CArbon-14 Source Term

CAST

Final evaluation of leach rates of treated and untreated i-graphite from the Rossendorf Research Reactor (D5.12)

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CAST – Project Overview

The CAST project (CArbon-14 Source Term) aims to develop an understanding of the potential release mechanisms of carbon-14 from radioactive waste materials under conditions relevant to waste packaging and disposal in underground geological disposal facilities. The project focuses on the release of carbon-14 as dissolved and gaseous species from irradiated metals (steels, Zircaloys), irradiated graphite and from ion-exchange materials.

The CAST consortium brings together 33 partners with a range of skills and competencies in the management of radioactive wastes containing carbon-14, geological disposal research, safety case development and experimental work on gas generation. The consortium consists of national waste management organisations, research institutes, universities and commercial organisations.

The objectives of the CAST project are to gain new scientific understanding of the rate of release of carbon-14 from the corrosion of irradiated steels and Zircaloys and from the leaching of ion-exchange resins and irradiated graphites under geological disposal conditions, its speciation and how this relates to the carbon-14 inventory and e.g. aqueous conditions. These results will be evaluated in the context of national safety assessments and disseminated to interested stakeholders. The new understanding should be of relevance to national safety assessment stakeholders and will also provide an opportunity for training for early career researchers.

For more information, please visit the CAST website at:
http://www.projectcast.eu

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Final evaluation of the leaching rates of treated and untreated i-graphite from the Rossendorf Research Reactor

Executive summary

Work Package 5 of the EC CAST project considers the behaviour of ^{14}C i-graphite. In particular, the work is focused on understanding the factors determining the release of ^{14}C from irradiated graphite (hereafter “i-graphite") under disposal conditions (including surface disposal facilities and deep geological disposal facilities). In this study, the release of ^{14}C was investigated in model experiments with i-graphite from the Rossendorf Research Reactor (RFR).

For RFR, different storage conditions were investigated by using 1M NaOH as a leaching media to simulate a cementitious media and deionized water (DIW) in order to enable comparison between different experimental facilities within CAST WP5 (for details see D5.4). All experiments were carried out on ambient conditions. In case of RFR graphite different temperature regimes typical for underground disposal (RT and 50°C) were tested.

Previously in the CAST project and in relation to the necessary leaching experiments, the development of an analytical method suitable for the detection of a low activity level fraction of ^{14}C released from i-graphite and its speciation in the gaseous phase has been completed. The method developed allows for the detection of activity levels of ^{14}C relevant for the Waste Acceptance Criteria of Schacht Konrad, where the German i-graphite is supposed to be disposed.

This work demonstrated that the dominant fraction of ^{14}C, i.e. >83%, is released in the form of CO_2, which mostly remains in the leaching solution (DIW or NaOH). Relatively small fractions of volatile CO and/or C_{org} were also detected. The highest fraction of volatile $^{14}CO_2$ is released in i-graphite/DIW systems at 50°C. Simulation of i-graphite behaviour in cementitious media demonstrated that the ^{14}C volatile fraction is strongly retained in the solution, presumably as carbonate. A relatively small fraction of volatile organic ^{14}C-species and/or ^{14}CO was also detected; this fraction was not affected by temperatures up to 50°C. The respective annual release rate for volatile ^{14}C was determined to be 7.3 10^{-3} %/year (if encapsulated in the cementitious material). Referred to the Waste Acceptance Criteria

(WAC) of Schacht Konrad, the limit is $1.8 \cdot 10^{10}$ Bq ^{14}C per container (with respect either to individual containers or the average of a batch of containers), if a release of <1% of the total ^{14}C inventory can be guaranteed during the operational phase of the repository [1]. In other words, this would enable to utilize the maximum permitted highest container loading for i-graphite even without preliminary treatment (e.g. thermal decontamination).

The effect of thermal treatment of i-graphite was shown to selectively separate up to 8% of the ^{14}C inventory. Subsequent leaching tests demonstrated the release rates of volatile ^{14}C below the detection limit of the method. Given that a proper encapsulation of i-graphite in a cementitious material alone may provide for the WAC to be met, a preliminary thermal treatment step of RFR graphite is considered to be unnecessary.

List of content

1. Introduction

According to the current nuclear waste management strategy in Germany, discharged irradiated graphite (i-graphite) will be disposed of in the deep geological repository for low and intermediate level radioactive waste (i.e. waste with negligible heat generation) Schacht Konrad. This requires reliable information on the radionuclide inventory of i-graphite and information about i-graphite behaviour under the conditions relevant to the repository. The former is relatively easy to obtain from routine analyses of i-graphite. However, the latter is concerned with comprehensive investigations of the radionuclide behaviour in i-graphite, namely the understanding of release mechanisms and the availability of reliable models capable of predicting the radionuclide release and transport in the short-and long-term.

^{14}C is a radionuclide of major concern regarding the disposal of i-graphite and. has relatively long half-life (5,700 years). It is a weak β-emitter (156 keV) and if incorporated in the human body may cause internal radiation hazard. ^{14}C can be present in i-graphite in different chemical forms, like elemental C, CO_2 or organic C species, which have different retention behaviour in i-graphite. Besides that, a partitioning of released ^{14}C between gaseous phase and aqueous solution ubiquitous for the underground repository may be affected by a number of factors, e.g. pH, temperature, salinity etc.

The main objective of the present work is to investigate the release of ^{14}C from i-graphite under conditions relevant to the repository Schacht Konrad and the effect of an upstream decontamination by thermal treatment on the behaviour of the labile ^{14}C fraction in i-graphite. The conditions of thermal treatment were selected based on the methods developed within the EU project CARBOWASTE. Different destructive (total incineration, LCS) and non-destructive (autoradiography, SEM) techniques were used to characterize the i-graphite. The kinetics of ^{14}C release from i-graphite and the corresponding speciation of volatile ^{14}C-species were investigated in order to answer the question, whether and to what extent German i-graphite can be disposed of in Schacht Konrad.

2. Experimental part

2.1. Sampling of i-graphite

The irradiated graphite for leaching tests and thermal treatment was sampled from the block 4 of the head part of thermal column of the Rossendorf Research Reactor (RFR, see Figure 1A) [2]. The block was cut into plates of 3 cm thickness resulting in 10 plates in total. Plates No. 5 and 6, which correspond to a distance of 15 cm from the reactor core, were selected for further sampling. The samples for leaching tests were taken in form of cylinders of 30 mm height and 25 mm diameter. The positions and labelling of the i-graphite samples for the leaching tests are given in Figure 1B.

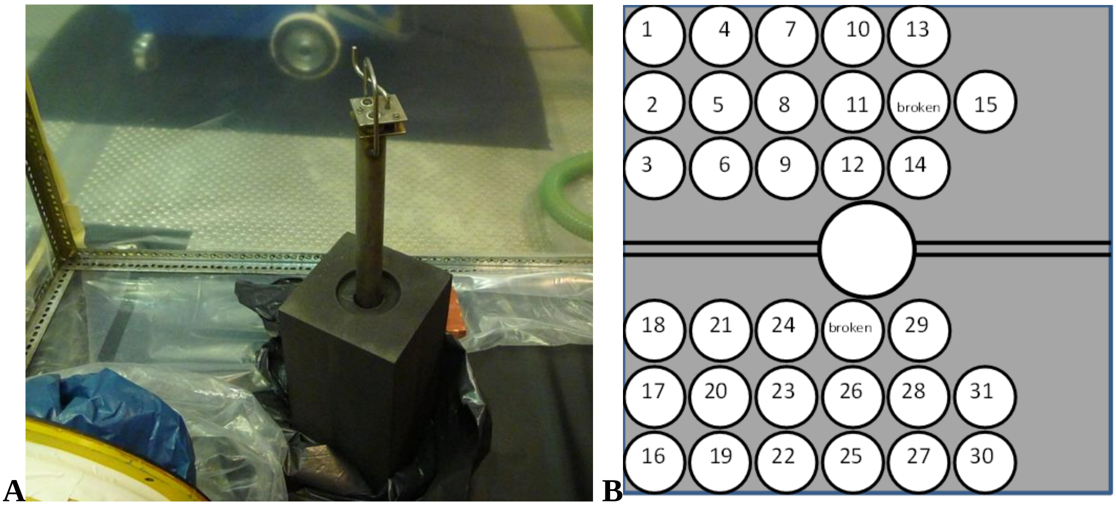

Figure 1: The sampling of irradiated nuclear graphite from Research Reactor Rossendorf: (**A**) - Block 4 taken from thermal column (TC); (**B**) - sampling positions on plates 5 and 6.

2.2. Pre-leaching characterization of i-graphite

Characterization of graphite samples was performed using γ-spectrometry, autoradiography, scanning electron microscopy (SEM) and total oxidation technique.

The inventory of activation products (APs) in i-graphite was evaluated by means of γ-spectrometry. For that, a semi-conductor coaxial HPGe detector (Type PGC 2018) with beryllium window (Model Gr3018 by Canberra) was used (voltage +2500 V). The spectra were acquired for 24 hours. The evaluation of the spectra was performed using GammaVision software (ORTEC). As a 30 x 25 mm sample cannot be considered as a point source, the detection efficiency was evaluated in a separate test (see Figure 2).

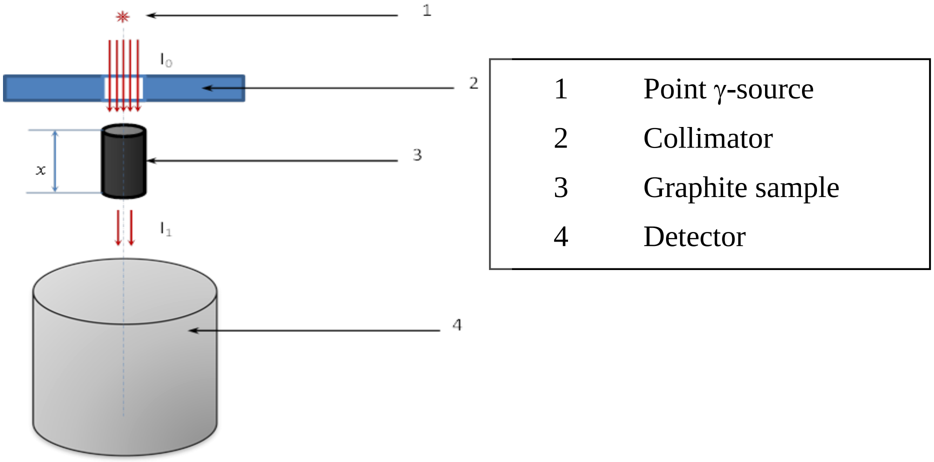

Figure 2: A method for the evaluation of absorption coefficients μ.

The correction factor of self-absorption, K_{sa}, was evaluated using Equation 1:

$$K_{sa} = \frac{\mu\rho x}{1 - e^{-\mu\rho x}} \qquad \text{(Eq. 1)}$$

where x – sample thickness; ρ – density of graphite; μ - linear absorption coefficient (independent on the material and γ-energy).

As the density of i-graphite may vary, the linear absorption coefficient was calculated using Equation 2. For that, as follows from Figure 2, a graphite sample was placed 20 cm above the detector. Above the sample, a ^{152}Eu point source was positioned. Between the sample and the ^{152}Eu source, a collimator with known window width was installed, in order to define the initial intensity of specific γ-lines of ^{152}Eu. Measuring the initial intensity of a γ-line at energy E ($I_{0,E}$) and the intensity of the same γ-line with energy E transmitted through the graphite sample ($I_{1,E}$), the linear absorption coefficient μ of γ-radiation at the defined energy E can be calculated (Equation 2).

$$\mu_E \rho = \frac{-\ln\left(\frac{I_{1,E}}{I_{0,E}}\right)}{x} \qquad \text{(Eq. 2)}$$

where $I_{0,E}$ – initial intensity of a γ-line with energy E; $I_{1,E}$ – intensity of a γ-line with energy E, measured behind the sample.

Figure 3 represents the linear absorption coefficient, a material and geometry specific parameter, as a function of energy measured for an ^{152}Eu-standard (a point source) in the energy region of 121.8 – 1408 keV.

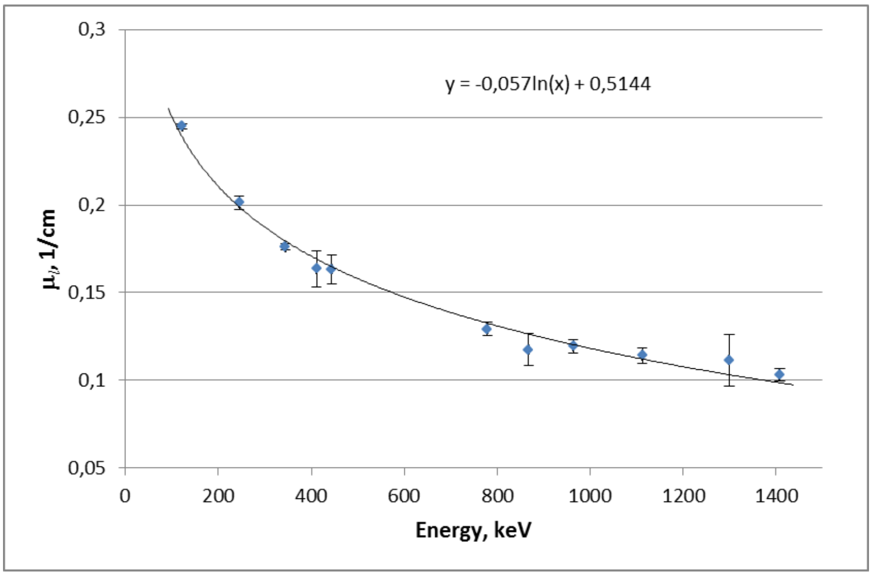

Figure 3: The dependence of a linear absorption coefficient on γ-Energy.

For autoradiography, the samples were selected to cover graphite from the center as well as the periphery of the plate exposed to different neutron fluxes, i.e. RFR-7, RFR-11, RFR-17, RFR-5 and RFR-29. Autoradiography was carried out with sensitive plates and following scanning of the plates with a CR-35 image scanner (Raytest, Germany). The image data analysis program AIDA (Raytest, Germany) was used for data evaluation. The contact time varied from 3.5 to 5 hours, which allows for a scan resolution of 50 µm.

The microstructure of i-graphite was investigated by SEM with energy dispersive X-Ray spectroscopy (EDX) using a Quanta 200 FEG instrument (FEI Comp.) coupled to an EDX-Modul (EDAX, Inc.).

Quantification of the total inventory of ^{14}C was carried out by the incineration method. Quantification was carried out using the graphite powder collected during the drilling of cylindrical graphite samples. The powder was thoroughly mixed and three random batches of ca. 1.5 g (hereafter S1 – S3) were i-graphite from RFR were taken and incinerated in the setup shown in Figure 4.

Figure 4: Experimental setup used for the quantification of total ^{3}H and ^{14}C inventories in i-graphite.

A sample of ca. 1.5 g is placed in the quartz tube and positioned in the oven. The quartz tube is coupled to an oxygen line on the one side and connected to a sequence of three washing bottles (WBs, 200 mL each) on the other side. Incineration is performed for 2 hours at 800°C. A stream of oxygen of 6 mL/min is used for oxidation of graphite, as well as carrier gas to bubble the resulting products $^{14}CO_2$ and $^{3}H_2O$ through the WBs. The first WB is filled with 0.1 M HNO_3, which retains ^{3}H as ^{3}HHO and ^{36}Cl as chloride; in the second WB is 4 M NaOH for retaining $^{14}CO_2$ as $Na_2{}^{14}CO_3$. The third WB is used as a control, in order to provide for a quantitative retention of ^{14}C. After the incineration is over, the aliquots from WBs1 and WB2 are sampled and analyzed by Liquid Scintillation Counting (LSC) for the quantification of ^{3}H and ^{14}C, respectively.

2.3. Leaching tests

Figure 5 demonstrates the vessels used for the leaching tests. These are specially designed reactors (Berghof GmbH, Germany) and glass bottles equipped with a valve for gas sampling. Both setups allow for controlled heating of the system up to 70°C and regular stirring. The Berghof-system is also equipped with two additional valves for separate sampling of gas phase and aqueous phase. The leaching tests were run in parallel, in order to enable a comparison of i-graphite leaching behaviour with respect to various conditions within the available project time.

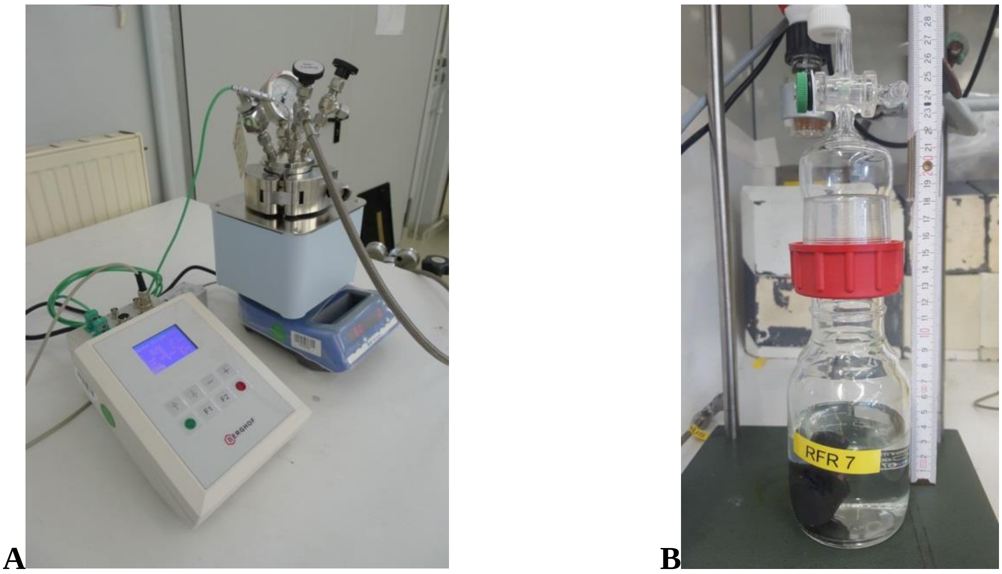

Figure 5: Vessels for leaching test with i-graphite: (**A**) an assembled reactor vessel (Berghof GmbH), (**B**) a glass bottles.

A sample of RFR i-graphite of known mass was put into 150 mL of DIW or a solution of 1 M NaOH (mimicking a cementitious environment); the reactor was sealed and left at constant temperature, i.e. RT or 50°C. All experiments were carried out at ambient atmospheric conditions (i.e. air as a gas phase and atmospheric pressure). Table 1 summarizes the main parameters used in the leaching tests. In order to evaluate the reproducibility of the results, two graphite samples (i.e. RFR-23 and RFR-28) were exposed to the same conditions.

Table 1: Parameters of the leaching tests with non-treated i-graphite from RFR.

Sample	Sample mass, g	Leaching solution	Leaching solution mass, g	Gas volume, mL	Duration, days
RFR-7	23.7	H_2O	149.0	51	139
RFR-11	23.3	H_2O	147.0	53	138

RFR-17	23.1	NaOH 1 M	153.3	59	137
RFR-23	22.698	NaOH 1 M	154.7	58	131
RFR-28	21.9	NaOH 1 M	154.3	58	103

The systems, i.e. gas phase and solution, were regularly sampled in order to analyze the gas phase and the solution composition. For that, a gas sample of 3 mL was taken in a gas-mouse (see Figure 6) and analyzed using a Gas-Chromatography (GC) system SiCHROMAT-2 (Siemens). This system is equipped with two chromatigraphic columns, Porapack and Molsieb, connected via a life-switch, and a thermal conductivity detector. Ar was used as a carrier gas. Generally, the main air components, i.e. N_2, O_2, CO, CO_2, and simple volatile organic compounds (e.g. CH_4) were quantified in the gas phase. The detection limits for corresponding permanent gases are listed in Table 2.

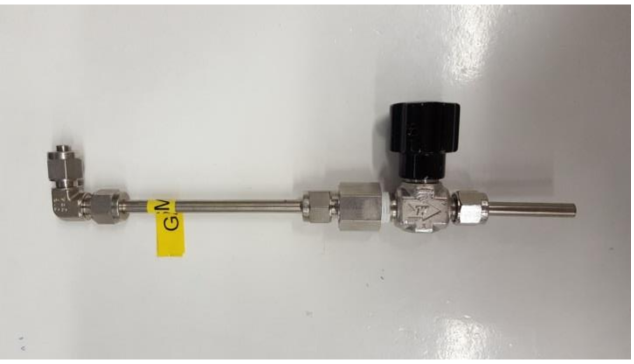

Figure 6: A gas-mouse used for sampling of the gas-phase during leaching tests with nuclear graphite.

Table 2: Detection limit of SiCHROMAT-2 GC for some permanent gases.

Component	H_2	N_2, CO_2, CH_4	O_2
Detection limit, Vol.-%	0.01	0.03	0.15

Total ^{14}C release into the gas phase and the speciation of ^{14}C volatile species were determined using a specifically designed setup for ^{14}C and ^{3}H fractionation, shown in Figure 7. The reactor with a graphite sample (1) is connected to an Ar-line on the one side (not shown, Ar used as a carrier gas) and WBs-line on the other side. The system includes 8 working WBs (3, 5, 9, 11), 3 control WBs (4, 8, 10) and a catalytic oven (7) with a quartz tube filled with CuO as a catalyzer. WBs 3 and 9 are filled with 4 ml 0.1 M HNO_3 to collect mainly HTO, whereas WBs 5 and 11 are filled with 4 ml of 2 M NaOH to absorb $^{14}CO_2$. If $^{14}CO_2$ or ^{3}HHO are present in the system, they are absorbed in WBs 3 and 5 respectively as H_2O and $Na_2{}^{14}CO_3$. Species like H_2 (or ^{3}HH), ^{14}CO or $^{14}C_{org}$. are not quantitatively absorbed in the acidic or basic solution, therefore they are oxidized in the catalytic oven at 800°C to $^{14}CO_2$ or ^{3}HHO and are absorbed in WBs 9 and 11 respectively. The flushing of volatile ^{3}H and ^{14}C compounds is considered to be complete within 4 hours; the solutions from WBs 3, 5, 9 and 11 are then removed and analyzed by LSC for quantification of ^{3}H and ^{14}C.

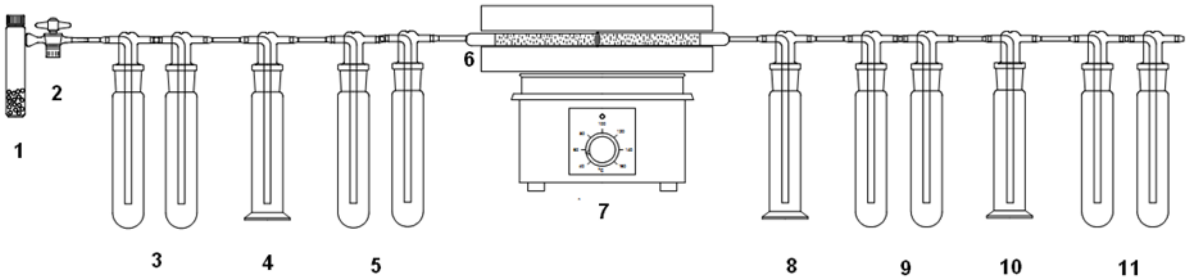

Figure 7: Experimental setup for fractionation of ^{3}H and ^{14}C in the gas phase.

1 – reactor vessel with graphite sample, 2 – gas-valve, 3 and 9- WBs with 0.1 M HNO_3, 4, 8, 10 – control WBs, 5 and 11 - WBs with 2 M NaOH, 6 – quartz tube with CuO catalyst, 7 – a catalytic oven.

After the analysis of the gas phase, the reactor vessel was opened and the aqueous phase was sampled for quantification of ^{14}C dissolved in the leachate (using LSC) as well as to account for the release of other γ-emitters into solution (using γ-spectrometry). Speciation of ^{14}C in the solution was not carried out.

2.4 High temperature treatment of i-graphite

The treatment of RFR i-graphite was carried out at 1300°C in Ar over a period of 19 hours. These conditions were earlier reported to be the most effective for a selective removal of ^{14}C from irradiated graphite with a relatively low mass loss of graphite [3]. During the treatment, the amount of released ^{14}C into the gas phase was controlled using the sequence of WBs described in chapter 2.3. Simultaneously the mass loss was controlled by weighing the sample after the treatment. The results are presented as a plot of relative ^{14}C release vs. the mass loss of the graphite sample.

2.5 Data evaluation

Evaluation of the results was carried out according to D5.4 “Definition of the scientific scope of leaching experiments”. Namely, the release kinetics was quantified as cumulative release fraction; F_n is represented by the released fraction calculated over the exposure time t (see Equation 3).

$$F_n = \frac{\sum a_n}{a_0} \cdot 100\% , \qquad \text{Eq. (3)}$$

where:

F_n - is a dimensionless cumulative leaching fraction in the n-step of an experiment,
a_o – the total initial activity of ^{14}C in the i-graphite sample, in Bq,
a_n - the activity of ^{14}C released in the n-step, in Bq.

Besides that, a release rate R_n was evaluated using Equation (4):

$$R_n = \frac{a_n \cdot V}{a_o \cdot S \cdot t_n} = K \cdot \frac{a_n}{a_0 \cdot t_n} , \qquad \text{Eq. (4)}$$

where, besides above mentioned:

V – is the volume of an i-graphite sample, in cm^3,
S - is the geometrical surface of the i-graphite sample, in cm^2,

K - is a characteristic constant equal to V/S ratio, in cm.

Given that all graphite specimens have the same geometry, a value of *K*=0.44 cm was applied for all samples used in the leaching experiments.

3. Results and discussion

For the disposal of ^{14}C-bearing waste in Konrad, the release rate must be evaluated within the safety analyses by means of leaching tests [4]. The total ^{14}C activity being allowed for Konrad is $4{\cdot}10^{14}$ Bq. With an overall storage capacity of 303,000 m^3 this results in $1.32{\cdot}10^{9}$ Bq/m^3, as an average. Most restrictive ^{14}C limits arise from safety issues for internal operation and are classified based on annual release of volatile ^{14}C from the waste container, which must not exceed 1% of the total ^{14}C inventory. This provides the limit of $1.8{\cdot}10^{10}$ Bq per container or about 22,000 waste-containers will be needed to accommodate the allowed total ^{14}C activity of $4{\cdot}10^{14}$ Bq.

A number of leaching and storage tests aimed at ^{14}C release have been carried out in the past. In most of these tests graphite powder was used, in order to obtain a measurable amount of released ^{14}C and to reliably estimate the annual release rates. The release of ^{14}C from i-graphite can be considered to be divided into two main stages: (1) release from the external graphite-water (or graphite-air, in case of the storage experiments) interface and (2) release from the open porosity of the graphite bulk. The first process is presumably faster, as the ^{14}C weakly bound to the interface (i.e. physisorbed) becomes immediately exposed to the leaching solution (or atmosphere). The second process is much slower, as it is mediated by the infiltration of the leaching solution into the open pore system of the graphite bulk. To some extent oxygen dissolved in the leaching solution may contribute to the release in this stage by oxidation of covalently bound ^{14}C. It is important to mention that a fraction of ^{14}C is ‘sealed’ in the closed porosity, which is unlikely to be leached at all, as this area is not accessible to the leaching solution. Due to the slow kinetics steady-state conditions were not reached in any of the tests; it was therefore not possible to quantify the fraction of accessible volatile ^{14}C in i-graphite. Therefore, in the interpretation of the results of the leaching tests the volatile ^{14}C fraction released is always referenced to the total ^{14}C inventory determined by the total incineration in the preliminary i-graphite characterization.

The graphite powder used in the previous experiments normally provides for a larger contact area for the leaching solution to interact with the interfacial ^{14}C, therefore by definition results it overestimated release rates, compared to the graphite blocks. The saturation of relatively small particles of i-graphite with leaching solution also proceeds faster than that of a massive i-graphite sample, providing a reason for the faster release of the bulk ^{14}C from powdered or crushed samples. This is why the tests with powdered graphite sample may result in facilitated release of ^{14}C and overestimate the annual release rates. Therefore, in the present study, we have selected massive monolithic samples (30 x 25 mm) in order to approach the real conditions in the repository and allow for more realistic insight into the release process in massive blocks of i-graphite in the waste packages. The release kinetics of ^{14}C described hereafter addresses the behaviour of ^{14}C when graphite is encapsulated in a cementitious matrix and exposed to conditions relevant to the Konrad repository (ambient atmosphere and pressure, T<50°C). A characterization of i-graphite (i.e. radionuclide inventory and microstructure) was carried out prior to the leaching tests, in order to enable the quantification of the released fractions of ^{14}C and other radionuclides.

3.1 Characterization of i-graphite from RFR

Quantification of the total ^{14}C inventory in the graphite is only possible using the total incineration method. Due to the inhomogeneous distribution of ^{14}C in i-graphite, an average ^{14}C inventory was evaluated by analyzing three different RFR-graphite samples (S.1 – S.3). The results of the ^{14}C quantification are shown in Table 3. The results variability calculated from three independent measurements comprised 17.4%. The average specific activity of $(1.21\pm0.21)\cdot10^4$ Bq/g was used to quantify the release rates of ^{14}C during the leaching tests irrespectively from the sampling position.

Table 3: Inventory of ^{14}C in i-graphite from RFR.

Radionuclide	Activity in S.1, Bq/g	Activity in S.2, Bq/g	Activity in S.3, Bq/g	Average, Bq/g
^{14}C	$1.06 \cdot 10^4$	$1.45 \cdot 10^4$	$1.13 \cdot 10^4$	$(1.21 \pm 0.21) \cdot 10^4$

Besides ^{14}C, a number of other activation products (APs) may be present in i-graphite in different amounts. These were quantified by direct γ-spectrometric analysis of i-graphite (see Table 4). Generally, the overall activity of γ-emitting isotopes was relatively low. The main source of γ-radiation is ^{60}Co. Some traces of ^{137}Cs and Eu isotopes are measurable. The isotopes ^{134}Cs and ^{133}Ba, which are normally present in i-graphite, were completely decayed within the storage time.

It should be noted that the activity distribution in the i-graphite is not uniform, mainly as a consequence of deviations in the neutron flux. As an example, Figure 8 depicts the distribution of the specific activity of ^{60}Co in the graphite plate. Here the ^{60}Co activity increases in the direction from top to bottom (vertically) and from left to right (horizontally), corresponding to the variation in the neutron flux in the reactor. As the distribution of ^{14}C in graphite linearly depends on the neutron flux, the ^{60}Co-mapping was used for the selection of the samples presumably more enriched in ^{14}C, e.g. samples RFR-17, RFR-27, and RFR-28. These samples may provide for a better confidence in the detection of ^{14}C activity during the leaching experiments.

Table 4: Results of γ-spectrometric characterization of i-graphite (TC) from RFR: block 4, plate 5 (only samples which were further investigated are shown).

Sample	Sample mass, g	Radionuclide inventory, Bq/g					
		^{152}Eu	^{154}Eu	^{155}Eu	^{137}Cs	^{60}Co	^{133}Ba
5	23.630	0.93	1.97	bdl	3.93	15.32	bdl
7	23.629	0.42	1.97	bdl	2.38	27.42	0.30
11	23.257	0.55	1.95	bdl	4.56	16.56	0.38
17	23.092	2.69	3.38	bdl	1.07	50.20	bdl
23	22.698	1.43	4.23	bdl	3.34	26.48	bdl
25	22.548	2.52	8.46	0.81	3.17	90.78	0.51

Sample	Sample mass, g	Radionuclide inventory, Bq/g					
		^{152}Eu	^{154}Eu	^{155}Eu	^{137}Cs	^{60}Co	^{133}Ba
27	22.149	2.09	8.79	0.74	1.71	112.77	0.41
28	21.949	0.99	6.79	0.80	2.25	36.16	0.36
29	22.188	0.84	4.81	0.59	2.78	39.68	0.58
30	21.990	2.09	10.79	1.42	2.70	141.28	1.55

*bdl – below detection limit: DL(^{155}Eu)=0.5 Bq/g, DL(^{133}Ba)=0.1 Bq/g

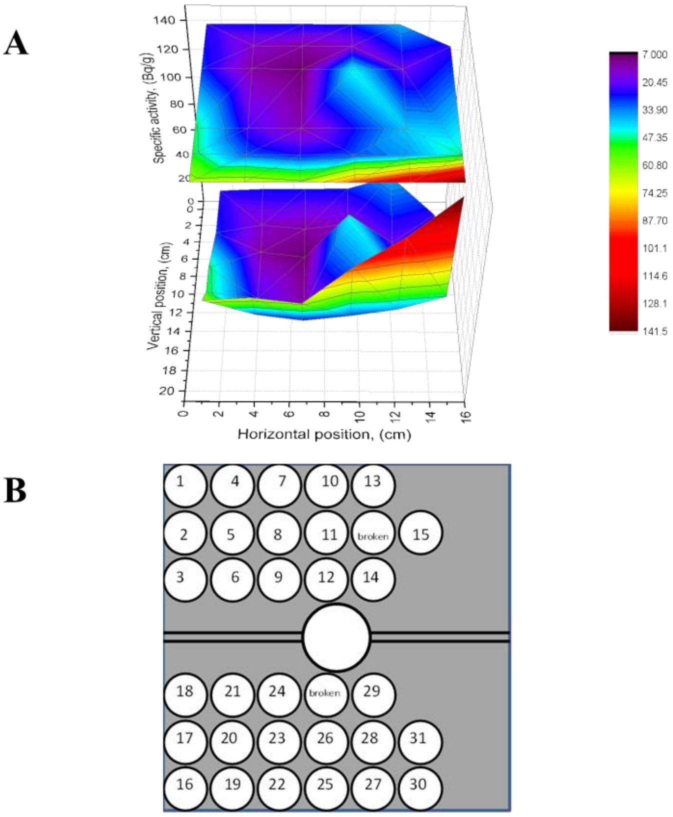

Figure 8: Distribution of the specific activity of ^{60}Co in irradiated nuclear graphite from RFR correlated to the sampling positions (block 4, plate 5, ca. 15 cm from the reactor core).

Former studies demonstrated that the distribution of APs in i-graphite is inhomogeneous and APs are usually present in the form of hot-spots [4]. For a more detailed investigation of the AP distribution in RFR graphite, a few samples were analyzed by autoradiography (e.g. RFR-7, RFR-11, RFR-17, RFR-5 and RFR-29). This non-destructive method allows for a rather quick determination of the spatial activity distribution and the identification of hot-spots. The method is sensitive to the radionuclides present in i-graphite, however it does not allow the qualitative or quantitative analysis of the hot-spot in voluminous samples.

Therefore, an SEM equipped with EDX was used for the investigation of hot-spots with higher precision. The results of the autoradiography given in Figure 9, demonstrated the presence of hot-spots in every investigated graphite sample, with. The contrast to the background indicating the degree of activation. White inclusions on the images are shielded areas from a copper tape, used for indication and localization of the hot-spots.

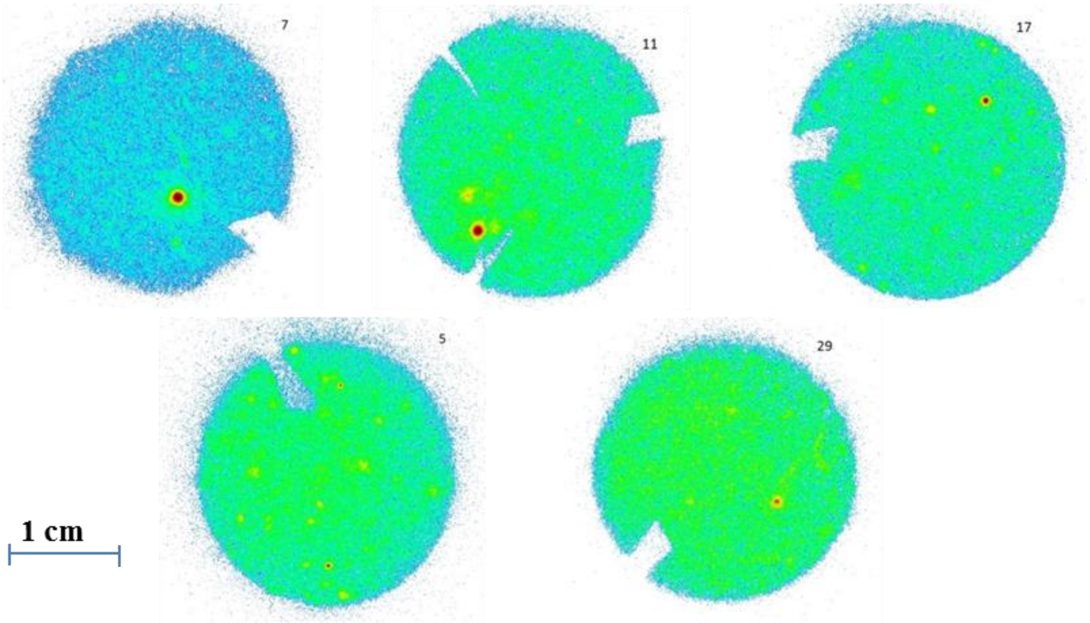

Figure 9: Autoradiography images of i-graphite samples from RFR; the colour other than blue corresponds to the activity above the background; red colour corresponds to the regions with the highest activity, white regions – Cu-markers.

For hot-spots found by an autoradiography (Figure 10A), EDX was performed to investigate their elemental composition. The results are shown in Figure 10B and C. It seems that most of radionuclides, detected by autoradiography, is concentrated in the pores.

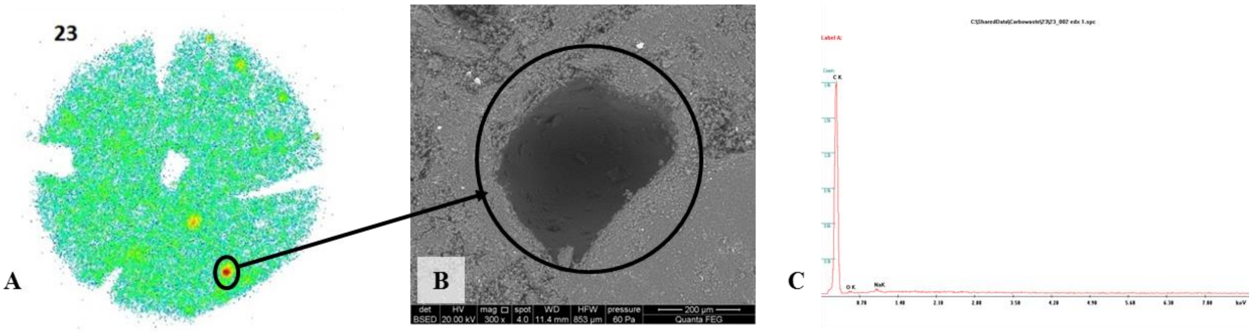

Figure 10: Graphite hot-spots characterization with autoradiography/SEM/EDX: (A) – autoradiography image, (B) - SEM image of the hot-spot area, (C) - EDX spectrum.

The result of EDX investigation of elemental composition in the hot-spot region clearly show no impurity other than a carbon, which may indicate that the increased activity in these areas was due to radioactive ^{14}C bound to the surface of the pore. This result was consistently observed in all graphite samples and is in a good agreement with the assumption that the highest fraction of ^{14}C inventory originated from the activation of ^{14}N (via $^{14}N(n,p)^{14}C$ reaction) or ^{17}O (via $^{17}O(n,\alpha)^{14}C$ reaction), trapped in the pores or absorbed on the pore surface. The ^{14}C activated from ^{13}C (via $^{13}C(n,\gamma)^{14}C$ reaction) would be uniformly distributed in the graphite, and therefore cannot be the reason for hot-spots, but would rather contribute to the background on the autoradiography images, as demonstrated in Figure 9 (e.g. samples RFR–7 and RFR–29).

3.2 Leaching behaviour of i-graphite

The results of the current leaching tests show the effect of elevated pH and temperature on the release kinetics of ^{14}C from i-graphite. Figure 11 shows the cumulative release fraction of volatile ^{14}C as a function of time in DIW (opened symbols) and in 1M NaOH (filled symbols) at room temperature. Different species of ^{14}C, like CO_2 or CO/C_{org}, were distinguished in the gas phase. As it was technically impossible to differentiate between CO and volatile organic species, a sum fraction of these species ($CO+C_{org}$) is shown on the graph. The results are summarized in Table 5.

Over the given exposure time of ca. 140 days, the total release of volatile ^{14}C from DIW at RT is $8.9 \cdot 10^{-3}$%, which is more than 3 times higher than from NaOH ($2.6\ 10^{-3}$%) at this temperature. In the volatile fraction released from an i-graphite/DIW system, the fraction of $^{14}CO_2$ prevails ($7.35 \cdot 10^{-3}$%), whereas the detected CO+C_{org} fraction is much lower, $1.5 \cdot 10^{-3}$%. In the system with NaOH, the release of $^{14}CO_2$ is much lower ($1.28 \cdot 10^{-3}$%) and very similar to the CO+C_{org} fraction ($1.28 \cdot 10^{-3}$%). The fractions of volatile CO+C_{org} released in systems with water and NaOH are rather similar, i.e. around $1.5 \cdot 10^{-3}$%.

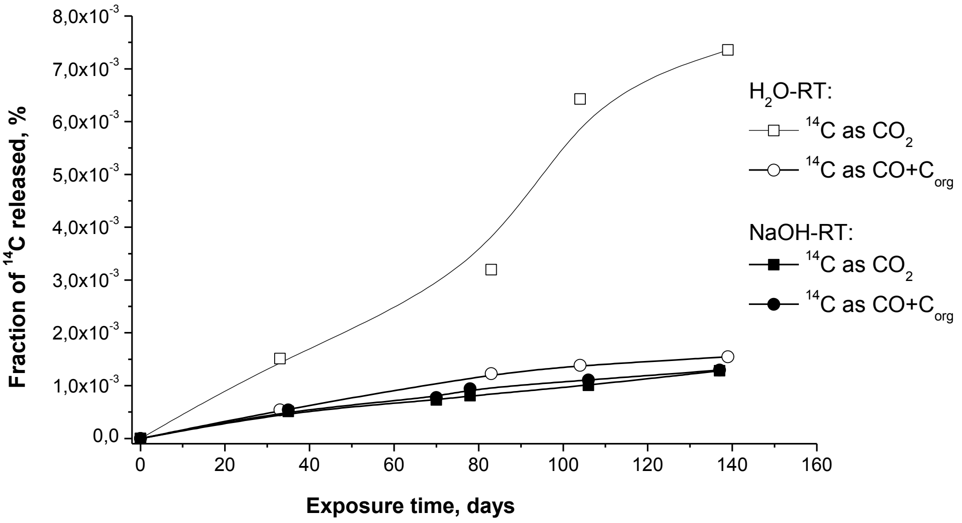

Figure 11: Kinetics of ^{14}C release from RFR-graphite at RT: in DIW (opened symbols) and in 1 M NaOH (filled symbols).

The fractions of non-volatile ^{14}C species released in DIW and NaOH at RT (i.e. ^{14}C in the leachates), are significantly higher than the respective volatile fractions (Table 5). Thus, the dominant fraction of ^{14}C leached from i-graphite remains in the solution. Here the higher amount of ^{14}C remains in the basic solution presumably in form of $Na^{14}CO_3^-$ and $^{14}CO_3^{2-}$ species in form of $H^{14}CO_3^-$ than in DIW at neutral pH. This consistently determines the lower volatile ^{14}C fraction from the i-graphite/NaOH system compared to the i-graphite/DIW system.

Table 5: Cumulative fractions of ^{14}C (in %) released into the leaching solution and the gas phase respectively (t=140 d).

Conditions	H_2O/RT	NaOH/RT	H_2O/50°C	NaOH/50°C
Gas phase	$8.9 \cdot 10^{-3}$	$2.6 \cdot 10^{-3}$	0.09	$8.9 \cdot 10^{-3}$
Solution	0.16	0.65	0.43	1.04

The release of volatile ^{14}C at 50°C is shown in Figure 12. Leaching in the DIW system at elevated temperature results in a total volatile ^{14}C fraction of 0.09 %, which is more than an order of magnitude higher than the respective release under RT conditions ($8.9 \cdot 10^{-3}$%). Speciation of volatile ^{14}C has shown that this increase is mainly due to CO_2 release, whereas the fraction of $CO+C_{org}$ is not significantly affected by the temperature increase. This behaviour is consistent with the decrease of CO_2 solubility in DIW with the temperature [5], however can be also explained by the higher release rates of volatile ^{14}C compared to the RT. In contrast to the system with DIW, the total release of volatile ^{14}C-spiecies in leaching experiments in NaOH is slightly lower ($1.3 \cdot 10^{-3}$%) than the respective release at RT. The resulting speciation of ^{14}C in the gas phase indicated almost equal fractions of CO_2 and $CO+C_{org}$ similar to the RT experiments. Examination of the leaching solution demonstrated a rather high concentration of dissolved ^{14}C (1.04%), presumably in form of carbonate. Thus, it can be concluded that the release of volatile ^{14}C is generally higher in DIW and increases with the temperature. Besides that application of NaOH as a leaching solution results in the higher fraction of ^{14}C being absorbed in the aqueous phase.

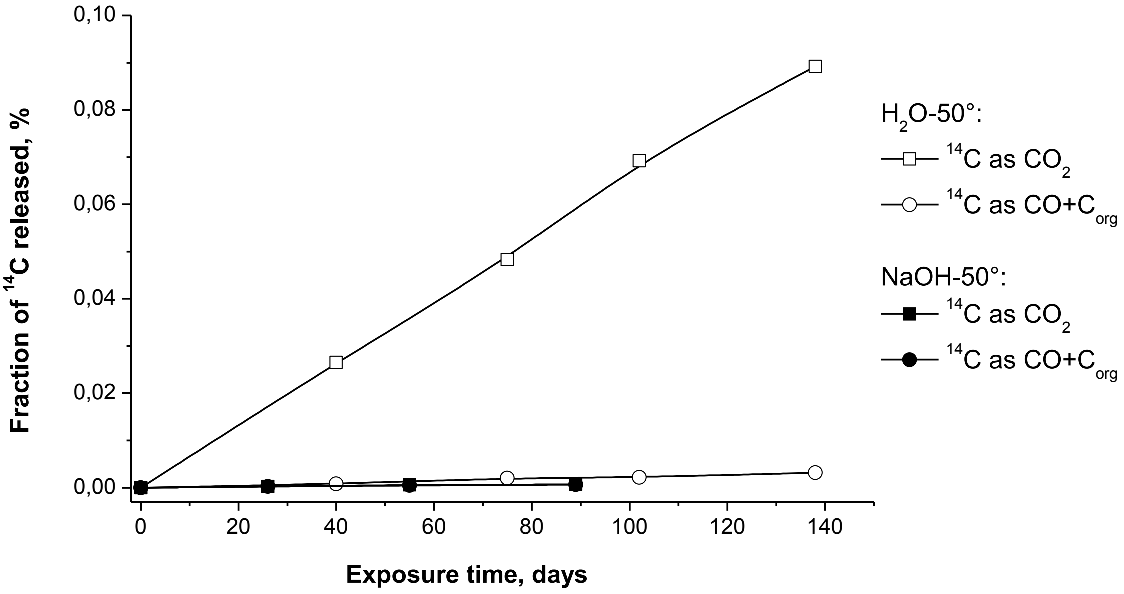

Figure 12: Kinetics of volatile ^{14}C release from RFR-graphite at 50°C: in DIW (opened symbols) and in 1 M NaOH (filled symbols).

The results of GC-analysis of the gas phase present over the leaching solution are given in Table 6. In all cases the oxygen concentration was found to deviate from that in air (20,9%). This is indicative of oxidation processes occurring in the systems, where the oxygen is consumed: the lower the O_2 concentration in the gas phase, the more extensive the oxidation of graphite is to be expected. Thus, the most extensive oxidation occurred in i-graphite/NaOH system at 50°C. This correlates with the highest inorganic ^{14}C content in the corresponding leaching solution (see Table 5). The concentration of other components, like CO or CO_2 in the gas phase, was determined to be below the detection limit (DL).

Table 6: Composition of the gas phase in the leaching tests.

Gas component	Relative concentration, vol. %			
	Water/RT	Water/50°C	NaOH/RT	NaOH/50°C
N_2	79.66	79.35	79.44	81.52

O_2	4	20.65	20.56	18.48
CO_2	<DL	<DL	<DL	<DL
CO	<DL	<DL	<DL	<DL

The obtained release fractions of volatile ^{14}C were subsequently used for the evaluation of the release rate R_n of ^{14}C (see Figure 13). The highest release rate was found for the i-graphite/DIW system at 50°C. Significantly lower is the R_n for i-graphite/water at RT. For both i-graphite/NaOH systems, the release rate was found to vary insignificantly. Hence, it can be concluded that the release of volatile ^{14}C from untreated i-graphite can be considerably retarded if i-graphite is encapsulated in some kind of cementitious environment.

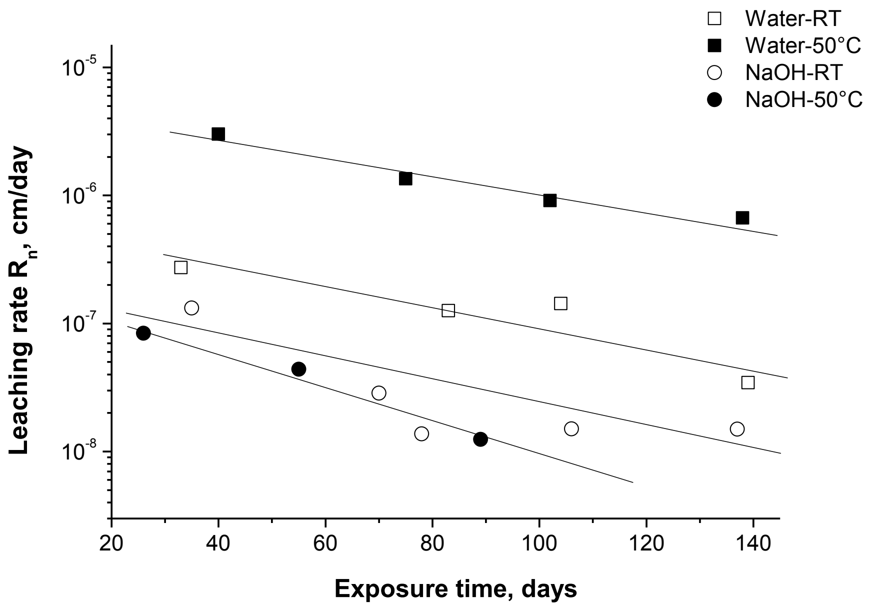

Figure 13: Release rate R_n of ^{14}C from RFR i-graphite in DIW and NaOH at RT and 50°C.

In order to assist the attainment of a conclusion about the disposability of i-graphite, to choose associated appropriate treatment steps (if required) and to select a suitable packaging approach, the annual release rates (RR) for ^{14}C are evaluated and compared to requirements from the Waste Acceptance Criteria (WAC) for the repository Schacht Konrad [6]. The corresponding values are summarized in Table 7. It is obvious that, in a case of i-graphite/NaOH system, which mimics the i-graphite encapsulation in cementitious material, the annual RR of ^{14}C does not exceed 0.1%.

Table 7: The annual RR for ^{14}C from RFR graphite, in %/year.

Radionuclide	i-graphite/water		i-graphite/1M NaOH		WAC
	RT	50°C	RT	50°C	
^{14}C	$2.56\cdot10^{-2}$	$2.56\cdot10^{-1}$	$7.3\cdot10^{-3}$	$6.9\cdot10^{-3}$	<1

A demonstrated RR of <1% provides for the highest allowed ^{14}C loading of RFR graphite, i.e. $1.8\cdot10^{10}$ Bq per container, which corresponds to 22,000 containers with i-graphite to be disposed of in Konrad with the total allowed ^{14}C activity of $4\cdot10^{14}$ Bq.

Various other radionuclides were also detected in the leaching solution. Their concentrations are summarized in Table 8. Only ^{137}Cs was systematically found in each sample, whereas ^{60}Co was detected only during leaching in NaOH at 50°C. No isotopes of Eu were detected in any leaching solution.

Table 8: Concentration of other radionuclides in the leaching solution after 140 days of leaching test.

Sample	**Specific activity, Bq/g**			
	^{60}Co	**^{137}Cs**	**^{152}Eu**	**^{154}Eu**
RFR-7 (H_2O, RT)	<DL	$(8.01\pm1.2)\cdot10^{-2}$	<DL	<DL
RFR-11 (H_2O, 50°)	<DL	$(64.4\pm4.4)\cdot10^{-2}$	<DL	<DL
RFR-17 (NaOH, RT)	<DL	$(11.5\pm1.2)\cdot10^{-2}$	<DL	<DL
RFR-28 (NaOH, 50°)	$(48.7\pm2)\cdot10^{-2}$	$(53.85\pm3.2)\cdot10^{-2}$	<DL	<DL

3.3 The effect of thermal treatment on the release of ^{14}C

The release of ^{14}C from i-graphite during thermal treatment was investigated under inert conditions at 1300°C. These conditions were earlier reported to be the most favourable regarding the selectivity of ^{14}C removal [3]. Figure 14 shows the results of the thermal treatment of i-graphite from RFR. The three independent tests on i-graphite treatment demonstrated a rather good reproducibility of the results. The results show that a selective separation of a ^{14}C fraction of 5.5 – 8 % can be achieved at rather a small mass loss of 0.4%.

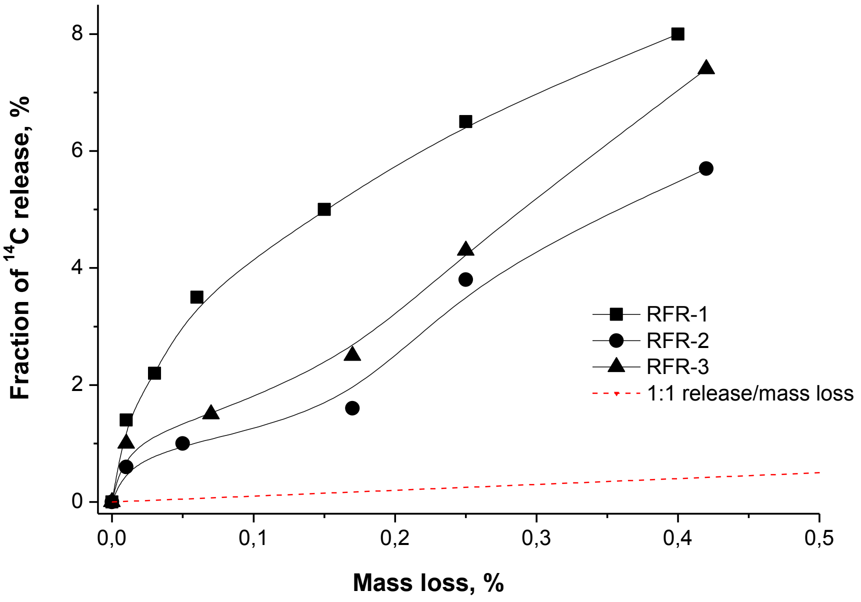

Figure 14: Dependence of ^{14}C fraction released during thermal treatment of RFR i-graphite on respective mass loss. Treatment conditions: carrier gas - Ar, 1300°C. Dashed line corresponds to 1:1 ^{14}C release/mass loss. Lines are shown as guidance for the eye.

For comparison, the dashed line in Figure 14 shows, a 1:1 ratio between ^{14}C release and mass loss, i.e. when the process becomes non-selective towards a ^{14}C separation. Since there is no oxidation of graphite expected in Ar stream, an easily-removable ^{14}C fraction, which is presumably bound to the outer graphite surfaces via physisorption, is suggested to be separated by desorption.

There is also an alternative explanation, proposed in earlier reports, where the release was suggested to be promoted by oxygen absorbed on the surface of i-graphite [3], that at higher temperatures becomes more active and oxidizes the weakly bound ^{14}C. The latter, due to recoil effects, is not integrated in the graphite lattice (i.e. layered structure - the system of graphene sheets) and therefore easier to oxidize than the remainder of the inactive C in the graphite lattice. In this case, both physisorbed and chemisorbed ^{14}C could be removed. Presumably, the treatment in the presence of some mild oxidizing agent, like CO or H_2O, may further improve the selectivity of the ^{14}C removal during thermal treatment. This is currently considered at FZJ as a promising decontamination step to enable the further reuse of i-graphite.

The effect of the thermal treatment on the structure of the i-graphite was investigated by SEM. Figure 15 shows images of i-graphite before and after the thermal treatment. Obviously, i-graphite retains its layered structure, however the sheets look more ordered after exposure to the 1300°C. This could be due to the re-graphitisation, a known property of graphite to restore its structure during exposure to the high temperatures [7]. At the same time, the mild oxidation of unordered regions (e.g. interstitial defects or interstitial loops [8]), which are known to be more reactive than the rest of the graphite lattice, may occur. Generally, some surface changes were identified, which can influence the ^{14}C release, e.g. due to the modified i-graphite structure.

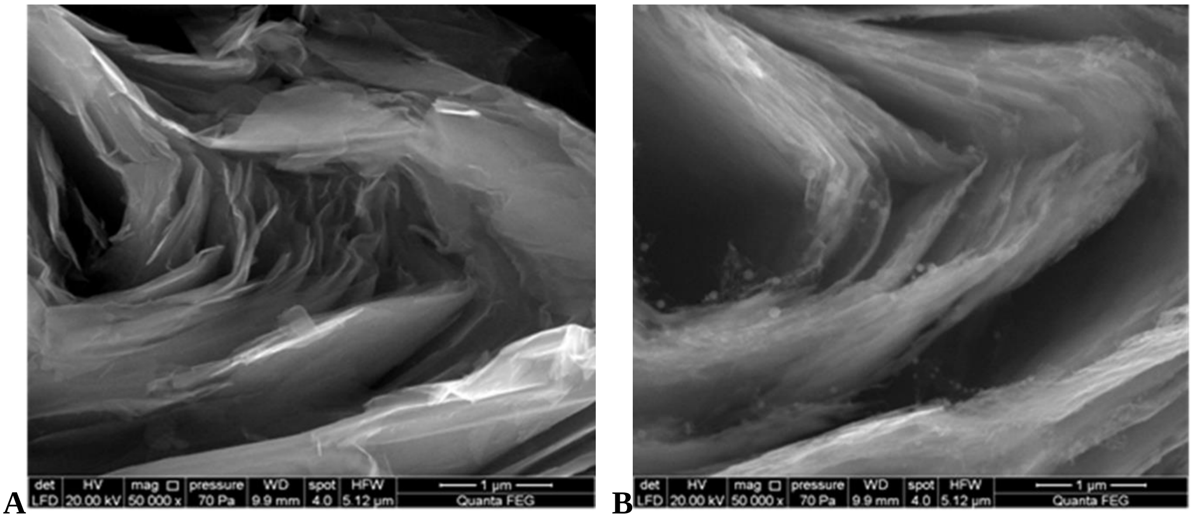

Figure 15: SEM of i-graphite before (**A**) and after (**B**) the thermal treatment.

After the thermal treatment, the leaching of ^{14}C was investigated under conditions similar to those used for the non-treated graphite, i.e. DIW and 1M NaOH were selected as leaching solutions. The tests were carried at 50°C for ca. 140 days. Within this period, only the background level of total released ^{14}C activity was detected. These results indicate that thermal treatment at 1300°C enables the separation of a relatively of easy removable fraction of ^{14}C (labile fraction) and improves the robustness of RFR i-graphite as a nuclear waste to be disposed in Konrad. On the other hand a thermal treatment in a given regime (i.e. Ar, 1300°C, ca. 19 hours of treatment) does not provide for a significant reduction of ^{14}C bound to i-graphite. A proper encapsulation of RFR i-graphite in a cementitious material alone provides for the WAC to be met, does not require costly energy consumption compared to the thermal treatment, and, therefore, is unlikely to be considered as a part of i-graphite disposal plan in Germany.

It should be further kept in mind that an application of the currently developed method for high-temperature separation of ^{14}C is concerned with the generation of secondary wastes, i.e. basic solution with ^{14}C trapped as CO_2, which has to be managed as well (e.g. immobilized in form of insoluble $Ba^{14}CO_3$). Therefore a thermal treatment makes more sense in case of low-activated i-graphite, like carbon bricks, when treatment may provide for a waste volume reduction by a concentration of ^{14}C in a relatively small volume of trap solution compared to the volume of i-graphite. The efficiency of the waste volume reduction will strongly depend on the selectivity of ^{14}C separation. For highly-activated graphite types, like moderator, where only a minor fraction of ^{14}C can be separated by thermal treatment, accumulation of secondary wastes may be concerned with additional costs outbalancing the advantage of the waste volume reduction. Therefore a high-temperature treatment would presumably make sense if a strategy of i-graphite recycling (e.g. returning it into the nuclear industry after decontamination) is pursued.

4. Conclusions

A number of leaching tests under different conditions were performed, in order to evaluate the release rates of ^{14}C from RFR i-graphite. The release of radiocarbon was found to occur into the aqueous and gas phase, and in both cases the inorganic ^{14}C species (i.e. $^{14}CO_2$) represent the dominant fraction. The release of volatile $^{14}CO_2$ is enhanced at higher temperature and under neutral conditions compared to basic solution. Investigation of i-graphite behaviour in cementitious media by using 1M NaOH as a leaching solution demonstrated that the major part of leached ^{14}C remains in the aqueous phase. The volatile fraction of radiocarbon is mostly comprised of $^{14}CO_2$, with a relatively small amount of organic ^{14}C-species or ^{14}CO. In contrast to $^{14}CO_2$, this fraction is not affected by the temperature up to 50°C. At a respective annual release rate of ^{14}C $<7.3 \cdot 10^{-3}$ %/year (if encapsulated in the cementitious material), the highest allowed storage capacity of i-graphite in the Schacht Konrad can be achieved even without prior treatment (e.g. thermal decontamination). An application of thermal treatment of i-graphite allows a selective separation of only a minor ^{14}C fraction, i.e. 8%, but results in unmeasurable release rates of volatile ^{14}C from treated i-graphite in neutral and basic solution. This finding indicates that thermal treatment on the given conditions does not provide for separation of a significant part of ^{14}C to achieve the clearance level, requires costly energy consumption and may result in unwanted secondary waste generation. Given that a proper encapsulation of i-graphite in a cementitious material alone may provide for WAC to be met, a thermal treatment of RFR i-graphite is considered to be redundant.

5. References

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