CArbon-14 Source Term

CAST

Final report on C-14 release and inorganic/organic ratio in leachates from TRIGA irradiated graphite (Task 5.3)

Author(s):

Crina BUCUR, Camelia ICHIM, Ionut FLOREA, Relu Dobrin, Liliana BUJOREANU, Cristina DIACONESCU

Date of issue of this report: 16/11/2017

The project has received funding from the European Union’s Seventh Framework Programme for research, technological development and demonstration under grant agreement no. 604779, the CAST project		
Dissemination Level		
PU	Public	**X**
RE	Restricted to the partners of the CAST project	
CO	Confidential, only for specific distribution list defined on this document	

CAST – Project Overview

The CAST project (CArbon-14 Source Term) aims to develop understanding of the potential release mechanisms of carbon-14 from radioactive waste materials under conditions relevant to waste packaging and disposal to 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 these relate to carbon-14 inventory and 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

CAST		
Work Package: 5	CAST Document no. :	Document type:
Task: 5.3	CAST-2017-D5.10	R = report
Issued by: RATEN ICN		Document status:
Internal no. 11652/30.08.2017		Final

Document title
Final report on C-14 release and inorganic/organic ratio in leachates from TRIGA irradiated graphite (Task 5.3) (D5.10)

Executive Summary

Leaching tests performed by RATEN ICN were carried out in aerobic and anaerobic conditions to assess the ^{14}C release as dissolved species in alkaline solution simulating the cementitious environment.

The irradiated graphite available for the leaching tests is originating from a brick dismantled in 2000 from the thermal column of the TRIGA research reactor in operation at RATEN ICN.

The total ^{14}C measurement in the powder graphite samples taken during mechanical cutting of the specimens used in the leaching tests was achieved by combustion in an oxygen rich atmosphere. Also gamma emitting radionuclides were measured by gamma spectrometry on the same powder graphite samples.

For the measurement of inorganic and organic fraction of the ^{14}C released in leachate solutions, an analytical method based on acid stripping and wet oxidation was applied.

The ^{14}C measurement was carried out by liquid scintillation counting (LSC) using a Tri-Carb® analyser Model 3110 TR.

The experimental results obtained from the leaching tests both in aerobic and anaerobic conditions confirm the low ^{14}C release in alkaline environment. Less than 2% from the total ^{14}C inventory in the specimens subject to the leaching tests was released as dissolved species.

Under aerobic conditions, the ^{14}C released was found to be predominantly in inorganic forms (around 68% from the total ^{14}C released), while in anaerobic conditions, the ^{14}C is released mainly as organic species (around 65% from the total ^{14}C released).

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1 Introduction

The thermal column of TRIGA Reactor is a graphite block (1716x1144x710 mm) made up of 98 rectangular graphite cells (12 rows x 8 bricks) in Aluminium cladding and it is placed into the reactor pool on the North side of the steady-state core. It was built up in 1985, using sintered graphite blocks with a density of 1.72 g/cm^3 and various geometries. The graphite was imported in the ‘50s from a UK producer but documents of its origin were lost. No information on its characteristics and on the impurity content could be found.

First experiments to measure the radionuclide inventory in TRIGA i-graphite were carried out under CARBOWASTE project. The measured data were complemented with data obtained by modeling, based on impurity content of the virgin graphite and the irradiation history [Toulhoat *et al.*, 2016].

In CAST WP5, RATEN ICN proposed to update the ^{14}C inventory in the irradiated graphite from thermal column of the TRIGA 14MW reactor and to evaluate the ^{14}C release in alkaline conditions (relevant to disposal in cementitious environment), both in terms of total ^{14}C as well as inorganic and organic fractions.

2 Materials and Methods

2.1 *Irradiated graphite used in the leaching tests*

Two cylindrical bars (Figure 1) originating from a brick extracted and dismantled in 2000 from the thermal column of TRIGA reactor were available for the experimental programme carried out in RATEN ICN under CAST WP5: one cylinder with a diameter of 50 mm and length of 200 mm (noted B1), and the second one with diameter of 60 mm (noted B2) and length of 250 mm. From the extraction from the thermal column until their usage in the experimental programme, the irradiated graphite bars were stored in air. No information regarding their position in the thermal column was found.

By mechanical cutting, four cylindrical samples whose dimensions respect the ratio of diameter to height of 1 to 1 were obtained: two with 50 mm diameter and 50 mm height (from B1 bar) and two with 60 mm diameter and 50 mm height (from B2 bar).

Figure 1. The irradiated graphite cylindrical bars used to cut intact samples for leaching experiments and powder samples to measure the radionuclide content

The two intact specimens obtained from B 1 bar (Figure 2) were used for the leaching tests carried out in aerobic conditions, while those obtained from B2 bar were used in the leaching tests performed in anaerobic conditions [Toulhoat *et al.*, 2016].

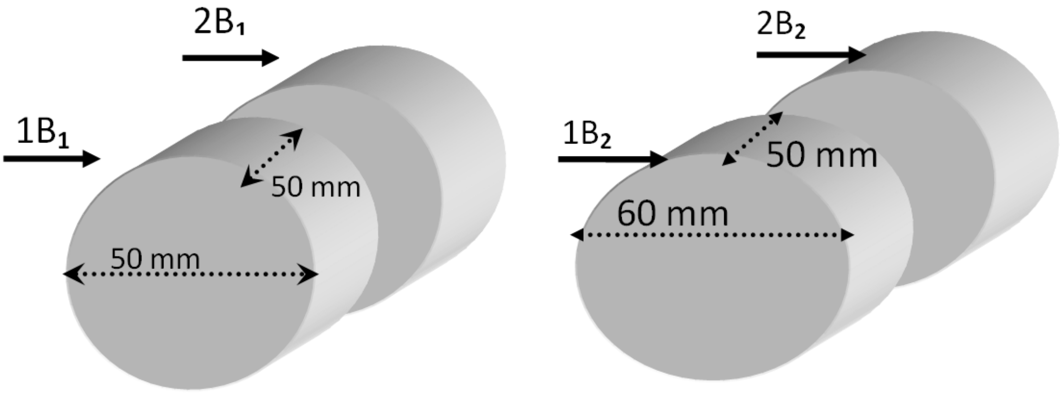

Figure 2. Intact specimens obtained from B 1 and B2 bars

The physical characteristics of the four irradiated graphite samples used in the leaching tests are reported in Table 1.

The powder graphite that resulted from cutting was sampled both from the ends of the cylindrical bars and from their middle and the resulting powder samples were used to measure the radionuclide content (^{14}C and gamma emitters). Four powder samples were taken from the B1 bar (two from the end of the bar and two from the middle).

Table 1. Characteristics of the irradiated graphite samples used for leaching tests

Sample ID	Type of leaching test	Mass, g	Geometric volume, cm^3	Volumetric density, g/cm^2	Surface area, cm^2
1B1	aerobic	172.72	98.13	1.76	117.75
2B1		168.24	98.12	1.72	117.75
1B2	anaerobic	250.10	141.30	1.77	150.72
2B2		249.70	141.30	1.76	150.72

To get more information on the ^{14}C distribution inside the irradiated graphite bar, powder samples were taken from different position from the B2 bar, by cutting one cylinder of 60x50 mm in half and then in quarters (Figure 3).

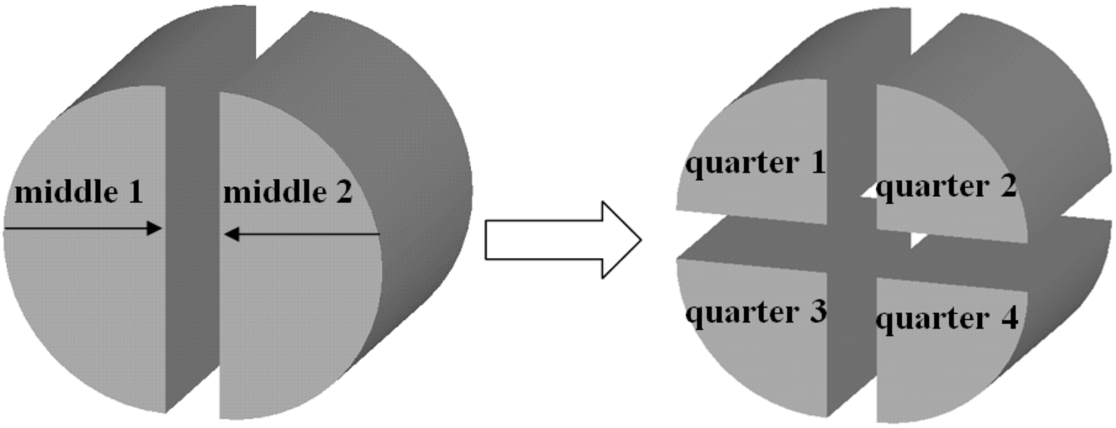

Figure 3. Cutting of one cylindrical piece of B2 bar for powder sampling

By this supplementary cutting of one cylindrical piece obtained from B2 bar, 12 powder samples were taken: 3 samples from the first half, 3 from the second half, 3 samples taken during first half cutting in quarters and 3 more samples taken during the second half cutting in quarters.

2.2 *Experimental conditions for leaching tests*

To evaluate the ^{14}C release from TRIGA irradiated graphite in chemical conditions relevant to geological disposal (cementitious environment), leaching tests in aerobic and anaerobic conditions were performed.

The leaching tests were carried out in 0.1 M NaOH solution (pH ~ 13) and room temperature (25±3°C), in inert Pyrex glass vessels.

All leaching tests were performed in semi-dynamic conditions, with a precise time scale for leachate sampling/replacement, until equilibrium was reached. The ratio of leachate volume to exposed surface area of the cylindrical samples was held constant (it does not exceed 0.1 m) by replacing the volume of leachate sampled at each sampling time with the same volume of fresh 0.1 M NaOH solution.

The volume of leachate solution was 1118 cm^3 in the aerobic leaching tests and 1500 cm^3 in the anaerobic ones.

The anaerobic leaching tests were carried out in N_2 atmosphere, in closed Pyrex glass vessels placed on a magnetic stirrer. The lids of the glass bottles were adapted to allow N_2 purging (Figure 4) before starting the leaching tests (to ensure the anaerobic conditions) and sampling the leachate solution without opening the vessels.

Figure 4. Photo of the leaching set-up for anaerobic conditions

According to D5.4 [Petrova et al., 2015], the leachate solution was sampled and renewed after 1, 3, 7, 10, 14 days, twice on week II, once on weeks III to VI and after that monthly until the equilibrium is reached.

2.3 *Methods used for total ^{14}C measurement*

For total ^{14}C measurement both in irradiated graphite and in leachate solutions sampled from the leaching tests, non-catalytic combustion by flame oxidation method was used.

For inorganic and organic ^{14}C measurement, an analytical method adapted after the one developed by Magnusson [Magnusson et al., 2008] for ^{14}C measurement in spent ion exchange resins and process waters was used. This method distinguishes between $^{14}CO_2$ released during acid stripping and $^{14}CO_2$ released by wet oxidation of hydrocarbons allowing determination of the inorganic and organic fractions of ^{14}C in irradiated graphite and leachate solutions.

2.3.1 Method for total ^{14}C measurement

For total ^{14}C measurement in irradiated graphite, non-catalytic combustion by flame oxidation method was used. By this method, the graphite samples are combusted in an oxygen-enriched atmosphere with a continuous flow of oxygen using Sample Oxidizer, Model 307 PerkinElmer® (Figure 5). During the combustion process any hydrogen is oxidized to H_2O and any carbon is oxidized to CO_2.

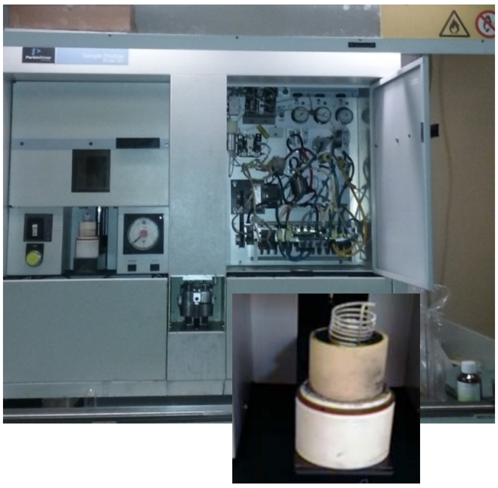

Figure 5. The experimental device used for total ^{14}C measurements in liquid samples

The Sample Oxidizer consists of the following major functional areas: combustion system, tritium collection system, ^{14}C and ^{3}H collection systems, water injection system, nitrogen system and programmer.

Since the carbon dioxide readily reacts with compounds containing amines, Carbo-Sorb® E was chosen to absorb the $^{14}CO_2$ released during combustion process. The absorption reaction of carbon dioxide can be described as follows [Ahn at al., 2013]:

$$^{14}CO_2 + RNH_2 \rightarrow RNH_2^{+}{}^{14}COO^{-} \qquad \text{(eq. 1)}$$

$$RNH_2^{+}{}^{14}COO^{-} + \begin{bmatrix} RNH_2 \rightarrow RNH^{14}COO^{-} + RNH_3^{+} \\ H_2O \rightarrow RNH^{14}COO^{-} + H_3O^{+} \\ OH^{-} \rightarrow RNH^{14}COO^{-} + H_2O \end{bmatrix} \qquad \text{(eq. 2)}$$

$$RNH^{14}COO^{-} + H_2O \rightarrow RNH_2 + H^{14}CO_3^{-} \qquad \text{(eq. 3)}$$

As shown in eq. 2, the amine contained by the Carbo-sorb E solution reacts with ^{14}C-labelled carbon dioxide to form a zwitterion, which reacts with H_2O to form a stable carbonate compound (eq. 3). This resulting carbonate compound is mixed with the LSC cocktail (Perma-fluor® E+) directly in the counting vial.

The $^{3}H_2O$ resulting from the combustion process is condensed in a cooled coil, washed into a counting vial where it is mixed with LSC cocktail (Monophase®S).

At the end of combustion process, two separate samples, one for ^{14}C measurement and one for ^{3}H measurement, are trapped at ambient temperature minimizing the cross-contamination.

The ^{14}C and ^{3}H radioactivity in the samples resulted from irradiated graphite combustion was measured by liquid scintillation counting (LSC) using a Tri-Carb® analyser Model 3110 TR. This analyser allows for ultra-low level counting mode with typical count rate in the range of 1 – 20 CPM (counts per minute) above background.

2.3.2 Analytical method for inorganic and organic ^{14}C measurement

The analytical method used for inorganic and organic ^{14}C measurement in leachate solutions consists in a sequential extraction of inorganic ^{14}C and organic ^{14}C using acid stripping and wet oxidation, adapted after the method developed by Magnusson [Magnusson et al., 2008] for ^{14}C measurement in spent ion exchange resins and process waters.

The experimental set-up used to separate the inorganic and organic ^{14}C from the leachate solutions is schematically presented in Figure 6. It consists in a reaction vessel, a separatory funnel, a nitrogen supply and a vacuum pump, two gas washing lines with a catalytic furnace between them.

An Erlenmayer flask (300 ml) with a three-hole rubber stopper (two for gas and separatory funnel inlets and one for gas outlet) was used as a reaction vessel, with a tap-water cooling loop, made of copper tubing that was fitted on the outer side of the Erlenmeyer flask (Figure 6) for vapour condensation. The reaction vessel was placed on a heater with magnetic stirring.

To ensure that no gases are released from the system, all tests were carried out under vacuum (0.2 bar below atmospheric pressure) and the carrier gas (N_2) was introduced into the system with a flow rate around 50 ml/min (controlled by a flow meter).

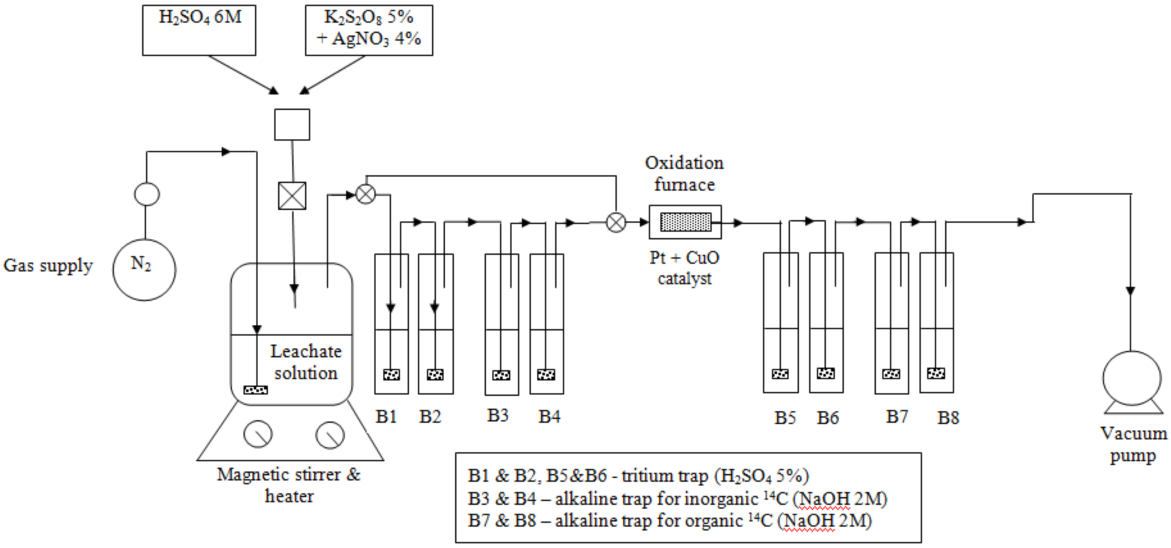

Figure 6. The experimental set-up for separation and purification of inorganic and organic ^{14}C from the solutions sampled from leaching tests

Since the irradiated graphite contains, besides ^{14}C, also tritium and other beta emitters that could be released during the leaching tests and interfere with ^{14}C measurement by LSC, the gas washing lines contain slightly acidic traps with sulphuric acid (5% H_2SO_4) for absorption of tritium and other potential interfering radionuclides (placed both before the catalytic furnace and after it) and four alkaline traps (two placed before the catalytic furnace and two after it) with 2M sodium hydroxide (NaOH).

Since the inorganic ^{14}C compounds (i.e. carbonates and bicarbonates) are easily decomposed by weak acids to carbon dioxide, the inorganic ^{14}C is released during the acid stripping step of the analytical method, mainly as $^{14}CO_2$, and the gases released are carried by the carrier gas through the first gas washing line (Figure 6). If any ^{14}C is released during this step as CO or other organic molecules, it passes through the scrubbing bottles of the first gas washing line and is oxidized to CO_2 in the catalytic furnace and subsequently absorbed in the alkaline scrubbing bottles of the second gas washing line. After the acid stripping step is accomplished, the first gas washing line is isolated from the system by means of three ways valves placed before the first scrubbing bottle and the fourth one.

Because the organic compounds have high bounding energies between atoms they are decomposed by strong oxidants such as potassium persulphate ($K_2S_2O_8$). The presence of a catalyser such as silver nitrate ($AgNO_3$) enhances the decomposition of the organic compounds. During the wet oxidation step the temperature of the solution in the reaction vessel is slightly increased to 90°C.

The mechanism of ^{14}C-labelled organic compounds decomposition is based on the $OH^{(*)}$ radicals and can be expressed by the following equations [Ahn et al., 2013]:

$$K_2S_2O_8 \xrightarrow{H_2O} 2K^+ + S_2O_8^{2-} \tag{eq. 4}$$

$$S_2O_8^{2-} + 4H_2O \underset{Ag}{\rightarrow} 2SO_4^{2-} + 2H^+ + 2OH^* \tag{eq. 5}$$

$$^{14}C_nH_m + (4n+m)OH^* \rightarrow n^{14}CO_2 + (2n+m)H_2O \tag{eq. 6}$$

The ^{14}C released during the wet oxidation step of the analytical procedure (both as CO_2, but also as CO or CH_4) is carried by the carrier gas through a catalytic furnace that ensures oxidation of any reduced compounds to CO_2, which is afterwards absorbed in the scrubbing bottles of the second gas washing line (Figure 6).

Two wet oxidation steps were carried out in order to ensure the complete decomposition of the organic ^{14}C-labelled compounds, and the carrier gas was purged into the system for one hour in each wet oxidation steps.

In order to not dilute the amount of $^{14}CO_2$ absorbed in the alkaline gas washing bottles too much, in the experimental set-up presented in Figure 6, scrubbers of small volume were used (15 ml).

The ^{14}C activity in the alkaline traps as well as ^3H activity in solutions sampled from the acid scrubbing bottles were measured by liquid scintillation counting (LSC), using a Tri-Carb® analyser Model 3110 TR.

An hionic fluor liquid scintillation cocktail was used for ^{14}C measurement by LCS, and Ultima Gold AB liquid scintillation cocktail for tritium measurement. The ratio between sample and scintillation cocktail was 1 to 10. All samples were kept in darkness over night before counting.

Aliquots from the reaction vessel solution, as well as from all scrubbing bottles, were sampled for gamma measurements. The system used for the gamma spectrometry comprises of the following components: HPGe ORTEC detector, digiDart analyser and GammaVision software. The spectrometer was calibrated in energy and efficiency using a standard liquid source containing ^{60}Co, ^{137}Cs, ^{241}Am, ^{152}Eu in 20 ml glass vials. The same geometry was used for gamma measurements on the sampled aliquots solutions from the acid stripping/wet oxidation experiments. The counting time was higher than 8 hours for each sample.

3 Results and discussion

3.1 *Total ^{14}C content in the irradiated graphite samples used in leaching tests*

Preliminary combustion tests were carried out using graphite samples spiked with radionuclides of interest (^{14}C – as Spec-Chec solution with known ^{14}C activity, ^{3}H, ^{60}Co, ^{137}Cs, ^{241}Am and ^{152}Eu) in order to optimize the combustion process and determine the recovery and memory effect of the combustion method. The memory effect represents the amount of ^{14}C, and other radionuclides of interest, absorbed on the components of the experimental set-up and the tubing used to connect them.

The optimised experimental conditions for complete graphite oxidation were the following:

- ✓ 0.14 – 0.16 g of graphite powder
- ✓ 10 ml CarbosorbE (liquid scintillation cocktail for ^{14}C)
- ✓ 10 ml PermafluorE+ (liquid scintillation cocktail for ^{3}H)

The labelled graphite sample was placed into a combusto-cone that was further placed into platinum ignition basket. The average combustion recovery by this method was 97%. Virgin graphite samples were also combusted for background measurements.

The memory effect was less than 0.04% and no gamma emitters were identified either in the counting vial for ^{14}C measurement or in the ^{3}H one.

The experimental results obtained for ^{14}C content in the powder samples originating from the B1 graphite bar used for aerobic leaching tests are reported in Table 2, while those obtained for the powder samples taken from B2 bar are reported in Table 3.

Table 2. ^{14}C content in the powder graphite sampled from B1 bar

Sample ID	Graphite mass used in combustion tests, g	^{14}C specific activity, Bq/sample	^{14}C specific activity, Bq/g	Observations
virgin graphite_1	0.16	5.17E-01	3.23E+00	^{14}C background
end B1_1	0.13	6.18E+01	4.75E+02	Sampled from the end of B1 bar
end B1_2	0.14	6.18E+01	4.42E+02	
middle B1_1	0.14	6.16E+01	4.40E+02	Sampled from the middle of B1 bar
middle B1_2	0.16	7.14E+01	4.46E+02	
		Average B1	**450.75±16.36**	

As it can be seen from data reported in Table 2, no notable difference in ^{14}C content in powder samples taken from the end and middle of B1 bar was observed.

For the total ^{14}C content in the irradiated graphite samples used for leaching tests carried out in aerobic conditions, a value of 450.74 Bq/g was considered (the average of the 4 measurements presented in Table 2).

Table 3. ^{14}C content in the powder graphite sampled from B2 bar of irradiated graphite

Sample ID	Graphite mass used in combustion tests, g	^{14}C specific activity, Bq/sample	^{14}C specific activity, Bq/g	Observations
H1_1	0.14	1.38E+01	9.88E+01	Sampled from the first half
H1_2	0.16	1.37E+01	8.55E+01	
H1_3	0.14	1.73E+01	1.24E+02	
Average H1			102.77±19.55	
H2_1	0.13	1.67E+01	1.29E+02	Sampled from the second half
H2_2	0.16	1.24E+01	7.72E+01	
H2_3	0.15	1.03E+01	6.90E+01	
Average H2			91.73±32.53	
Q1_1	0.16	1.50E+01	9.36E+01	Sampled from the first half cutting in quarters
Q1_2	0.12	1.45E+01	1.21E+02	
Q1_3	0.12	1.39E+01	1.16E+02	
Average Q1			110.20±14.59	
Q2_1	0.14	1.31E+01	9.39E+01	Sampled from the second half cutting in quarters
Q2_2	0.16	1.01E+01	6.28E+01	
Q2_3	0.15	1.24E+01	8.25E+01	
Average Q2			79.73±15.73	
Average B2			**96.11±21.20**	

For the total ^{14}C content in the irradiated graphite samples used for leaching tests carried out in anaerobic conditions, a value of 96.11 Bq/g was considered (the average of the 12 measurements presented in Table 3).

3.2 Recovery and memory effect of the acid stripping/wet oxidation method

Preliminary acid stripping/wet oxidation tests were carried out using aqueous solutions spiked with the radionuclides of interest: inorganic ^{14}C (in the form of sodium carbonate / bicarbonate), organic ^{14}C (sodium acetate and lauric acid), ^{3}H, and gamma emitters (^{60}Co, ^{137}Cs, ^{241}Am and ^{152}Eu).

The ^{14}C recovery was between 94.79% and 98.32% [Rizzo *et al.*, 2017]. The average recovery was 96.97 % with a standard deviation of 1.46 %. No gamma emitters were identified in any of the scrubbing bottles and the entire activity of ^{60}Co, ^{137}Cs, ^{241}Am and ^{152}Eu were found in the solutions sampled from the reaction vessel (with average recovery higher than 96%). Also the solutions sampled from the alkaline gas washing bottles were counted for tritium (using double labelled mode implemented on LCS counter) but tritium was not detected above the background in these samples. All tritium added in the reaction vessel was found in the acid scrubbing bottles. An average memory effect of less than 1% was observed.

To account for the uncertainty associated with this analytical method, 6 identical tests were carried out using solutions spiked both with inorganic and organic ^{14}C, as well as with tritium and gamma emitters. The standard deviation of the results of these tests was less than 15%.

3.3 *^{14}C release in alkaline solution*

The leaching behaviour is represented by the ^{14}C cumulative release fraction (F_n) in time and also by leaching rate (R_n), computed using equations (eq. 1) and (eq. 2):

$$F_n = \frac{\sum a_n}{a_o} \qquad \text{(eq. 7)}$$

$$R_n = \frac{a_n \cdot V}{a_0 \cdot S \cdot t_n} = K \cdot \frac{a_n}{t_n} \qquad \text{(eq. 8)}$$

where: F_n is the cumulative release fraction (%) at the moment *n* of the leaching test; R_n represents the release rate (cm/day) at the moment *n* of the test; a_0 is the initial ^{14}C content of the graphite sample (Bq); a_n represents the amount of ^{14}C released at the moment *n* of the test (Bq) in the leachate solution; t_n represent the time in the moment *n* of the test (days); V is the sample volume (cm^3); S is the geometric surface of the sample (cm^2); is a test constant (cm/Bq).

3.3.1 ^{14}C release in alkaline solution under aerobic conditions

As presented in the previous chapter, the leaching tests carried out in aerobic conditions were performed in 0.1 M NaOH solution, in semi-dynamic conditions. At the established leaching times, 30 ml of leachate were sampled and 30 ml of fresh NaOH solution were added in the leaching vessels. Two parallel tests were performed with the main parameters reported in Table 4.

Table 4. Tests parameters for aerobic leaching

Sample ID	Sample mass, g	Leachate volume, ml	Total ^{14}C content, Bq
1_B1	172.72	1118	7.79E+04
2_B1	168.24	1118	7.58E+04

The volume of NaOH solution was chosen to respect the ratio between the leachate volume to the sample surface not higher than 0.1 m.

To avoid kinetic effects at the graphite – leachate solution interface (e.g., heterogeneous distribution of ^{14}C in the solution), the leachate solution was stirred before sampling. At each sampling time, the leachate solutions were measured by gamma spectrometry and, if no beta-gamma emitters were identified in solution, sub-samples for LSC measurement were prepared. Both tritium and radiocarbon were measured by LSC using a double-labelled method implemented on TRICARB 3100 TR.

20 ml from the leachate solution was used to evaluate the inorganic and organic ^{14}C content by means of an acid stripping/wet oxidation method. This method also allows a good decontamination of other potential interfering radionuclides and the total ^{14}C measured directly by LSC was comparable with the sum of inorganic and organic ^{14}C measured by the acid stripping/wet oxidation method.

The values of ^{14}C measured in the leachate solution at each sampling times were used to compute the ^{14}C cumulative release fraction (F_n) and leaching rate (R_n). The measured ^{14}C activity in the leachate solution was corrected for the dilution factor due to the leachate sampling/renewal and divided by the initial ^{14}C activity in the i-graphite subject of the leaching test to get the cumulative release fraction. The results, both for the cumulative release fraction and for the leaching rate, are reported in Table 5.

The results obtained by the two parallel are very similar (see Figure 7) confirming the reproducibility of the leaching tests.

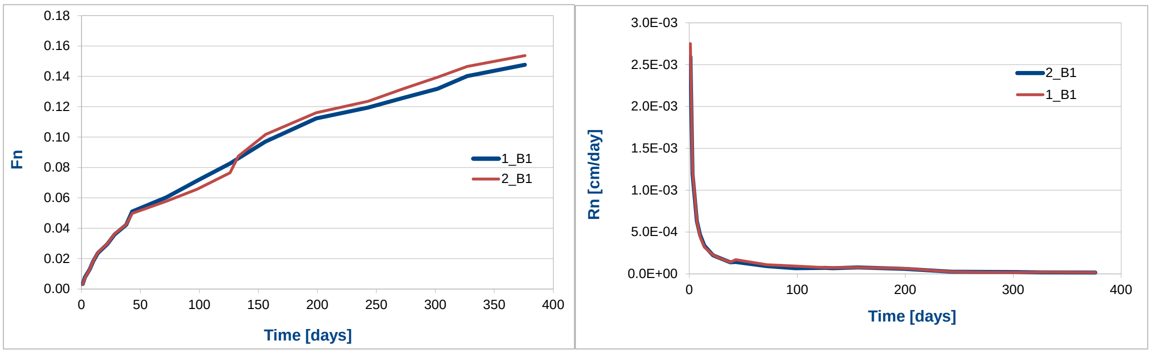

Figure 7. Evolution of the leaching rate (right) and ^{14}C cumulative release fraction (left)

Table 5. ^{14}C cumulative release fraction (F_n) and leaching rate (R_n) for the aerobic leaching tests

	Sample 1_B1		**Sample 2_B1**	
Time, days	**Rn [cm/day]**	**Fn [%]**	**Rn [cm/day]**	**Fn [%]**
1	2.75E-03	3.30E-03	2.59E-03	3.11E-03
3	1.22E-03	7.69E-03	1.20E-03	7.42E-03
7	6.29E-04	1.30E-02	6.32E-04	1.27E-02
10	4.42E-04	1.83E-02	4.66E-04	1.83E-02
14	3.17E-04	2.36E-02	3.36E-04	2.40E-02
22	2.24E-04	2.95E-02	2.22E-04	2.98E-02
28	1.89E-04	3.59E-02	1.90E-04	3.62E-02
38	1.39E-04	4.22E-02	1.38E-04	4.25E-02
43	1.14E-04	5.10E-02	1.42E-04	4.98E-02
72	1.07E-04	6.03E-02	9.25E-05	5.78E-02
98	9.36E-05	7.13E-02	6.70E-05	6.57E-02
126	7.47E-05	8.26E-02	7.16E-05	7.65E-02
156	7.68E-05	9.70E-02	6.83E-05	8.74E-02
199	6.40E-05	1.12E-01	7.62E-05	1.02E-01
243	2.47E-05	1.19E-01	5.99E-05	1.16E-01
272	1.90E-05	1.26E-01	2.59E-05	1.24E-01
302	1.71E-05	1.32E-01	2.45E-05	1.32E-01
327	2.13E-05	1.40E-01	2.17E-05	1.39E-01
376	1.65E-05	1.48E-01	1.82E-05	1.47E-01

The results of the aerobic leaching tests confirm a very low release rate of the ^{14}C. After 376 days of immersion in alkaline solution, around 1.33E3 Bq of ^{14}C was released as dissolved species, representing 1.75% of the initial ^{14}C activity of the i-graphite subject of the leaching test.

The leaching rate is higher in the first days of immersion and it decreases after that, indicating a two stage process: an initial quick release with an average release rate of 5.48E-02 % of inventory/day* during the first 48 days, followed by a slower release of around 4.62E-3 % of inventory/day. These two stages of ^{14}C release could be associated with the initial release of the more labile species arising from the ^{14}N impurities or from the ^{13}C from different depositions, while the second stage is most probably linked to ^{14}C created in the matrix [Carlsson et al., 2014].

The acid stripping/wet oxidation tests carried out on the leachate solutions show that in all solutions more inorganic than organic ^{14}C was released. The ratio between inorganic and organic ^{14}C release during the leaching test is almost constant during the test. The inorganic fraction of ^{14}C measured in the leachant solution sampled at different leaching intervals ranges between 66% and 70% from the total ^{14}C released as dissolved species, with an average of 67.89% and a standard deviation of 1.84%. The organic ^{14}C on leachant solution sampled at different leaching intervals is ranging between 30% and 34% from the total ^{14}C released as dissolved species, with an average of 32.11%.

3.3.2 ^{14}C release in alkaline solution under anaerobic conditions

The experimental conditions for anaerobic leaching tests were similar with those described in the aerobic leaching tests, except for the volume of the leachate solution that was increased to 1500 cm^3 due to the larger diameter of the irradiated graphite available for these anaerobic leaching tests (Table 6).

Table 6. Tests parameters for anaerobic leaching

Sample ID	Sample mass, g	Leachate volume, ml	Total ^{14}C content, Bq
1_B2	250.10	1500	2.404E+04
2_B2	249.7	1500	2.400E+04

The volume of leachate solution sampled/renewed at each testing time was 50 ml. The values of ^{14}C measured in the sampled solutions at each sampling times were used to

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* % of inventory/day represent the ^{14}C activity release in each time interval divided by the initial inventory in irradiated graphite, divided by the leaching time and multiplied by 100.

compute the ^{14}C cumulative release fraction (F_n) and leaching rate (R_n). The results are reported in Table 7.

Table 7. ^{14}C cumulative release fraction (F_n) and leaching rate (R_n) for the anaerobic leaching tests

Time, days	Sample 1_B1		Sample 2_B1	
	Rn [cm/day]	**Fn**	**Rn [cm/day]**	**Fn**
1	7.80E-03	9.36E-03	8.67E-03	1.04E-02
3	2.69E-03	1.90E-02	2.98E-03	2.12E-02
7	1.28E-03	2.97E-02	1.65E-03	3.51E-02
10	8.95E-04	4.05E-02	1.16E-03	4.91E-02
14	7.02E-04	5.23E-02	9.55E-04	6.51E-02
21	5.10E-04	6.51E-02	6.40E-04	8.13E-02
28	4.77E-04	8.11E-02	5.73E-04	1.01E-01
35	2.65E-04	9.23E-02	2.38E-04	1.11E-01
46	1.99E-04	1.03E-01	1.75E-04	1.20E-01
91	1.12E-04	1.15E-01	1.40E-04	1.36E-01
126	1.14E-04	1.33E-01	1.22E-04	1.54E-01
175	8.29E-05	1.50E-01	8.80E-05	1.72E-01
205	4.79E-05	1.62E-01	5.06E-05	1.85E-01
244	2.90E-05	1.70E-01	3.33E-05	1.94E-01
314	3.88E-05	1.85E-01	2.73E-05	2.05E-01
364	2.97E-05	1.98E-01	2.93E-05	2.18E-01

Similar to the aerobic leaching tests, the experimental results indicate a good reproducibility of the tests (Figure 8).

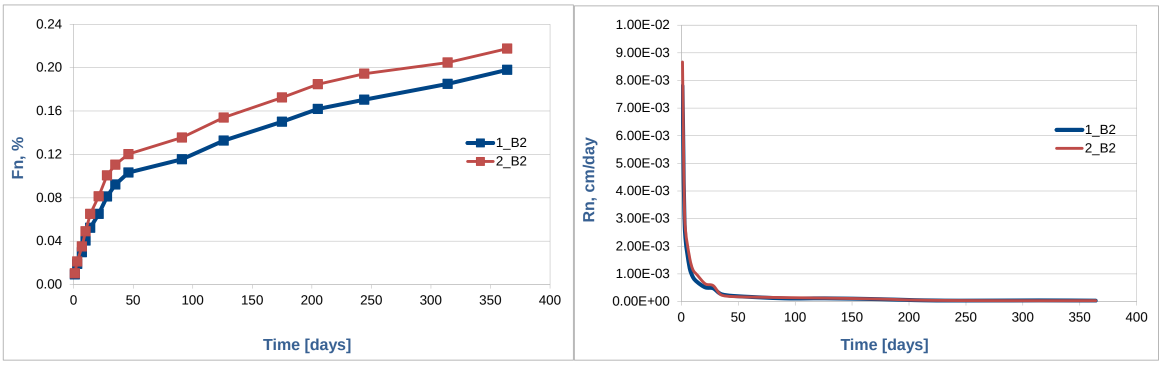

Figure 8. Evolution of the ^{14}C cumulative release fraction (left) and leaching rate (right)

The results of the anaerobic leaching tests also show a low ^{14}C release. After 364 days of test, less than 450 Bq of ^{14}C was released as dissolved species, representing 1.85% from the initial ^{14}C activity of the i-graphite subject to the leaching test.

As it was also observed in the tests carried out in aerobic conditions, the leaching rate is high in the first days of immersion. The initial quick release takes place with an average rate of 9E-02 % of inventory/day during the first 48 days while the slower release has a rate of around 4E-3 % of inventory/day.

The acid stripping/wet oxidation tests carried out on the leachate solutions sampled at different leaching intervals show that under anaerobic conditions, more organic than inorganic ^{14}C was released, with an almost constant ratio between organic and inorganic ^{14}C. The organic ^{14}C released as dissolved species under anaerobic conditions was between 61% and 66%, with an average of 64.57% (and a standard deviation of 3.08%).

No ^{14}C was measured in gas phase, but it is expected for this high-pH conditions that any $^{14}CO_2$ released from the irradiated graphite to remain in solution as carbonate.

4 Conclusions

The results of the leaching tests confirm the very low release rate of the ^{14}C. At the end of the leaching tests (376 days), around 1.33E3 Bq of ^{14}C in aerobic conditions and 450 Bq in anaerobic condition was released as dissolved species, representing 1.75% and 1.85%, respectively of the initial ^{14}C activity of the i-graphite subject of the leaching test.

Both for anaerobic and aerobic conditions, the leaching rates are high in the first days of immersion and decrease after that, indicating a two stage process: an initial quick release (less than 9E-02 % of inventory/day for the first 48 days) followed by a slower release rate (around 4E-3 % of inventory/day).

The ratio between inorganic and organic ^{14}C release during the leaching test is almost constant, with more organic than inorganic ^{14}C released under anaerobic conditions (with an average fraction of organic ^{14}C of around 65% from the total ^{14}C released) and more inorganic than organic ^{14}C in aerobic conditions (with an average fraction of inorganic ^{14}C of around 68% from the total ^{14}C released).

No ^{14}C was measured in gas phase, but it is expected for this high-pH conditions that any $^{14}CO_2$ released from the irradiated graphite to remain in solution as carbonate.

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