QUANTITATIVE DETERMINATION OF THE AMOUNT OF ^{3}H AND ^{14}C IN REACTOR GRAPHITE

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Up to the present time, 19 domestic reactors have been taken out of service, of which 15 are water-cooled and graphite-moderated, viz. two Beloyarsk reactors, three at Chernobyl Nuclear Generating Station (NGS), and 10 industrial.

The contemporary concept of decommissioning a NGS envisages mothballing the reactor for a period of not less than 50 years, then dismantling it and burying or salvaging the materials. The technology of dismantling is determined by the composition and activity of radionuclides in the construction materials of the nuclear power plant.

An investigation of the problems of decommissioning graphite-moderated reactors began in earnest in the USA and France in the mid 80's, and in Britain much experience has been garnered about the mothballing of damaged gas-cooled graphite reactors [1-4]. Studies show that graphite is the main source of radioactivity at the time of dismantling. Each reactor contains thousands of tonnes of graphite. Its high activity is a consequence of neutron reactions with the carbon and impurities contained therein, and also of fragments of fuel dropping into the moderator as a result of leakage of fuel elements and pressure tubes. The activity of the irradiated graphite is determined by the content of such radionuclides as ^{3}H, ^{14}C, ^{63}Ni, ^{60}Co, ^{36}Cl, ^{55}Fe ^{41}Ca, ^{154}Eu, ^{152}Eu, etc., but in the first few years after shutdown 80-90% of the activity comes from ^{3}H and ^{14}C.

Attempts to arrive at a calculated estimates of the radioactive contamination of reactor graphite run into difficulties because of the absence of evidence about the initial nuclide composition of the graphite, and about the migration of radionuclides in the reactor core media. In such a situation, a reliable prediction of the radionuclide composition is impossible without an experimental test and validation of the method of calculation. At the present time, the necessary experimental data on impurity levels of graphite in domestic reactors do not exist. The available foreign data can not be used on account of differences in the technology of manufacturing graphite and in the reactor operating conditions.

The present work is the beginning of systematic all-round studies of the radionuclide content in reactor graphite; it is devoted to ^{3}H and ^{14}C. The aim of the work was to design a method and apparatus for studying the contamination of reactor graphite with ^{3}H and ^{14}C, to analyze the first 17 samples of graphite from the moderator of the shut-down reactors AV-2 and ÉI-2, to obtain calculated estimates of the ^{3}H and ^{14}C contents, and to compare them with the results of the experimental investigations.

Method of Measuring ^{3}H and ^{14}C. With a view to a large number of planned analyses, the requirements were determined for a method which had to guarantee an acceptable time and accuracy (not worse than 30%) of analysis when measuring ^{3}H and ^{14}C in samples of reactor graphite; the method had also to be based on the simplest possible procedures and equipment. The gist of the method developed was to separate ^{3}H and ^{14}C from a sample by two-component oxidation and to transfer the gaseous products into a liquid phase for measurement of the activity with a liquid scintillator. A mixture of CuO and V_2O_5 was chosen as the two-component oxidant, which made it possible to have a low temperature of melting at around 660°C, and readily fusible reduction products. As a result of the oxidation reactions, the nuclides being studied were evolved from the sample in the gaseous form as CO_2 and HTO, but interfering nuclides were contained in the melt. On oxidizing graphite. CO can be formed besides CO_2, and this leads to loss of ^{14}C. To prevent such losses, a stage for oxidation of the gaseous products was introduced. For this, the gases were filtered through heated copper oxide.

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TABLE 1. Efficiency of Counting ^3H and ^{14}C

Nuclide	Standard			Efficiency, %
	chemical content	A_{sp}, 10^5 Bq/g	mass, g	
^3H	HTO	1,00	0,030	24±1
^{14}C	Thymine, 2-^{14}C	1,03	0,030	65±2

The tritium-containing phase was separated in an apparatus with a liquid nitrogen trap. A graphite sample of mass 50 mg was placed in a reaction vessel, covered with a moistened mixture of the solid oxidants (1.6 g CuO + 7.28 g V_2O_5), and the CuO filter was attached. After heating the reaction vessel, it was placed in a furnace, and the trap was immersed in liquid nitrogen. Then the reaction vessel was heated to 700°C and kept at about that temperature for 5 h. As the sample is oxidized, the trace impurity HTO is blown by the carbon dioxide formed into the free volume of the reaction vessel filled with water vapor. After completion of the process, the apparatus is evacuated, and the tritium-containing phase is condensed in the liquid-nitrogen trap. The water collected is put in a 20 cm^3 measuring flask with a dioxane scintillator, and a homogeneous scintillation mixture is formed.

In order to analyze the ^{14}C content in the graphite, the CO_2 formed by oxidation was absorbed using NaOH. A phase containing ^{14}C was separated according to the following scheme. A graphite sample of mass 50 mg was placed in a reaction vessel, and covered with a mixture of solid oxidants (1.6 g CuO + 7.28 g V_2O_5). After attaching filters filled with CuO and NaOH, the reaction vessel was placed in a furnace, and the trap was immersed in liquid nitrogen. The reaction vessel was heated to 700°C, and kept at about that temperature for 5 h. The apparatus was then evacuated, and the CO_2 remaining in the reaction vessel was absorbed in NaOH. The contents of the trap and alkali filter were washed out with distilled water, and a portion of the solution formed was introduced into a liquid scintillator having the following composition: toluene 180 g + TRITON X-100 80 g + PPO 0.8 g + POPOP 0.2 g. Activity was measured on a "Mark III" scintillator system from the firm "Tracor Analytic". The efficiency of recording ^3H and ^{14}C was determined by the internal standard method [5]. The calibration results and data on the standards used are shown in Table 1.

To test the method, series of experiments were performed on special samples having known ^3H and ^{14}C activity. Two types of samples were used, differing in the additive introduced into graphite powder. In the first case, this was lithium carbonate powder which had been irradiated with thermal neutrons. The source of the tritium in the powder was the reaction $^6Li(n,\alpha)^3H$, the thermal neutron cross section of which was known with high accuracy. Knowing the quantity of ^6Li nuclei and the absolute value of the neutron emission rate from the neutron source, the activity of tritium formed was calculated. In the second type of samples, thymine labeled with ^{14}C was used as additive.

The tests performed showed that almost all the ^{14}C was transferred from the sample into the liquid phase, but the degree of extraction of tritium from a sample reached 75%. This result is close to the value obtained in [6].

Some features of the method developed are as follows:

Possibility of simultaneous analysis of a sample for ^3H and ^{14}C content;

High sensitivity: limit of detection of ^3H content is about 4 Bq/g, for ^{14}C it is 1 Bq/g;

Comparative simplicity of the experimental procedure and equipment, and also the absence of expensive and scarce reagents used to decompose a sample.

Experimental Results. The samples for analysis were obtained in 1991 after the reactors had finally been shut down. The graphite had been irradiated for more than 30 years. Ten samples of moderator graphite were removed from the center of the core of AV-2 reactor. Locations of sample removal from ÉI-2 reactor (7 samples) were distributed both in the core center, and at the periphery at different distances from the center according to height. Graphite samples of activity ~100-300 kBq were studied.

The main results of studying the graphite samples are shown in Fig. 1.

Analysis of the results of measurement shows that the specific activity of radionuclides in the graphite samples is characterized by a marked inequality of distribution, especially for ÉI-2. In all the samples analyzed, the activity was determined by ^{14}C; the ^3H activity was ≈100 fold less in samples from reactor AV-2, and 10-100 fold less for reactor ÉI-2.

Calculated Estimates of ^3H and ^{14}C in Graphite Samples. The method of calculating the specific activity of radionuclides in the reactor graphite consists of the following stages:

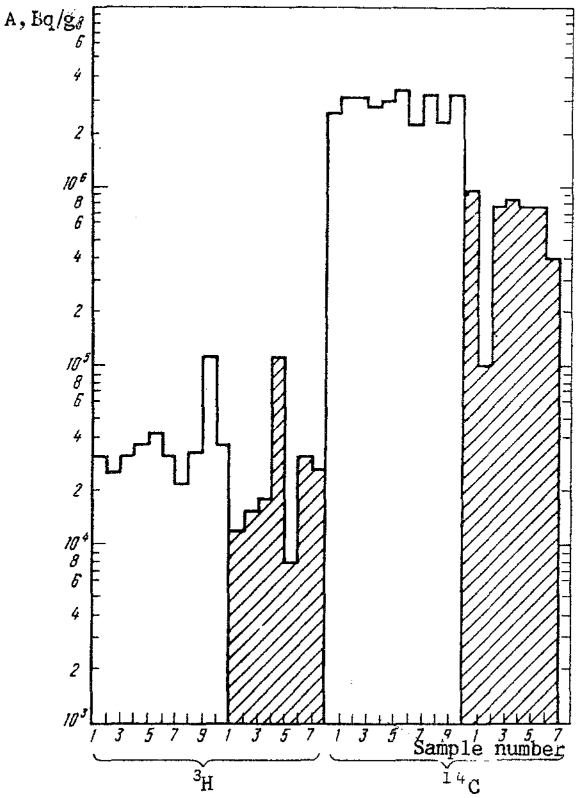

Fig. 1. Histogram of radionuclide content in samples from reactors AV-2 and ÉI-2 (crosshatched).

1. Calculation of the distribution of the flux density of thermal neutrons Φ in the graphite moderator for every period of reactor operation. A program for calculation of the spatio-energetic distribution of neutron flux density, viz. DOT III, was used, with the CASK library of neutron constants correlated with the help of the program WIMS. Changes in reactor power during operation were allowed for.

2. An estimate of the spectral characteristics of the neutron field, the rigidity of the spectrum γ and the temperature of the neutron gas T_n. This was performed with the help of the program WIMS (calculation of the spatio-energetic distribution of neutron flux density for all energy ranges), and of special additional programs.

3. Calculation of the changing (during irradiation) concentration of radionuclides of interest, for known irradiation parameters (i.e., Φ, γ, T_n) and for a given initial state of the moderator graphite. A specially written program was used to solve the kinetic equations of nuclide transmutation.

It was assumed that the following reactions play the main role in the formation of ^3H and ^{14}C in graphite: $^6Li(n,\alpha)^3H$, $^{14}N(n,t)^{14}C$, $^3He(n,p)^3H$, $^{13}C(n,\gamma)^{14}C$, $^{14}N(n,p)^{14}C$.

Lithium and nitrogen can be contained in the original graphite as impurities; nitrogen, moreover, is a basic component of the gaseous mixture for purging the moderator; ^3He is formed as a result of tritium decay.

A very high uncertainty in obtaining calculated estimates of the radionuclide content arises because of the absence of reliable data for the initial impurity content of the materials. In Table 2 some data are provided from domestic and foreign sources of information about the impurity content in reactor graphite.

In view of the uncertainty of data on the initial impurity content of graphite, all known values of the initial concentration of impurities were considered. Moreover, in some variants, the concentration of nitrogen was assigned taking account of its filling the pores in graphite. For this purpose, it was assumed that the total porosity of graphite is 25%, comprising 15% open pores and 10% closed. In the calculations no account was taken of removal of ^3H and ^{14}C from the graphite moderator because of gas purging, washing, and the like.

TABLE. 2. Content of Impurities in Reactor Graphites 10^{-6} by Mass

Nuclide	Source of information		
	[2]	[3]	[7]
N	4,0	15,0	4
Li	0,1	0,046	—

Comparison of the results of calculations with experimental data on the measured specific activity of ^3H and ^{14}C in the samples of graphite moderator from AV-2 and ÉI-2 shows that taking account of nitrogen filling both open and closed pores in the graphite enables one to obtain a calculated estimate of the ^{14}C content in the graphite with an uncertainty coefficient of 1.5-2. The reaction $^{14}N(n,p)^{14}C$ dominates in the formation of ^{14}C; the contribution of the reactions $^6Li(n,\alpha)^3H$ and $^{14}N(n,t)^{12}C$ in the formation of tritium is compatible with a concentration of $(1\text{-}4.6)\cdot10^{-6}\%$ by mass. However, the experimental specific activity of ^3H in all the graphite samples investigated was only 5-10% of the calculated. Apparently, the greater part of the tritium formed is carried away out of the graphite in the process of operating the reactor; it is swept out with a gaseous mixture owing to wetting of the graphite, etc. At the present time, we do not have the necessary volume of evidence available about processes controlling the removal of tritium from graphite; therefore it does not seem possible to take these factors into consideration when making calculated estimates.

Analysis of foreign data [1-3] shows that, in the first few years after shutdown of the reactors, in all cases the tritium activity in the graphite was 5-6 times higher than the ^{14}C activity. The results of experimental studies of samples of graphite from AV-2 and ÉI-2 tell the opposite story: the ^{14}C activity is hundreds of times higher than the ^3H activity. This can be explained both by essential differences in the initial composition of the graphite as between domestic and foreign reactors, and also by essential differences in the moderator service conditions.

As a model, experimental data on the ^3H and ^{14}C content in graphite of shut-down reactors at Hanford (USA) [1] were recalculated for AV-2 taking account of the corresponding neutron fluence, mass of graphite, and time lag. The resulting estimates of the mean specific activities of radionuclides are far from the experimental values: $1.6\cdot10^6$ and $3.7\cdot10^5$ Bq/g for ^3H and ^{14}C respectively. Hence it follows that the use of foreign experimental data about ^3H and ^{14}C activity in reactor graphite to estimate their amount in graphite from shut-down domestic reactors can lead to large errors (by a factor of tens).

Thus, obtaining reliable estimates of the activity of radionuclides, particularly tritium, in graphite of shut-down reactors, is possible only on the basis of experimental investigations of samples of reactor graphite.

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