not exceed 2 mm.
- Sources of radiocarbon formation are the isotope ^{13}C naturally present in graphite to 1.1%, and ^{14}N both in coupled state and in pores. Radiocarbon

formed from nitrogen is mainly present (in the form of (CN)n) on pore surfaces and is not included into graphite crystal lattice [15], [16].

The abovementioned facts give reasons to develop decontamination technologies for graphite waste which provide a decrease of specific activity due to removal of labile ^{14}C and radionuclides ^{137}Cs, ^{90}Sr, ^{238}Pu, ^{239}Pu, ^{241}Am, ^{243}Am, ^{244}Cm from the outer layers of graphite waste. Thus the main aim of such decontamination is separation of significant part of radioactive contamination from main volume of graphite waste.

In laboratory conditions the experimental research of the possibility of irradiated graphite waste decontamination from loosely coupled radionuclides was carried out by the following methods:

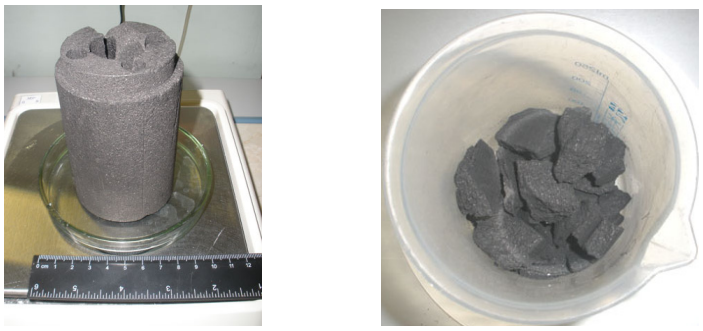
- molten salt treatment of graphite waste with and without use of oxidizer-catalyst;
- thermal treatment of graphite waste in air flux at different temperatures;
- thermal treatment of graphite waste in water vapor flux.

Two types of irradiated graphite waste have been studied – fragments of a graphite sleeve from the AM-type research reactor at the Physical-Energy Institute "A.I. Leypunsky" (Fig. 8a,b) and graphite rings from RBMK (LWRG) type reactor at Kursk NPP (Fig. 8d). The characteristics of the waste are presented in Table 5.

TABLE 5. RESEARCH SUBJECTS CHARACTERISTICS

Research subject	Radionuclide composition, $Bq.kg^{-1}$	Experiment samples
Graphite sleeve	^{14}C – $(0.9\text{-}1.4)\cdot 10^6$, ^{3}H – 7.6×10^5, ^{60}Co – 2.88×10^4 ^{137}Cs – 2.27×10^6 ^{241}Am – 4.78×10^4 ^{154}Eu – 1.5×10^3 ^{144}Ce – 5.3×10^3 $\sum\alpha$ by ^{239}Pu – $3{,}7\cdot 10^4$	Rectangular parallelepipeds. Mass of samples ~ 12 g Total activity – 1.1×10^4 Bq by ^{137}Cs and 1.4×10^2 Bq by ^{60}Co.
Graphite rings	^{14}C – $(2.2\text{-}3.2) \times 10^8$, ^{3}H – $(1\text{–}2.8) \times 10^7$ ^{60}Co – 3.31×10^6, ^{137}Cs – 6×10^4, ^{54}Mn – 1.3×10^5, ^{134}Cs – 1×10^4, ^{95}Nb – 1×10^4, ^{94}Nb – 7×10^4, ^{65}Zn – 1.1×10^5.	Rectangular parallelepipeds. Mass of samples 4.7–5.8 g.

(a) (b)



(c)

FIG. 8. Outward appearance of irradiated graphite: (a) graphite sleeve (b) fragments of graphite sleeve for the experiments; (c) graphite rings from RBMK (LWRG) type reactor

3.1 Thermal molten salt decontamination

The possibility of irradiated graphite molten salt decontamination by complete oxidation in molten salts of outer graphite layers was estimated based on the results of the experimental set. Samples of graphite sleeve (Table 5, Fig. 8b) were used. Working salt melts for experiments were compositions made of alkali metal carbonates with oxidizing catalysts in form of sodium sulphate (Na_2SO_4), boron oxide (B_2O_3), barium and potassium chromates ($BaCrO_4$ and K_2CrO_4). The mass of the oxidizing catalysts was 25 % above the mass of the initial batch. Temperatures used for decontamination were dependent on the batch melting temperatures and were limited to 870–1270 K. More precisely experiments' conditions are presented in Table 6. The controlling parameters for irradiated graphite MSO decontamination were the activities of ^{137}Cs and ^{60}Co in samples before and after the decontamination process.

The decontamination efficiency (βD) was estimated based on the removal of radionuclides from the irradiated graphite using the equation:

$$\beta_D = (A_i - A_e)/A_i * 100\% \qquad (1),$$

where Ai is the initial contamination, $Bq.kg^{-1}$; Ae is the final contamination achieved, Bq/kg.

TABLE 6 – MOLTEN SALT BATCH COMPOSITIONS USED IN EXPERIMENTS

Index	Batch composition, mass fraction %	Process temperature, K	Melting temperature, K
L	Basic composition: Li_2CO_3 – 0.39; Na_2CO_3 – 0,28; K_2CO_3 – 0,33 Without oxidizer	870–1170	620
LS	Basic composition: Li_2CO_3 – 0,39; Na_2CO_3 – 0,28; K_2CO_3 – 0,33; Oxidizer: Na_2SO_4 – 25% above 100% of basic composition	870–1170	740
S	Basic composition: Na_2CO_3 – 0,56; K_2CO_3 – 0,44; Oxidizer: Na_2SO_4 – 25% above 100% of basic composition	1170 - 1270	1120
B	Basic composition: Na_2CO_3 – 0,56; K_2CO_3 – 0,44; Oxidizer: B_2O_3 – 25% above 100% of basic composition	1170 - 1270	~1070
XBa	Basic composition: Na_2CO_3 – 0,56; K_2CO_3 – 0,44; Oxidizer: $BaCrO_4$ – 25% above 100% of basic composition	1170 - 1270	~1070
XK	Basic composition: Na_2CO_3 – 0,56; K_2CO_3 – 0,44; Oxidizer: K_2CrO_4 – 25% above 100% of basic composition	1170 - 1270	~1070

The irradiated graphite MSO decontamination efficiencies are given in Table 7 and Fig. 9 as a function of batch composition, processing time and temperature.

Figure 9 (a) shows the decontamination efficiency for real reactor graphite waste for ^{137}Cs at various temperatures in experiments with processing time of three hours. A maximum decontamination efficiency of reactor graphite for ^{137}Cs (e.g. 96%) was obtained in the melt with oxidizer-catalyst in form of sodium sulphate (batch labels LS and S) at 1170 K.

Figure 9 (b) shows the efficiency of MSO decontamination for ^{137}Cs at various temperatures in experiments with a processing time of 1 hour. From the plot given in Figure 9 (b), it can be seen that the highest decontamination efficiency for ^{137}Cs (e.g. 95%) was achieved in 1 h at 1270 K in the molten salt batch labelled S, which contained sodium sulphate as the oxidizer-catalyst.

TABLE 7 – IRRADIATED GRAPHITE MSO DECONTAMINATION EFFICIENCIES

Sample label	T, K	Decontamination efficiency, %					
		^{137}Cs			^{60}Co		
		Process duration, h					
		1	2	3	1	2	3
L	870	14	25	28	11	16	18
L	970	22	23	30	6	9	18
L	1070	27	38	44	9	6	6
L	1170	65	78	86	0	0	0
LS	870	16	29	33	24	31	32
LS	970	24	38	49	18	21	29
LS	1070	37	57	63	8	14	18
LS	1170	65	88	96	45	60	73
S	1170	66	87	96	40	60	77
S	1270	95	-	-	85	-	-
B	1070	47	60	78	11	15	27
B	1170	54	68	82	12	11	17
XBa	1070	29	33	35	0	0	0
XBa	1170	50	56	62	10	5	10
XK	1070	35	37	33	7	10	4
XK	1170	43	57	77	12	14	15

(a) (b)

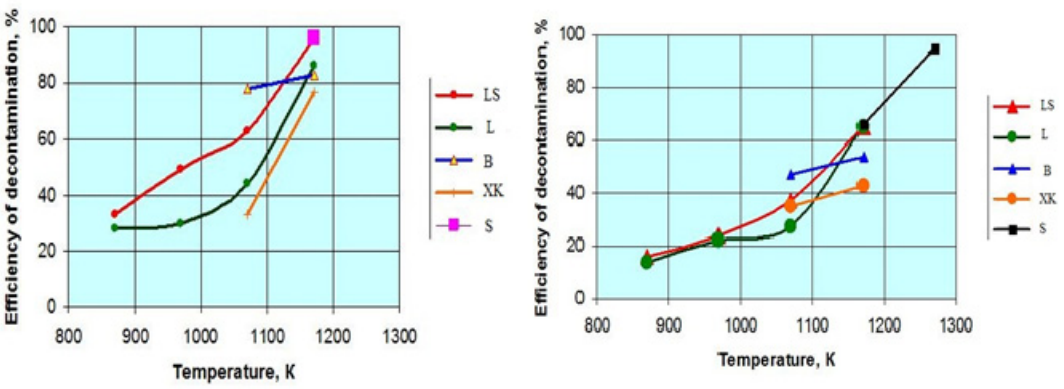


FIG. 9. Decontamination efficiency ^{137}Cs removal at processing time – 3 h (a) and at processing time – 1 h (b).

The overall efficiency for ^{60}Co (as seen from Table 7) is not high (< 32%) except for molten salt batch compositions which have sodium sulphate oxidizer-catalysts. Within the temperature interval 870–1070 K the decontamination efficiency for ^{60}Co gradually decreases for all batches. In the temperature interval 1070–1170 K the temperature dependency of MSO decontamination efficiency for ^{60}Co has various trends. In the melt with boron oxide and without an oxidizer the efficiency decreases whereas in the melts with potassium chromate and sodium sulphate it increases. The efficiency of MSO decontamination for ^{60}Co at various temperatures in experiments with a processing time of 1 hour has reached maximum (e.g. 85 %) in the melt with oxidizer-catalyst in the form of sodium sulphate (batch label S) at 1270 K. [13].

3.2 Decontamination in air flux at different temperatures

The experiments were carried out with the help of the laboratory test bench which general layout is shown in Figure 10.

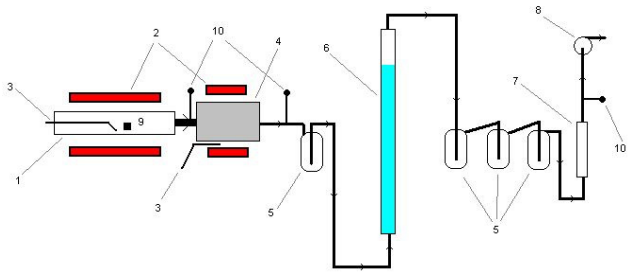


FIG. 10 – General layout of the laboratory test bench: 1– shaft furnace, 2– electrical heaters, 3 – thermal couples, 4 – catalytic afterburner of CO, 5 – protective flasks, 6 – absorption column, 7 – flow meter, 8 – vacuum pump, 9 – graphite sample, 10 – gas sampling points

The electrical pipe furnace 1 is the main element of the test bench. It is intended for thermal treatment of graphite sample in a flowing mode. At the output of the furnace there is a catalytic afterburner 4 intended for oxidation of carbon oxide to carbon dioxide. The absorption column is for absorption of CO_2 and radionuclides evolving in the gaseous phase during thermal treatment of graphite waste in the pipe furnace. Air flow through the whole system (furnace, catalytic afterburner 4, and absorption column 6) is provided by the vacuum pump 8.

In order to determine the acceptable temperature for decontamination of graphite sleeve samples (Table 5, Fig. 8) a set of preliminary experiments has been carried out at temperatures 400-900°C. The results are presented in Table 8 and Figure 11.

So it was determined that significant oxidation of graphite in air flux and removal of radiocarbon and tritium from it begins at temperatures above 600 °C. Initial mass loss of the sample at 400 is likely to be because of moisture removal from graphite sample.

At temperatures above 700°C oxidation starts to be intensive – with graphite mass loss of more than 1 % per hour. Hence the interval of temperatures for mild oxidation of graphite for removal of loosely coupled radiocarbon is 600–700°C.

TABLE 8 – GRAPHITE MASS LOSS IN DEPENDANCE ON TEMPERATURE*

Temperature, °C	**Graphite mass loss %**
400	4.7 (moisture)
500	0
600	1.2
700	5.9
800	62.4

900 (complete oxidation)	100

*Duration - 5 hours, air flow rate 315–378 l/h

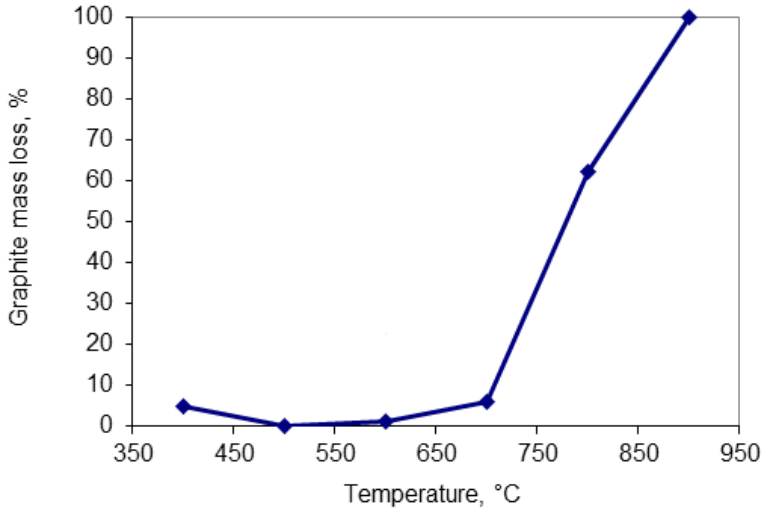


FIG. 11 – Graphite mass loss (%) at different temperatures

The results of oxidation of the graphite samples (maximum length 2.5 cm) in the determined temperature range (600-700 ºC) are presented in Table 9 and Figure 12.

For graphite sleeve samples it was impossible to determine tritium because of the high specific activity of radiocarbon.

According to the presented curve it can be seen that at that temperature interval gradual removal of radiocarbon from graphite occurs and removal of 90-95 % of radiocarbon is accompanied by about 25-35 % mass loss of carbon waste itself.

TABLE 9 – OXIDATION OF GRAPHITE SLEEVE SAMPLES

T, °C	Oxidation time, h	Total graphite mass loss %	Proportion of ^{14}C removed %
600	6	2.5	0.7
	11	5.0	2.4
	17	10.1	7.1
	23	10.1	24.5
	29	12.6	31.5

	34	13.9	42.4
	40	15.2	60.9
650	46	24	88.1
	51	26.6	95.1
	57	44.3	95.1
	Total oxidation	100	100

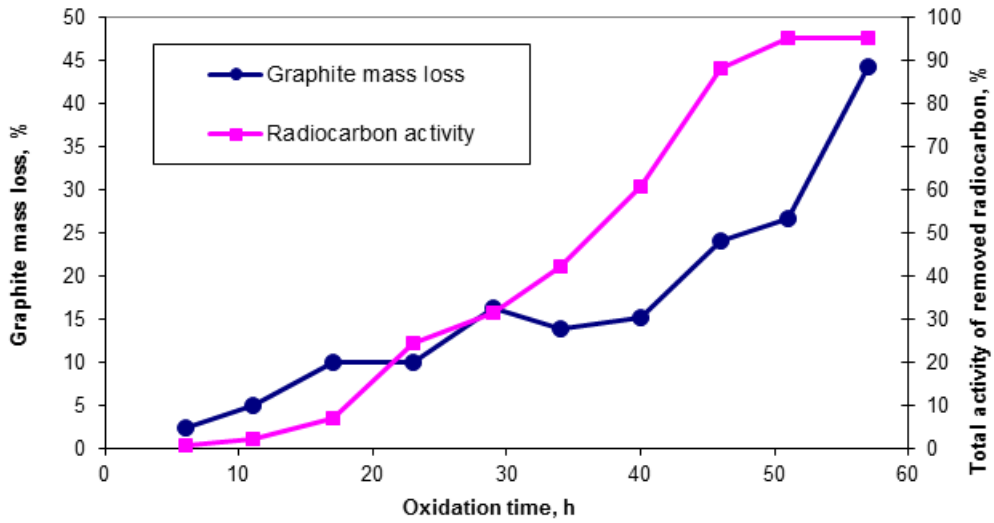


FIG. 12 – Oxidation of graphite sleeve samples at 600-650 °C.

The results of the decontamination process at the same conditions (temperature interval 600-650 °C, air flow rate 315 $l.h^{-1}$) for samples of RBMK (LWRG) reactor graphite (Table 5, Fig. 8) are quite different as for the samples of a graphite sleeve from AM reactor.

During the first 5-6 hours almost complete removal of radiocarbon (1.2–1.6 × 10^6 Bq) from samples of RBMK graphite occurs at abovementioned conditions. During the following thermal treatment removal of radiocarbon was not detected until almost complete oxidation of the samples had occurred.

Removal of tritium from RBMK reactor samples continuously increases with time (Table 10, 11, Fig. 13, 14).

TABLE 10 – OXIDATION OF RBMK REACTOR GRAPHITE SAMPLES AT 600°C

Time of oxidation, h	**Graphite mass loss %**	**Total activity of removed ^3H %**
22	14,5	41,3
28	21,3	76,1
34	25,5	100
Complete oxidation	100	100

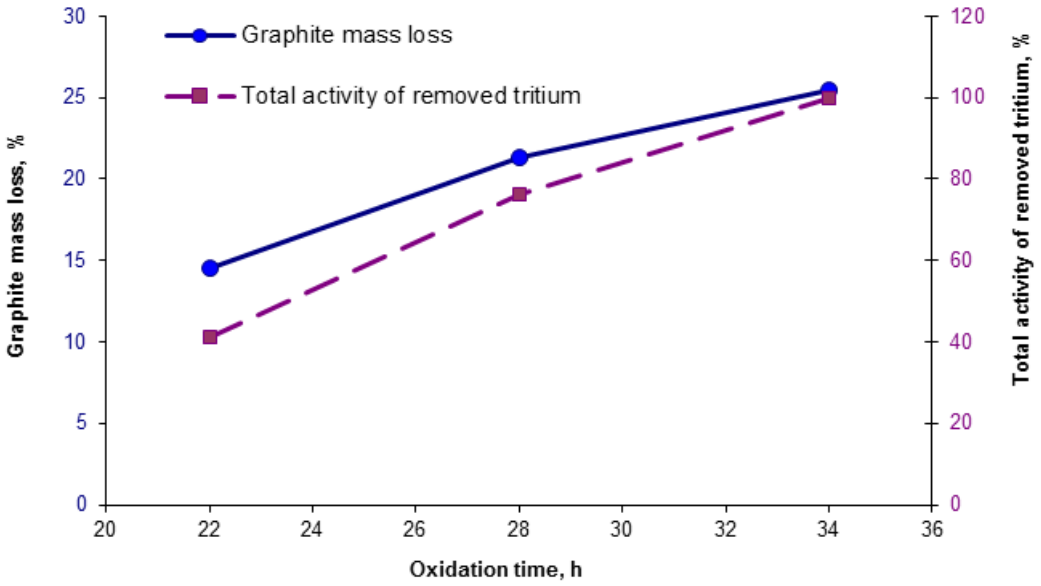


FIG. 13. – Removal of ^{3}H from RBMK reactor graphite samples at 600 ºC

TABLE 11 – OXIDATION OF RBMK REACTOR GRAPHITE SAMPLES AT 650°C

Time of oxidation, h	Graphite mass loss %	Proportion of ^{3}H removed %
6	17.2	11.9
11	36.2	23.1
17	53.4	33.1
22	56.9	68.8
Complete oxidation	100	100

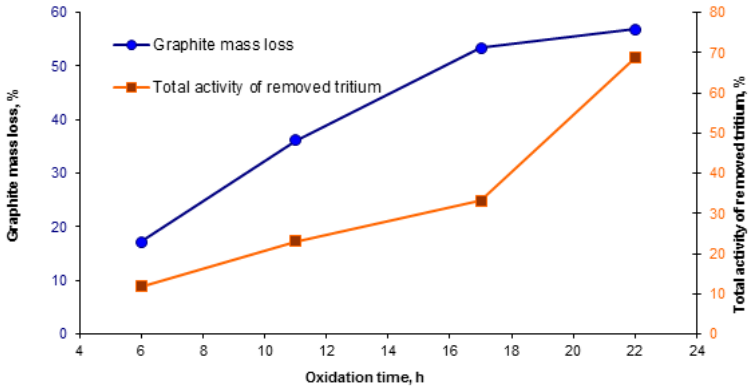


FIG. 14 – Removal of ^{3}H from RBMK reactor graphite samples at 650 ºC

3.3 Decontamination in water vapor flux

The experiments were carried out with the help of the laboratory test bench with a general layout as shown in Figure 15:

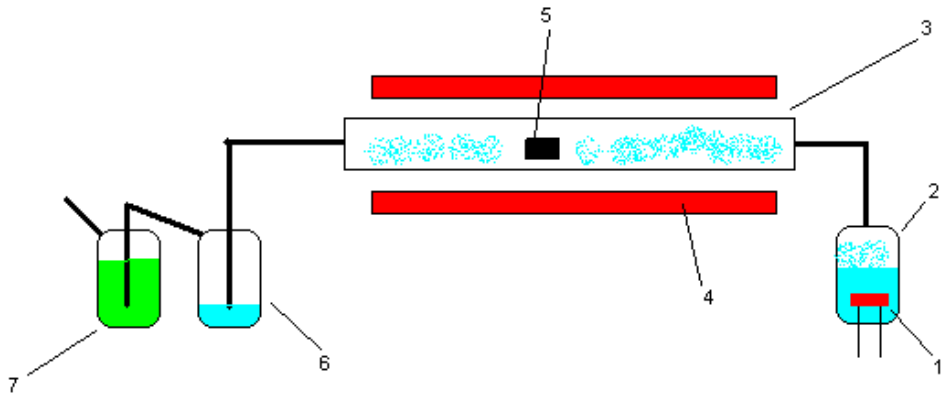


FIG. 15 –General layout of the test bench: 1 – adjustable electric heater of evaporator, 2 – evaporator, 3 – quartz pipe furnace, 4 – electric heater, 5 – graphite sample, 6 – flask for water condensate, 7 – absorption flask

The graphite sample of PBMK reactor (Table 5, Fig. 8) was placed into a pipe furnace 3. At a temperature of 350 ºC the electric heater 1of the evaporator 2 (filled with distilled water) was switched on. At a temperature of about 700 °C the absorbing system was connected. Water vapor flow rate through the system was 30-40 g/h. The flask 6 is for condensed water and the flask 7 was filled with 96% ethanol for absorbing of CO forming in the result of the reaction: $C + H_2O = CO + H_2$.

After the end of treatment samples were dried at 110 °C, weighed to determine mass loss and then completely oxidised for determination of residual content of radionuclides. The results of decontamination are presented in Table 12.

Activity of ^{14}C at ethanol absorbing solution after 5 hours of treatment was about 3 kBq and did not increase more with time.

TABLE 12 – RESIDUAL ACTIVITY OF RADIONUCLIDES IN WATER VAPOR CONDENSATE AFTER TREATMENT AT 700 °C

Treatment time, h	**Total activity of condensate, Bq**				
	^{3}H	**^{14}C**	**^{137}Cs**	**^{60}Co**	**^{65}Zn**
15	3400	550	10	20	210
24			10	30	250

The residual activity of radionuclides in samples after 24 hours of treatment by water vapor at 700 °C was: for tritium – 2.6×10^5 Bq; for radiocarbon – 7.6×10^5 Bq. Taking into regard the initial activity of radiocarbon at graphite samples from Kursk NPP (Table 5) it was proved that at abovementioned conditions of treatment about 23-47 % of ^{14}C activity was removed from graphite samples with a mass loss of graphite sample within 9 %.

DISCUSSION

The results of graphite incineration in air flux studies reviewed in this report show that according to the results of thermal gravimetric analysis of powdered graphite, incineration in air starts at about 570 °C, the maximum incineration speed is observed at temperatures higher than 750 °C with further constant incineration speed. It was determined that graphite monolith samples incinerate with remarkable speed in air flow. By the experimental data a linear dependence has been determined which can be described by the following equation (where v is the oxidation speed and T the treatment temperature (K):

$$\lg v = -(2{,}75 \pm 0{,}35)\cdot 10^4 \cdot 1/T;$$

By the example of graphite samples with initial area from 600 to 1800 mm^2 at 900 °C incineration it was determined that incineration speed related to a surface unit is more or less the same and is $(0.74 \pm 0{,}15)\cdot 10^{-3}$ $kg.m^{-2}.s^{-1}$. Incineration of graphite with enough amount of oxygen in air occurs with formation of almost CO_2 with a maximum formation in the beginning of the process and subsequent continuous decrease. CO content during the whole experiment does not exceed 20 ppm.

The results of studies of molten salt oxidation treatment show the efficiency of this method for treatment of such radioactive waste and prove the possibility of receiving a final solid glasslike product with durable fixation of radionuclides without increase of the initial waste volume. Thermodynamic modelling has shown that both sodium sulphate and potassium chromate are effective oxidizer-catalysts for molten salt oxidation due to their decomposition temperatures close to the temperature of active carbon oxidation. Potassium chromate can be used as an effective oxidizer-catalyst which does not form aggressive gases on decomposition.

MSO decontamination of real reactor graphite by removal of near-surface contamination is feasible. Decontamination efficiency depends on the oxidizer and temperature. The most effective media for MSO decontamination of ^{137}Cs and ^{60}Co is melt based on alkali metal carbonates with oxidizing-catalyst additives in the form of sodium sulphate and Na_2SO_4.

Oxidation of graphite samples in air flux at a temperature of 600-650 °C makes it possible to remove more than 90% of radiocarbon with mass loss of graphite itself not exceeding 20-30%. The necessary duration of treatment significantly depends on graphite irradiation history. Thus for Kursk NPP graphite samples it takes about 5-6 hours to remove more than 90% of ^{14}C and for graphite samples from IPPE it takes 30-50 hours (depending on temperature). Also it was determined that oxidation of graphite samples in air flux at temperature below 600 °C was not enough for significant removal of ^{14}C.

Graphite oxidation is accompanied by ^{3}H removal. The share of removed tritium significantly depends on graphite irradiation history, mode of treatment and in some cases (graphite samples from Kursk NPP, 600°C, 34 hours, air) can approach 100%.

Oxidation of IPPE graphite samples in water vapor atmosphere flux for 24 hours at temperature 700°C makes it possible to remove 20-50% of ^{14}C with graphite mass loss within 10%

CONCLUSIONS

Based on the results reviewed in this report it is possible to make the following conclusions:

1. Incineration of reactor graphite waste in air flux can be efficient only for low level waste for effective waste volume decrease. The process runs effectively only at temperatures above 750°C when oxidation speed does not depend on oxidized surface area and it depends only on air-flow i.e. after reaching thegaseous-diffusion-limited mode of graphite incineration.
2. Irradiated graphite molten salt oxidation makes it possible to receive final solid vitrified product for subsequent conditioning and placement for disposal. The technology has several significant advantages such as there is no need for graphite waste crushing, radionuclides remain in the salt melt and, if the oxidizer-catalyst and temperature are chosen correctly, then there are no acidic corrosion-active gases in off-gases.
3. The results received during study of graphite decontamination processes show that after treatment the characteristics of irradiated graphite waste can meet requirements of the acceptance criteria for waste intended for near-surface disposal because of decrease of ^{14}C specific activity. Activity of graphite waste contaminated with nuclear fuel spills with high radioactive toxicity can be significantly reduced with the help of molten salt decontamination.

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