Carbon-14 and Tritium Content in Contaminated Reactor Graphite After Long-Term Storage - 11043

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ABSTRACT

Graphite waste arises from different sources such as moderator and reflector of neutrons in more than 100 nuclear power plants and in many research and plutonium-production reactors world wide. Therefore the characterization and treatment of radioactive graphite became an important issue in respect of its final disposal. This is the subject of a German-Russian collaboration between the Institute for Energy Research, Safety Research and Reactor Technology at the Research Centre Juelich and the Department 5 of the National Research Nuclear University Moscow Engineering Physics Institute (NRNU-MEPhI).

The amount of several radionuclides such as C-14 arising from activation of N-14 in graphite, H-3, Cl-36 etc. must be determined. C-14 is one of the main contributors to the total radioactivity of the irradiated graphite. Furthermore, for the KONRAD repository in Germany wastes containing C-14 are classified according to its volatility. In this investigation, the radioactive inventory of graphite samples take from stacks and sleeves of Russian water-graphite reactors were determined before and after 10-years of storage as well as after additional mechanical treatment (milling).

The comparison of the experimental data for the investigated samples led to the conclusion that the C-14 activity level after 10-years storage is consistent in the frame of the experimental error range (< 20 %). On the other hand, after milling the C-14 activity level in the graphite decreased drastically (15 40 %). Further investigations are necessary before a graphite-treatment process can be developed. For this reason, the investigations will be further accomplished and verified.

INTRODUCTION

Graphite has been widely used as a moderator, reflector in various types of nuclear reactors in Germany, Russia, England, France, USA and other countries. The attractive properties of graphite, so as the low absorption cross section for thermal neutrons, high-temperature strength, stability and thermal conductivity make it suitable for the nuclear reactor industry.

At the end of the reactor life the contaminated graphite and carbon installations are radioactive waste, which requires a special waste management strategy.

The incineration and deep geological disposal are considered as the main waste management options [1, 2]. Disposal in deep geological formation is one of the most probable ways of final contaminated graphite management. However, the large volume of contaminated graphite significantly reduced the cost efficiency of this management route. Incineration is not presently accepted, due to the potential release of ^{14}C unless expensive separation techniques are employed. Therefore, the modern technologies on the preliminary waste treatment should be developed to reduce activity of the contaminated graphite and its volume and prevent the release of the radionuclides.

Moreover, in Germany, LAW and MAW wastes shall be disposed in the final repository mine KONRAd in the near future. Radioactive graphite has to achieve special conditions in order to fullfill the waste acceptance criteria for the disposal. Wastes containing C-14 are classified according to release rates of volatile c-14 from the waste or waste products under operating conditions. Concerning these release rates out of various types of graphite and the chemical form of possibly volatile C-14 a reliable basis of valuation is still missing.
Therefore research activities have been initiated within a German-Russian collaboration.

RESULTS AND DISCUSSIONS

Radioactivity in graphite results from the neutron capture reaction on carbon itself and on impurities like cobalt, iron, lithium, nitrogen, etc. However, during the long term storage the dominant source of radioactivity is ^{14}C radionuclide, which is beta-emitter with the maximal energy of β-spectra in 156,475 кeV, and has half-life of 5730 years.

The basic reactions of the graphite activation with the formation of ^{14}C and ^{3}H radionuclides can be written as following:

$$^{6}_{3}Li(n,\alpha)^{3}_{1}H \xrightarrow[\beta^-]{12.3\,years} {}^{3}_{2}He \qquad \text{(Eq. 1)}$$

$$^{13}_{6}C(n,\gamma)^{14}_{6}C \xrightarrow[\beta^-]{5730\,years} {}^{14}_{7}N \qquad \text{(Eq. 2)}$$

$$^{14}_{7}N(n,p)^{14}_{6}C \xrightarrow[\beta^-]{5730\,years} {}^{14}_{7}N \qquad \text{(Eq. 3)}$$

In graphite, nitrogen is present as an impurity, as a part of air in pores, and as carrier gas during the reactor operating.

In the work [3], the graphite samples with the different density (1.55 – 1.70 g/см^3) were irradiated with the neutron fluence (5*10^{21} neutron/см^2). The pore structure of graphite changes due to the neutron radiation. The porosity value of the irradiated graphite was higher than that for the initial graphite. The total pore volume increases at the average by 16%. The relative volume of the closed pore increases from 0.5 – 1.5% to 4 – 12%, hence the open pore volume decreases significantly.

In the present work, ^{14}C and ^{3}H content in the contaminated graphite has been investigated after storage during 10 and 20 years. The release of ^{14}C and ^{3}H from the contaminated graphite was also studied after fine milling.

The contaminated graphite used in our work was exposed to the prolonged radiation treatment (nearly 30 years) which was finished in 1990. The last 10 years the graphite was kept in the special repository.

The special technology was used for the sampling. The core samples were born from graphite block as shown in Fig. 1. For the following investigation, five samples were cut out from the obtained core with the distance between them in 12 mm. The diameter and thickness of the prepared sample were 8 and 2 mm, correspondingly. The mass of the sample equals 200 mg.

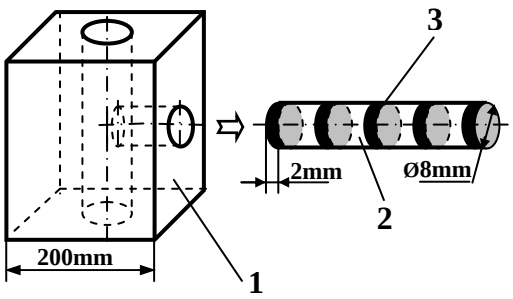

Fig. 1. Sample preparation scheme:
1- graphite block; 2-core; 3-sample

The graphite samples were stored in scientific laboratories under normal (NPT) conditions shrink-wrapped in polyethylene films.

For the determination of ^{14}C and ^{3}H contents in the graphite, the part of a sample (~ 50 mg) was burned in melt with the two-component oxidant comprising V_2O_5 and CuO. ^{14}C and ^{3}H in gas phase were passed through the nitrogen cooler and NaOH-containing trap for the forming of the water-soluble compounds. The traps were washed off the distilled water after full burning of the graphite sample. The ^{14}C recovery factor amounts to 0.95 ± 0.05. The part of the obtained solution was studied in the liquid scintillator for the analysis of the ^{14}C activity. From the residual part of the obtained solution ^{14}C was removed by the vacuum distillation, and ^{3}H activity was measured also in the liquid scintillator.

The first investigations were made in Moscow State Engineering Physics Institute in the years 1997-2001 [4]. The content of the different radionuclides in the contaminated graphite was measured. Moreover, the direct relation between ^{14}C content and the magnitude of the neutron fluence and the uniform distribution of ^{14}C in graphite was found [4]. Last investigations were made in 2010. Some results of this study for the six samples are presented in Table I.

Table I. ^{14}C content in contaminated graphite

Data	Sample №	№ 1	№ 2	№ 3	№ 4
1999/2001	^{14}C content, Bq/g	$(5.0\pm1.0) * 10^5$	$(1.65\pm0.30) * 10^6$	$(1.62\pm0.32) * 10^6$	$(8.0\pm1.6) * 10^5$
2009/2010	^{14}C content, Bq/g	$(4.4\pm0.9) * 10^5$	$(1.60\pm0.35) * 10^6$	$(1.47\pm0.29) * 10^6$	$(9.6\pm1.8) * 10^5$

The precision of ^{14}C content measurement is nearly 10 % (1 σ). Therefore, we can assume that ^{14}C content in the contaminated graphite did not change during the last ten years. The obtained result is important and should be taken into account at the designing of special waste management strategy for the contaminated graphite.

The relative contributions of reactions (2) and (3) to the ^{14}C accumulation in graphite were calculated on the basis of the information on the porosity and with the assumption that the pores are filled up the air. The values of the capture cross sections were estimated by Monte Carlo method with using module SAS2H of the program system SCALE4.4a [5] with taking into account the data on the fuel type, geometrical size of the fuel cell [6-8] and reference data [9]. It was shown that the contribution of the reaction (3) to the ^{14}C accumulation in the contaminated graphite was up to ten times more than that of the reaction (2).

It is known that the full neutron fluence through the graphite components in plutonium-production uranium-graphite (PUGR) reactor during the reactor's life equaled 10^{21}-10^{22} neutron/см^2. Therefore, the value of the ^{14}C accumulation in the contaminated graphite can be estimated from the values of the cross-section of the reaction (3) and from the concentration of the nitrogen in graphite. ^{14}C content in contaminated graphite equals $1.1*10^6$ Bq/g. The estimated and measured values of the ^{14}C accumulation have a good agreement.

Moreover, the release of ^{14}C and ^{3}H from the investigated samples was studied after fine milling. Grained graphite may be used as aggregate in cement used for the infilling of various wastes in radwaste containers (in this case disposal of graphite does not need any additional volume in waste containers).

The experimental results of the ^{14}C and ^{3}H content in the contaminated graphite samples before and after milling for the several samples are presented in Table II.

Table II. ^{14}C and ^{3}H content in the contaminated graphite samples before and after milling

Sample	Condition	^{3}H content, Bq/g	^{14}C content, Bq/g	^{3}H release, %	^{14}C release, %
№ 1	before	---	$4.24*10^{5}$	---	42.7
	after	---	$2.43*10^{5}$		
№ 2	before	$1.02*10^{2}$	$4.27*10^{5}$	13.5	4.4
	after	8.82*10	$4.08*10^{5}$		
№ 3	before	$5.30*10^{3}$	$4.52*10^{5}$	93.3	18.7
	after	$3.56*10^{2}$	$3.67*10^{5}$		
№ 4	before	$6.35*10^{3}$	$8.29*10^{5}$	89.6	28.1
	after	$6.57*10^{2}$	$5.96*10^{5}$		
№ 5	before	$7.57*10^{3}$	$8.96*10^{5}$	81.1	15.4
	after	$1.43*10^{3}$	$7.58*10^{5}$		
№ 6	before	$1.21*10^{3}$	$1.14*10^{6}$	31.3	26.2
	after	$8.31*10^{2}$	$8.42*10^{5}$		
№ 7	before	$2.95*10^{3}$	$1.04*10^{6}$	83.6	32.3
	after	$4.85*10^{2}$	$7.05*10^{5}$		

As shown in Table II, the ^{14}C content in the milled powders decreases at the average by 24 % in comparison with initial samples. After milling, the graphite samples consist of the particles with the characteristic size about 1 μm. Thus, the characteristic size of the graphite particles and porous in initial samples are comparable [10].

The reaction (3) is exoenergic, and kinetic energy of the generated ^{14}C ions equals a few keV. Therefore, these ions can embed and be retained in the graphite crystal lattice, i. e. these radionuclides are in the bonded state in most cases.

Thus, we can assumed that the milling of the contaminated graphite is accompanied by the rupture of the closed pores and the release of the carbon gaseous products (CO, CO_2), including ^{14}C.

The values of ^{3}H content in the investigated samples are characterized by the significant spread in values (see Tables 2) what also takes place in our preliminary investigations [4. 11]. For the reliable estimation of the values of ^{3}H content in the contaminated graphite and its release during the storage and at the mechanical treatments, it is necessary to perform a lot of additional investigations.

CONCLUSIONS

- In the present work, ^{14}C and ^{3}H content in the contaminated graphite, which was irradiated with neutron fluence 10^{21}-10^{22} neutron/см^{2}, after storage during 10 and 20 years was investigated. It was shown that ^{14}C content in the contaminated graphite did not change during the last ten years.
- The additional milling of the contaminated graphite results in decreasing of ^{14}C content at the average by 24 % in comparison with initial samples.

If ^{14}C in spent reactor graphite proves to be volatile above 1 percent of the total ^{14}C content, this would limit the possibility of disposal in the Final Repository KONRAD. Higher amounts of this waste have to remain in the interim storage facilities.

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