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Carbon-14 speciation in solution and gas from French graphite waste (D5.8)

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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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Carbon-14 speciation in solution and gas from French graphite waste

Executive summary

Carbon 14 is one of the key radionuclides for the future disposal of French irradiated graphite waste. It is one of the main long-lived radionuclides, and depending on its speciation, it can be more or less mobile in a disposal facility and more or less incorporated into living organisms. Following a first report concerning a review of the available leaching data of French irradiated graphite, particularly focused on carbon 14 release rates (D5.1, see reminder in Annex 8.1), this second report (D5.8) addresses the speciation of the released carbon 14.

Because of the low release rate of carbon 14 in graphite leaching experiments (D5.1, see reminder in Annex 8.1), an experimental methodology was specifically designed in order to increase carbon 14 release so as to identify the organic and inorganic released species in the gas and liquid phases. Two powdered samples of two French reactors were tested: SLA2 and G2. The leaching experiments were carried out at pH 13 (NaOH 0.1M) under inert atmosphere.

As a result, these experiments showed that more than 95% of the released carbon 14 was found in the liquid phase mainly as inorganic species (carbonates). However, some carbon 14 is also released as organic species. After 100 to 200 days, the speciation of the released carbon 14 reaches a quasi-steady state to around 30% of the total carbon 14 released as organic species. In the gas phase, due to the pH of the solution no carbon dioxide is observed. The released carbon 14 in the gas phase samples is as a mixture of organic species

and/or CO. Because of the analytical procedure, it is not possible to differentiate these forms.

Some parameters that can influence the release of carbon 14 were also studied. The water chemistry and the specific surface area seem to have an impact. Other parameters have not been studied yet (temperature, initial activity of the samples, location in the reactor).

The main consequence of these studies is that some additional work has to be done to clearly quantify the organic fraction of released carbon 14. Moreover, the experimental parameters of the leaching test have to be chosen carefully, in accordance with the conditions of the future waste disposal facility.

List of content

CAST – Project Overview ii
Executive summary iii
1 Introduction 6
2 Material description 8
2.1 SLA2 reactor – graphite samples 8
2.2 G2 reactor – graphite samples 9
2.3 Sample characteristics 10
3 Experimental methodology 12
3.1 Leaching test methodology 12
3.2 Carbon 14 measurements 14
  3.2.1 Carbon 14 in the graphite samples 14
  3.2.2 Carbon 14 in the gas phase 15
  3.2.3 Carbon 14 in the leaching liquid and speciation 17
4 Results 19
5 Influence of leaching parameters 22
5.1 Water chemistry: Leachant chemical composition and experimental parameters 22
5.2 Specific surface area of samples 25
5.3 Other parameters 26
6 Conclusion 28
7 References 30
8 Annexes 31
8.1 Brief reminder of D5.1 – Review on carbon 14 leaching data in French irradiated graphite (Petit et al., 2014) 31
8.2 Extract from D5.1 (chapter 2): Reactors and material description (Petit et al., 2014) 34
  8.2.1 G2 reactor 34
  8.2.2 Saint Laurent A2 reactor (SLA2) 38

1 Introduction

Carbon 14 is one of the key radionuclides to study for the future disposal of French irradiated graphite waste. This radionuclide is of particular interest because it is one of the main long-lived species (half-life: 5,700 years) present in graphite (up to 10^3 to 10^6 Bq/g for French irradiated graphite). Carbon 14 is a weak β-emitter (156 keV) which doesn't cause any external radiation hazard, but as some of its chemical forms can easily be incorporated in living organisms, it is important to assess and understand its release rate, its speciation and its behavior as relevant to future disposal. Moreover, depending on its chemical form, carbon 14 can be more or less mobile in the disposal facility: the inorganic forms of carbon 14[1] are not mobile in a cementitious environment (as envisaged for the future disposal facility) unlike the organic forms, which are probably more mobile. As a consequence, in France, some recent studies were dedicated to this radionuclide in order to determine its release rate and its speciation.

After a first report in 2014 (D5.1, see reminder in Annex 8.1) concerning a review of the available leaching data of French irradiated graphite, particularly focused on carbon 14 release rates, this second report addresses the speciation of the released carbon 14. Two leaching tests were specifically designed for the analysis of carbon 14 speciation. These two leaching tests are the same as the ones described in the previous report, D5.1 (see reminder in Annex 8.1). They were carried out on irradiated graphite samples coming from the stack Saint Laurent A2 (SLA2) and G2 reactors.

This report is divided into 4 main sections. A first part is dedicated to the description of the graphite samples used for the leaching tests. Then, the experimental conditions of leaching tests are described. The next part focuses on the results of the leaching experimentations. The last section gives some information about the experimental parameters which can

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[1] In this document, the term "inorganic forms of carbon 14" refers to CO_2 and corresponds to molecules in the liquid phase (i.e. carbonates). Due to the experimental methodology, CO can't be separated from organic molecules and is not taken into account in the mineral fraction of carbon 14 (but it is taken into account in the organic fraction).

influence the release and the speciation of carbon 14. At the end, as part of a conclusion, the main uncertainties are pointed out.

2 Material description

This section focuses on the samples coming from two out of the nine French UNGG reactors: G2 and SLA2. A more detailed description of these two reactors is given in the annex 8.2, which is an extract of D5.1 report. Studies have been carried out on these two reactors in order to characterize the speciation of leached carbon 14. The leaching tests used in this report are the same as for deliverable D5.1 (see reminder in Annex 8.1). Consequently, the samples have already been described, and the following text is a reminder of the previous report (see Annex 8.2).

2.1 *SLA2 reactor – graphite samples*

Initially, SLA2 graphite cores (cylinder diameter: 19 mm; height: 50 mm) were taken from one single channel with variable sampling heights (variable neutron flux and irradiation temperature). They were crushed, milled and mixed together in order to obtain a sufficient quantity of a "mean" graphite sample. After the mixing, the graphite was divided into 3 identical batches + 1 additional (smaller). 3 batches were used for leaching tests, only one in NaOH solution at pH 13, the other ones in demineralized water and dismantling water (pH 8.2). The smallest batch was used for radiochemical characterization and particles size measurement.

Thanks to the location of the graphite cores, the whole range of temperature and neutron flux is contained in the mixed powder. As a consequence, the results will give an overview of the behavior of the reactor.

Table 1 gives some details of the initial graphite cores used to produce the "mean" graphite sample. This graphite was made of Lima coke, underwent impregnation and was purified using MgF_2.

Table 1. Graphite samples from SLA2 reactor

Sample N°	Height (mm)	Mass (g)	Contact dose rate in 2010 (µSv/h)
SLA2-101	300	25.86	8
SLA2-107	3450	25.00	132
SLA2-112	5900	18.55	67
SLA2-115	7280	21.47	112
SLA2-118	8660	21.69	164

2.2 *G2 reactor – graphite samples*

Concerning G2 reactor, the core used is originally 13 to 20 cm long and has a diameter of 6.3 cm. A cut of this core was crushed, milled and mixed in order to obtain approximately 80 g of graphite powder for this leaching test. When the sample was chosen, it was supposed to be representative of the whole reactor.

Table 2 gives the characteristics of the original core.

Table 2. Graphite sample from G2 reactor

Sample n°	Location	Coke	Height (m)	Temperature (°C)
G2-27	Stack graphite	Supposed to be coke special A[2]	13.6 – 13.8	327

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[2] Most of the bricks constituting the stack are made of graphite coming from coke special A. However, a few of them are made of graphite coming from coke Lockport L. It is not possible to differentiate them. As a consequence, the samples used for leaching tests were probably produced with coke special A, but there is a limited possibility that this graphite comes from coke Lockport L.

2.3 *Sample characteristics*

Some characterizations of the graphite samples were carried out before leaching tests. Table 3 shows the initial activities of samples. Results are in Bq.g^{-1}.

Table 4 and Figure 1 show the particle size distribution of the samples, which is similar for the two reactors (same milling procedure for both).

Table 3. Sample activities

SLA2 (mixed powder from F4M10-C19 channel)		**G2 – 27**	
^{14}C (Bq.g^{-1})	Date of measurement	^{14}C (Bq.g^{-1})	Date of measurement
$5.26 \pm 0.42 \cdot 10^4$	March 2011	$4.36 \pm 0.39 \cdot 10^4$	August 2011

Table 4. Sample particle size distribution before leaching

Particle size	**SLA2 before leaching test**	**G2 before leaching test**
µm	*% (mass)*	*% (mass)*
>1000	36 %	31 %
850-1000	7 %	6 %
500-850	14 %	17 %
250-500	13 %	16 %
180-250	6 %	8 %
90-180	12 %	12 %
63-90	5 %	3 %
45-63	5 %	3 %
<45	2 %	4 %

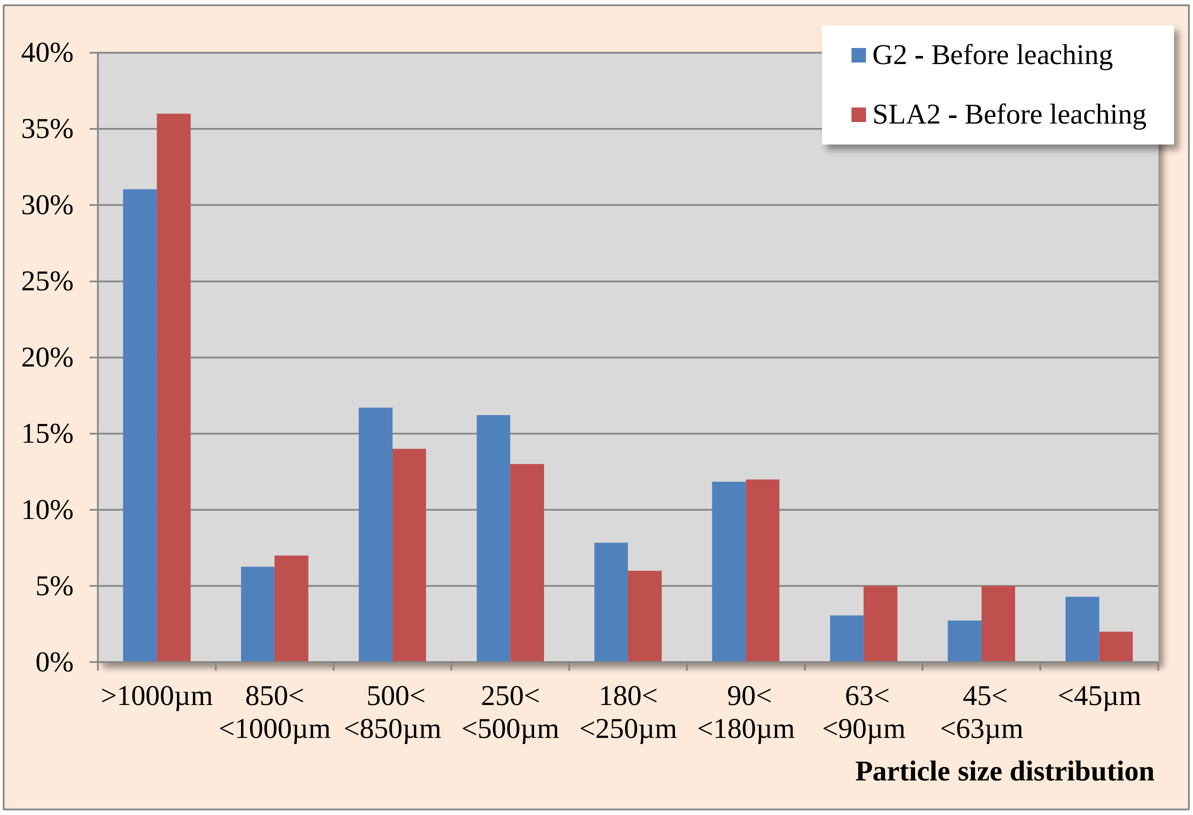

Figure 1. Particle size distribution of SLA2 and G2 graphite samples before leaching tests

3 Experimental methodology

3.1 *Leaching test methodology*

The methodology used for previous graphite leaching tests was initially designed for chlorine 36 study. The sampling sequence was based on the assumption that the labile fraction of chlorine 36 follows a diffusion law. The consequence of it is that the sampling timeframes were closely spaced at the beginning of the leaching test. Longer sampling timeframes were chosen once the released of chlorine 36 stabilized.

Concerning carbon 14, this sampling sequence had to be updated as it resulted in diluted concentration for carbon 14 because of its very low release rate. As a consequence, most of measurements were below quantification limits in the experimentations designed for chlorine 36.

Moreover, some other parameters had to be optimized in order to better fit with the characteristics of carbon 14 release. The following experimental conditions were changed over the time: dynamic or semi-dynamic sampling, mass to volume ratios, the use of graphite blocks or powder, the amount of graphite in each experiment, the pH of the leaching solution, etc.

Given these technical constraints, the parameters used for the present study were as follows:

- Dynamic/Semi-dynamic sampling: Due to very low concentration of carbon 14 in the leachate, a dynamic sampling methodology was not applicable to a carbon 14 release study. As a consequence, a semi-dynamic methodology was used. It consists of the partial removal of the leaching solution, which is replaced by fresh solution so that the liquid volume remains constant. The leachate concentration obtained is higher than in the case of a dynamic sampling. As a consequence, the released radionuclides are more concentrated in the solution, allowing a better measurement above the quantification limit. The experimentations were carried out in the Laboratory of Chemical and Radiochemical Analyses[3] in CEA Cadarache. This laboratory can manipulate a high amount of radioactive material. This higher amount of irradiated graphite allowed a higher mass on volume ratio (mass of irradiated graphite on volume of leaching solution) in order to obtain higher concentration of carbon 14 in leaching solution.

- The use of powdered samples was chosen in order to increase the carbon 14 release rate (increase of the ratio surface of graphite on volume of leaching solution), particularly for the tests dedicated to carbon 14 speciation.
- The pH of the leaching solution was chosen to be as representative as possible of the future disposal facility concept (made of concrete barriers). It was a solution of NaOH at 0.1 M, pH 13 under inert atmosphere.

Moreover, in order to increase the contact between the leaching solution and the irradiated graphite (powder), a continuous agitation was maintained.

Table 5 records the parameters used during the carbon 14 speciation tests presented in this document.

Table 5. Leaching test parameters

Reactor	Graphite sample mass	Leaching solution volume	Gas volume	Duration	Leaching solution
SLA2	24.97 g	100 mL	150 mL (N_2)	551 days	NaOH 0.1 M
G2	50.29 g	200 mL	300 mL (N_2)	548 days	NaOH 0.1 M

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[3] LARC (DEN/CAD/DEC/SA3C/LARC)

The leaching tests are carried out in a glass sealed reactor, as shown in Figure 2, in this case under inert atmosphere (anoxic conditions).

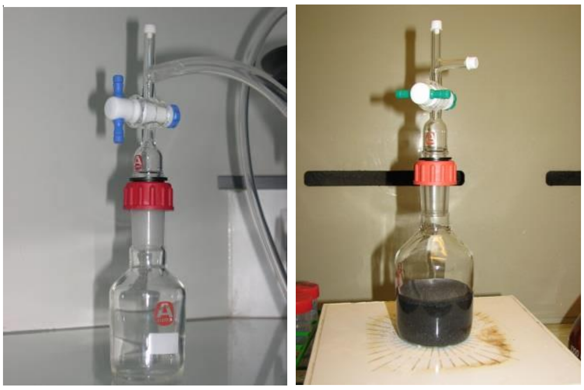

Figure 2. Gastight glass containers (without and with graphite powder) for leaching experiments

3.2 *Carbon 14 measurements*

3.2.1 Carbon 14 in the graphite samples

High discrepancies are observed on radionuclide measurements in irradiated graphite, especially for trace level radionuclides. For this reason, the carbon 14 mass balance in leaching tests has to be carried out on the whole graphite sample used for the leaching test, and not only for an aliquot of the sample.

As carbon 14 measurement in irradiated graphite is a destructive method, the initial activity of leached sample can be obtained only at the end of the leaching test, on the whole leached sample in addition with carbon 14 released in the leaching solution and in the gas phase.

The principle of the carbon 14 measurement for the two leaching tests of this document is the following one (LARC Methodology N° LARC MA001):

- A complete combustion of the sample is carried out under oxygen in a furnace at a temperature of approximately 900°C.

- The combustion gases are fully oxidized on a catalyzed bed (Pt and CuO catalyst) at about 680°C in order to fully convert carbon in CO_2. This CO_2 is trapped in a scintillation liquid cocktail specific to the carbon 14 (Zinsser analytical Oxysolve C400).

- The device used (Zinsser Oxidizer OX-501) ensures the separation of the tritium in vial before the recovery of carbon 14. Metals, salts, oxides with high melting points stay in combustion ashes.

The chemical yield of the combustion process of the graphite is determined by burning a carbon 14 standard solution mixed with non-irradiated graphite powder. The chemical yield is calculated by comparing the value obtained in the vial by liquid scintillation with the theoretical value. The selectivity of tritium/carbon 14 separation is also determined by applying the same procedure with a tritium standard.

3.2.2 Carbon 14 in the gas phase

The gas phase is sampled with the same sequence as for liquid phase. When required, the pump at the outlet of the system is switched on, in the same time as for the nitrogen inlet (see Figure 3). The inorganic species of tritium and carbon 14 in the gas phase are trapped in the HAG7000 system[4], as HTO for tritium and CO_2 for carbon 14. The organic species of tritium and carbon 14 in the gas phase (including HT and CO) are oxidized in a catalytic conversion furnace, and then trapped as HTO for tritium and CO_2 for carbon 14. This methodology enables the identification of the speciation of released carbon 14 as inorganic or organic species. With this experimental procedure, it has to be remembered that organic species correspond to real organic species (CH_4, etc.) but would also include any CO, which would be oxidized at the same time. For each gas sampling, a blank is carried out first.

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[4] HAG7000 system is certified according to the French standard « NF M60-812-1 Novembre 2006 - Énergie nucléaire Mesure de la radioactivité dans l'environnement - Partie 1 : guide du mesurage de l'activité volumique de l'air en C14 à partir d'un prélèvement atmosphérique »

Figure 3 clearly shows that the gas phase in the reactor is kept inert, even during gas sampling. The oxygen required for the catalytic conversion is added separately, after the leaching test reactor.

After each gas phase sampling, the pump is switched off, and the gas inlet are closed. There is no gas inlet between each gas phase sampling.

Figure 4 shows a photo of the experimental device with a leaching test reactor (left).

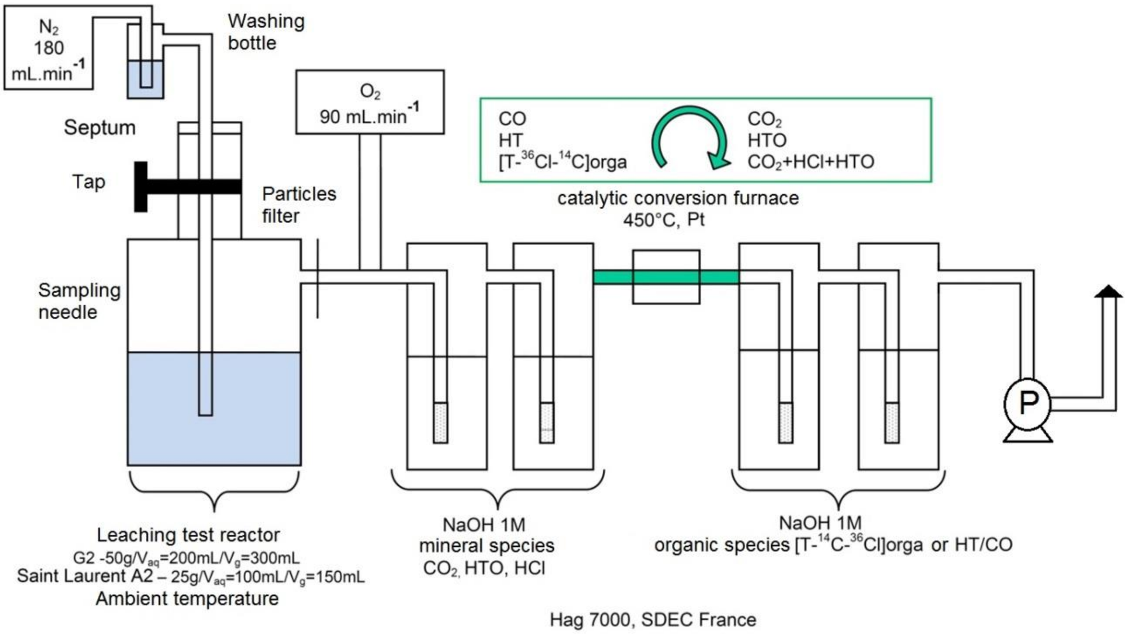

Figure 3. Experimental device for gas phase analysis

Figure 4. Experimental device HAG7000 (Vendé, 2012)

3.2.3 Carbon 14 in the leaching liquid and speciation

Due to the presence of many β/γ emitters in the leaching solution, it is not possible to measure directly carbon 14 in the solution. Consequently, after a first step of filtration of the solution, a thermal separation of the carbon 14 from the others β/γ-emitters is done (complete combustion). The methodology is the same as for a graphite sample (see section 3.2.1). The combustion gases are fully oxidized on a catalyzed bed (Pt and CuO catalyst) at about 680°C in order to fully convert carbon in CO_2. This CO_2 is trapped in a scintillation liquid specific to the carbon 14 (Zinsser analytical Oxysolve C400). Then, carbon 14 is measured by scintillating counting.

With this process, it is possible to determine organic and inorganic fractions of carbon 14 in the liquid phase (LARC methodology), as follows:

- First, a part of the sampled liquid is analyzed in order to obtain the total (organic + inorganic) carbon 14 content,

- Secondly, another part of the sampled liquid is acidified in order to remove the inorganic content (acidification into CO_2 of the carbonates form). Then, this sample is analyzed so as to obtain the organic carbon 14 content of the solution.
- Finally, the difference between these two analyses gives the inorganic carbon 14 content of the leaching solution.

4 Results

More than 50 carbon 14 leaching experiments were carried out on French irradiated graphites, especially for G2, SLA2 and Bugey 1 reactors. However, in most cases, carbon 14 is not measured as it is below the quantification limit (particularly because dynamic samplings were carried out in these tests). Even for the tests in which carbon 14 is measured, the quantity is very low (from 2 to 5 times the quantification limit) and the speciation is not analyzed.

Consequently, the tests on G2 and SLA2 graphite stack powder, and described hereafter, were specifically designed to increase the carbon 14 release and to allow carbon 14 speciation measurements (see section 3.1). Due to the design of these tests (graphite powder, agitation, etc.), it has to be reminded that the carbon 14 released fraction is overestimated compared to the release anticipated in a future disposal facility.

These tests were carried out for more than 500 days. However, despite this duration, the carbon 14 release had not yet stabilized at the end of the tests. The results are shown in Figure 5 for SLA2 reactor and in Figure 6 for G2 reactor (Andra, EDF & CEA, 2015).

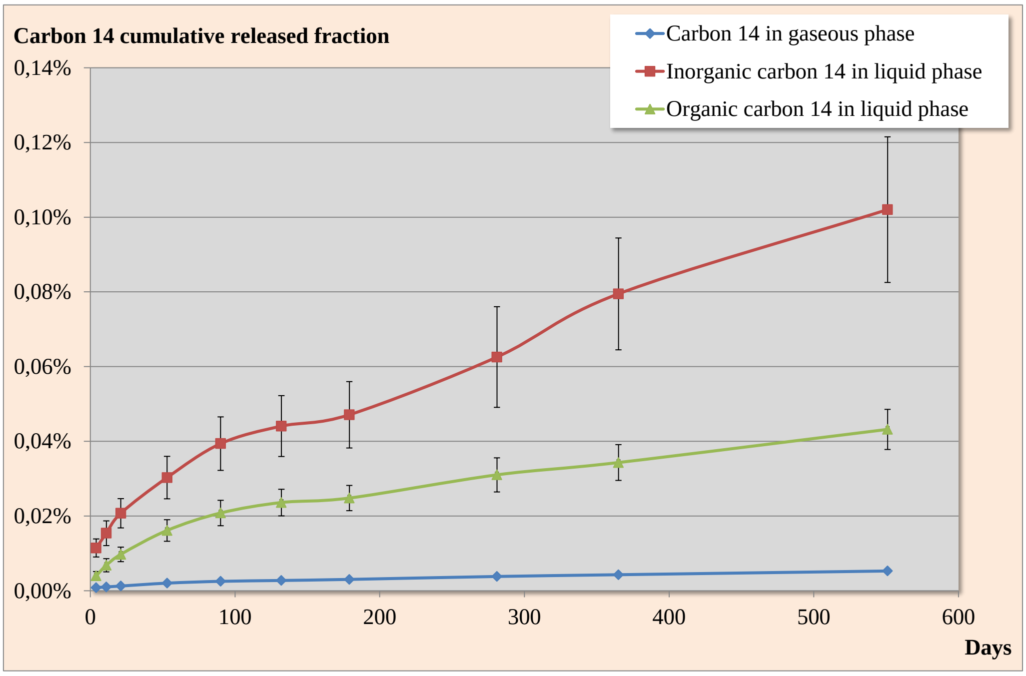

Figure 5. Carbon 14 release during leaching tests of SLA2 graphite (graphite powder, pH 13 NaOH 0.1 M)

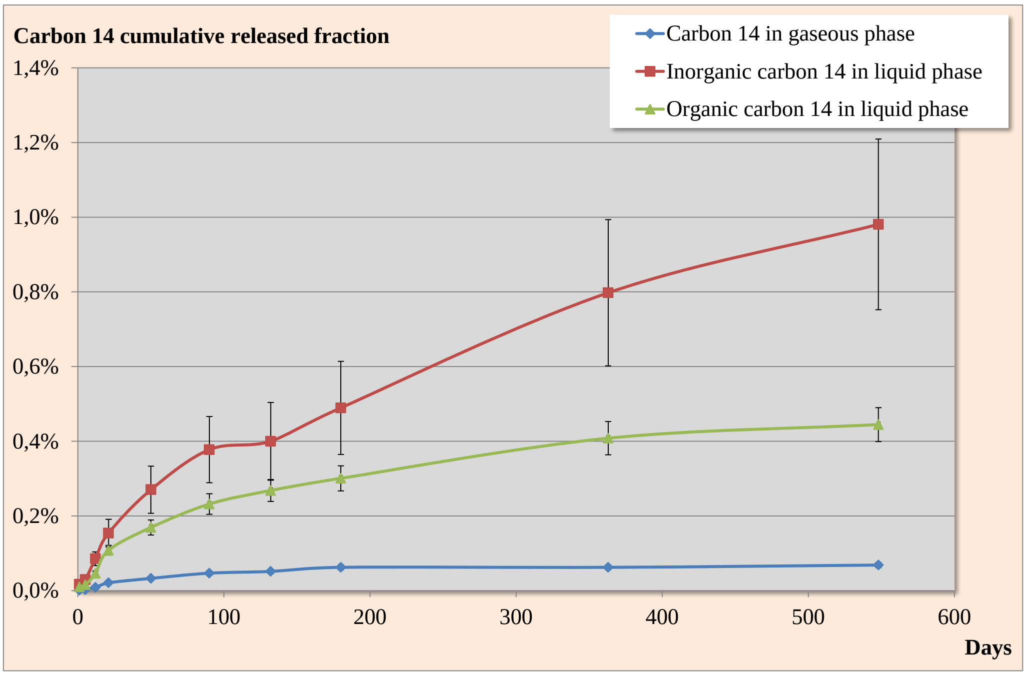

Figure 6. Carbon 14 release during leaching tests of G2 graphite (graphite powder, pH 13 NaOH 0.1 M)

Thanks to the design of these tests, release rates are measurable. As shown on Figure 5 and Figure 6, carbon 14 release rate for G2 graphite is approximately 10 times higher than for SLA2 graphite, in the liquid phase, but also in the gaseous phase.

Most of the carbon 14 is released in the liquid phase (>95 %) for both reactors. This distribution between the liquid and the gas phases is consistent with the data coming from a study carried out in the UK about the carbon 14 release from Oldbury graphite (Baston et al., 2014).

In the liquid phase, most of the carbon 14 is released as inorganic species (carbonates). However, some carbon 14 is also released as organic species. In the first part of the tests (t<180 days), the distribution of inorganic and organic species evolved. After 180 days, the distribution stabilized and approximately 30 % of the carbon 14 was released as organic species. This value is consistent with some tests carried out by Marshall et al. (2011).

In the gaseous phase, due to the pH of the leaching solution, carbon 14 can only be as organic species or as ^{14}CO. Because of the analytical procedure (see section 3.2.2), it is currently not possible to differentiate these two species. The inorganic molecules (CO_2 or carbonates) are soluble in the solution.

5 Influence of leaching parameters

The purpose of this section is to evaluate the influence of different parameters on carbon 14 release during leaching tests (Andra, EDF & CEA, 2015). Despite more than 50 leaching tests, just a few parameters have been tested because of the low release of carbon 14. Some important ones have not yet been tested.

5.1 *Water chemistry: Leachant chemical composition and experimental parameters*

The composition of the leaching solution is a key parameter of the carbon 14 release studies. This leaching solution has a direct effect on the solubility and the chemical form of carbon 14, but also on the distribution of carbon 14 in liquid and gaseous phases. This effect is due to the acid-base nature of the inorganic form of carbon 14 (CO_2, HCO_3^-, CO_3^{2-}) and some organic forms (carboxylic acid, etc.).

Figure 7 presents some tests in three different leaching solutions of SLA2 graphite powders coming from the same initial sample: demineralized water, dismantling water (pH 8,2) and NaOH 0.1 M (pH 13). The results include the fractions released in both gas and liquid phases. These tests were carried out in the same conditions, with exception of the agitation. Only the test in NaOH 0.1 M was carried out with continuous agitation. It is observed that the radionuclide release in NaOH 0.1 M is higher than in other solutions, whereas the release in demineralized water[5] and dismantling water is similar. This effect is not perfectly understood, but it is assumed that it could likely be the result of the graphite powder degradation due to one of these two effects or both at the same time: graphite hydrolysis and/or continuous agitation. Concerning the continuous agitation, the assumption is that it can potentially degrade (physical erosion for example) the powder and reduce the particle size and, consequently, increase the carbon 14 release rate.

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[5] In the case of carbon 14 release in demineralized water, the measures are under quantification limits.

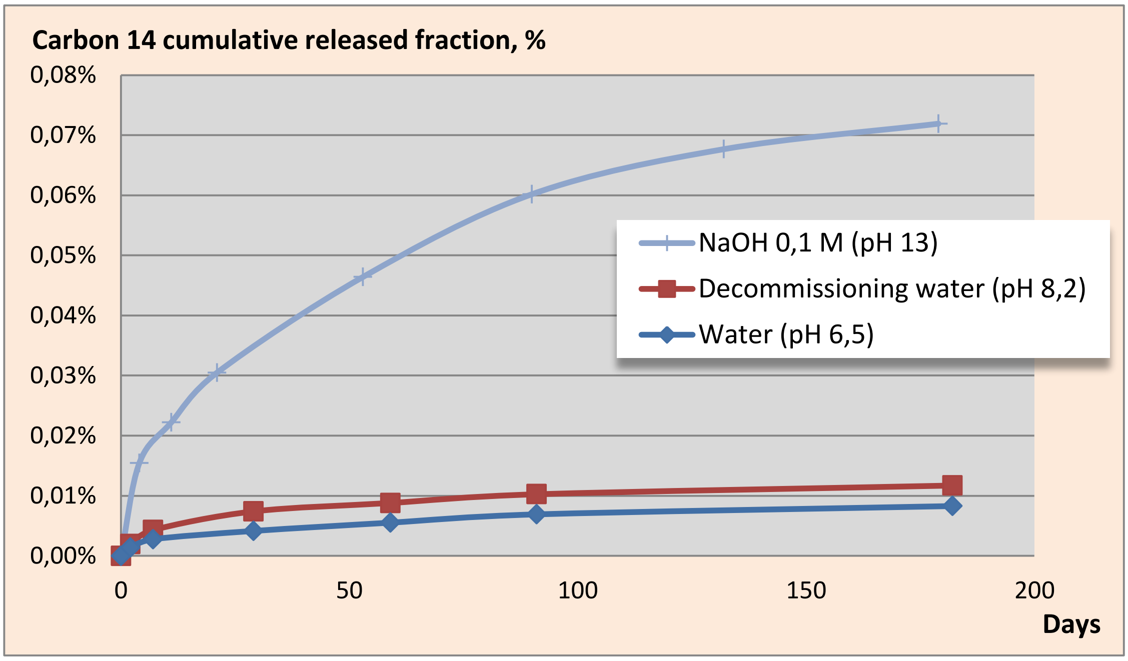

Figure 7. Carbon 14 release in three different leaching solutions

In order to confirm this hypothesis, some analyses of particle size distributions were performed before and after leaching tests. In case of a continuous agitation, the measured distribution shows that the particle size is approximately divided by 2. Furthermore, the smallest particles of graphite are aggregated in an amorphous form and can’t be separated when their size is lower than 63 µm.

Figure 8 shows the particle size distribution of G2 graphite powder before and after leaching in NaOH 0.1 M with continuous agitation.

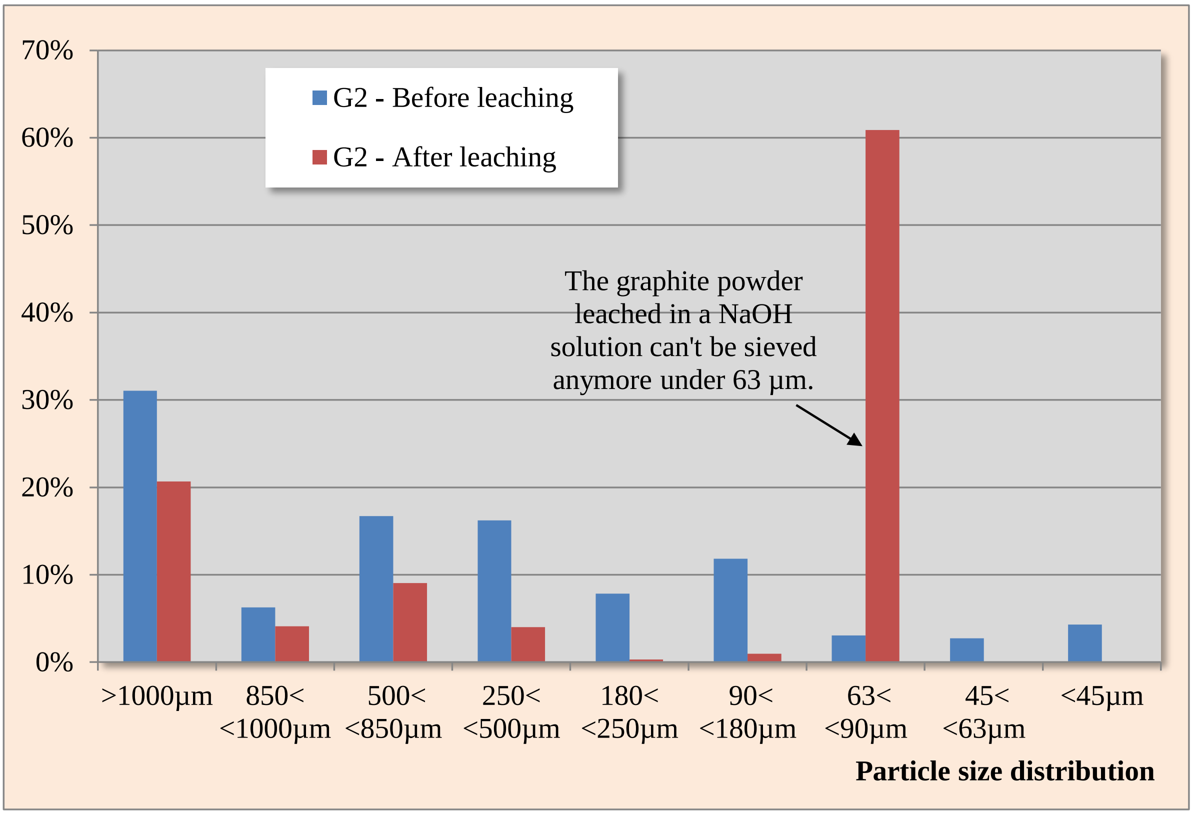

Figure 8. Particle size distribution of G2 irradiated graphite powder before and after leaching in a NaOH 0.1 M solution (pH 13)

Figure 9 illustrates the evolution of SLA2 graphite powder after leaching in the three different leaching solutions. As for G2 graphite powder, the smallest particles of graphite are aggregated in an amorphous form and can’t be separated when their size is lower than 63 µm.

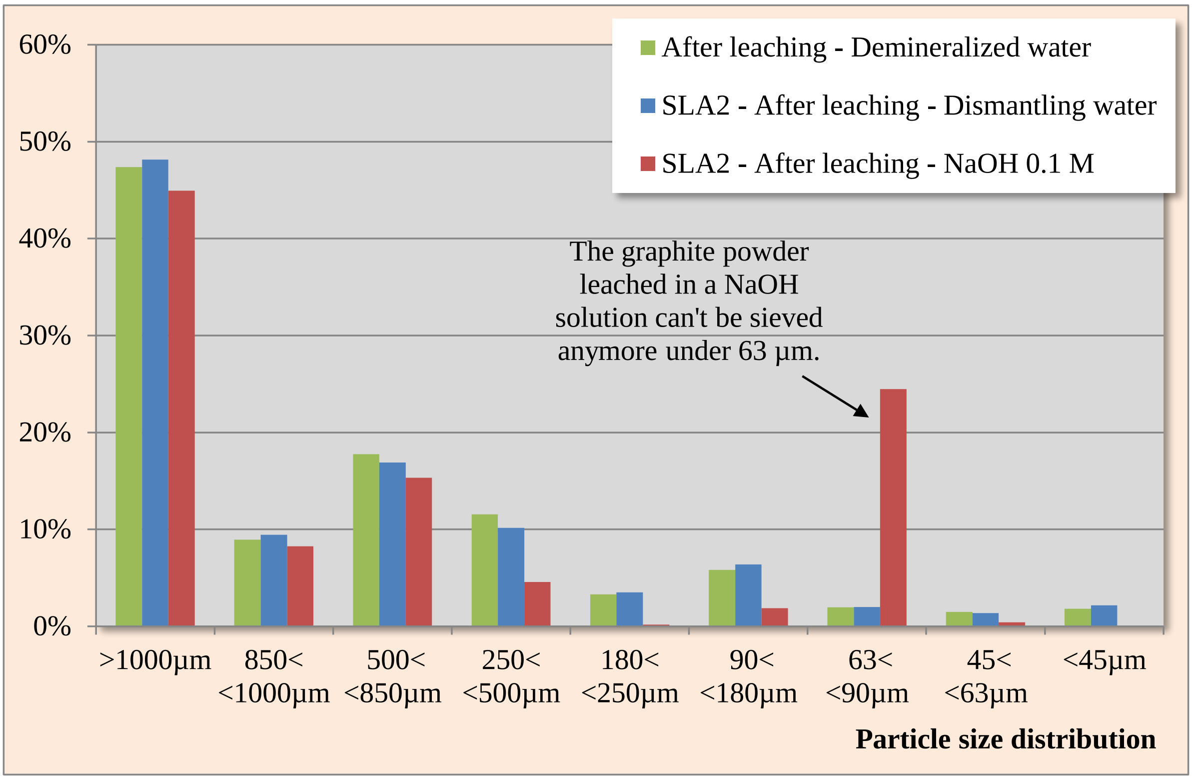

Figure 9. Particle size distribution of SLA2 irradiated graphite powder after leaching in different aqueous solutions

In order to be representative, the physicochemical conditions of the leaching solution have to be as close as possible to the conditions of the future disposal facility, particularly concerning the pH.

5.2 *Specific surface area of samples*

The effect of the specific surface area during leaching tests has not been studied yet for French irradiated graphites. As mentioned in D5.1 (see reminder in Annex 8.1), some comparison between tests carried out under water and under NaOH 0.1 M solution show an effect of the specific surface area. Carbon 14 release is increased when the ratio surface of graphite on volume of graphite is increased. However, some tests have to be done to quantify this effect.

The influence of the specific surface area has been precisely studied by Mc Dermott (2011). Some powder and block samples of BEPO graphite have been leached under water. The BET surface areas of these samples are 55.0 m^2/g for powder and 0.8 m^2/g for solid bloc. Figure 10 shows the results. Some similar results have been obtained in a basic leaching solution.

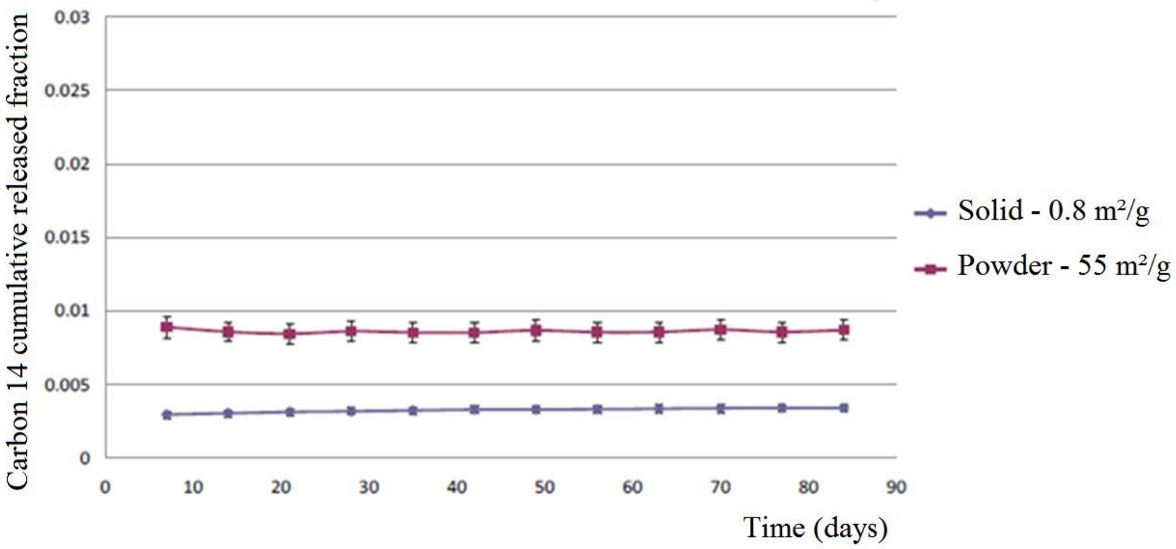

Figure 10. Surface ratio effect on carbon 14 release (BEPO Graphite, leaching under demineralized water)

It is observed that more carbon 14 is released when the ratio surface area on graphite volume is higher. It is also observed that this effect has mainly occurred during the first days of the leaching test. Then, the leaching rate stabilized. This observation suggests that the increase of the specific surface area increases the accessibility to some less leachable carbon 14 fractions.

These results underline the necessity to carry out leaching tests with graphite blocks in order to be representative of the waste in a future disposal facility.

5.3 *Other parameters*

Some other parameters could have an influence on carbon 14 release and speciation (Andra, EDF & CEA, 2015), such as: temperature, initial activity of the samples, location in the reactor. Even if these parameters have been studied with more than 50 leaching tests, these tests were not specifically designed for carbon 14. As a consequence, the carbon 14 measurement in most of these tests is under the quantification limit, and it is not possible to reach a conclusion with them. The effect of these parameters on carbon 14 release is not yet known for French irradiated graphites.

6 Conclusion

Carbon 14 is one of the key radionuclides for the future disposal of French irradiated graphite waste. It is one of the main long-lived radionuclides, and depending on its speciation, it can be more or less mobile in a disposal facility and more or less incorporated into living organisms. For this, the speciation of this radionuclide after being released has to be carefully studied.

As a consequence, some leaching tests have been specifically designed to identify the organic and inorganic fractions of the carbon 14 released from irradiated graphite stack. Two French reactors have been tested: SLA2 and G2. The results of these tests are given in two reports. A first report, D5.1 (see reminder in Annex 8.1), was dedicated to the leaching rate of carbon 14. This leaching rate is always low, lower than 1%/year. Some differences are observed between tests, but it is not obvious to identify the influence of each parameter. A second report, this document (D5.8), is dedicated to the speciation of the released carbon 14.

An experimental methodology was designed in order to identify the organic and inorganic fractions in gas and liquid phases. Concerning the gas phase, the experimental device HAG7000 was used. The inorganic fraction and the organic fraction were trapped separately in a caustic soda solution. Then, these solutions were analyzed. Concerning the liquid phase, a complete combustion was carried out on a sample of the solution to measure the total carbon 14 content, but also on a sample of an acidified solution in which inorganic forms of carbon 14 (carbonates) were removed. The carbon 14, after thermic separation, was trapped in a scintillation liquid cocktail and analyzed by liquid scintillation. This procedure gives two results: the organic + inorganic carbon 14 content and the organic carbon 14 content. The inorganic content is the difference between these two results.

As a result, these tests showed that more than 95% of the released carbon 14 was found into the liquid phase. In this liquid phase, most of the carbon 14 (70%) is in the form of inorganic species (carbonates). However, some carbon 14 in the liquid phase is also in the form of organic species. After a first period of evolution, the distribution stabilized and approximately 30% of the total carbon 14 in the liquid phase is in the form of organic species. In the gas phase, due to the pH of the solution, carbon 14 can be in the form of organic species or CO. Because of the analytical procedure, it is not possible to differentiate these two forms.

Some parameters that can influence the release of carbon 14 were also analyzed. The water chemistry seems to have an impact, but the effect of the continuous agitation during the tests presented in this report can be more or less important and has to be clarified. Moreover, the specific surface area of the sample seems to have an impact. Some parameters have not been studied, mainly because of the low leaching rate of carbon 14 in the corresponding tests, such as temperature, initial activity of the samples, and location in the reactor.

Concerning the implication of these studies for other i-graphites, it seems important to recall that radionuclide behavior might depends on the history and the background behind the used i-graphite. This is particularly true for carbon 14. In France, the presence of an organic form of carbon 14 in the leachate has an important impact on the future studies on graphite waste. Today, it is recognized that the leaching solution has to be representative in terms of pH of ground water considered likely to be present in the future disposal facility.

It is also important to mention that the tests presented in this document were carried out to increase the leaching rate and the concentration of carbon 14 in the liquid phase: semi-dynamic conditions, use of graphite powder, continuous agitation, liquid and gas sampling sequence. As a consequence, in France, studies on the carbon 14 release from graphite waste will be intensified, particularly to be more representative of the future disposal conditions. The organic fraction of carbon 14 has to be quantified more precisely.

7 References

(Andra, EDF & CEA, 2015) Andra, EDF & CEA, Référentiel graphite – Bilan des connaissances, FRPASCM150026 A, 2015

(Baston et al., 2014) G. Baston, S. Preston, R. Otlett, J. Walker, A. Clacher, M. Kirkham, B. Swift, Carbon-14 Release from Oldbury Graphite, AMEC, AMEC/5352/002 Issue 3 / NPO004819, 2014

(Marshall et al., 2011) T.A. Marshall et al., Longer-term release of carbon-14 from irradiated graphite, Serco technical report TAS/001190/001 Issue, 2011

(Mc Dermott, 2011) L. Mc Dermott, Characterization and chemical treatment of irradiated UK graphite waste, Thèse de Doctorat de l'université de Manchester, 2011

(Petit, 2009) L. Petit, WP1 – Review report – France, Carbowaste CW0904-D-1.1.4, 2009

(Petit et al., 2014) L. Petit (EDF), J. Comte (CEA), S. Catherin (Andra), Review on carbon 14 leaching data in French irradiated graphite (D5.1), CArbon-14 Source Term – CAST, 2014

(Vendé, 2012) L. Vendé, Comportement des déchets graphite en situation de stockage : relâchement et répartition des espèces organiques et inorganiques du carbone 14 et du tritium en milieu alcalin, Thèse de Doctorat, thèse n° 2012EMNA0018, 2012

8 Annexes

8.1 *Brief reminder of D5.1 – Review on carbon 14 leaching data in French irradiated graphite (Petit et al., 2014)*

The purpose of deliverable D5.1 was to give an overview of the results obtained on the leaching behavior of carbon 14 in French i-graphite. The results of studies carried out between the 90's and nowadays on French i-graphite were analyzed. The main conclusions are the following ones.

Concerning the graphite stack, the obvious result is that carbon 14 leaching rate is very slow in French i-graphites. In most of cases, a quasi-steady leach rate state seems to be achieved after around 100 to 200 days. Over that period, the measured carbon 14 release rate depends on the shape of the samples (block / powder). In order to standardize the results, a mean carbon 14 leaching rate (R_O) has been calculated. It takes into account the geometric volume ratio on the geometric surface of the leached sample. R_O is calculated as follows:

$$R_o = FAL\frac{V}{S}.\frac{1}{365}$$

With:

- **R_O**: Mean leach rate during the quasi-steady state (meter.day^{-1}).
- V and S: respectively the geometric volume in cubic meters and the geometric surface in square meters of the leached sample (geometric = calculated on external dimensions).

The FAL is the annual leached fraction. It is calculated as follows:

$$FAL = \frac{\sum_{i=t_d}^{t_f} a_i}{A_0} \times \frac{365}{(t_f - t_d)}$$

With:

- **FAL**: Annual leached fraction. It is determined during the quasi-steady state observed from the t_d time to the end of the leaching experiment t_f.
- $\sum_{i=t_d}^{t_f} a_i$ is the cumulative leached carbon 14 activity during the quasi-steady state.
- A_0 is the initial total activity of the leached graphite sample.
- t_d is the time (in days) at the beginning of the quasi-steady state (at least 100 days for carbon 14) and t_f the final time of the experiment.

In that case, the mean carbon 14 leaching rate lies in a wide range from $4.7\ 10^{-11}$ up to $4.2\ 10^{-8}$ $m.day^{-1}$. The reasons of the variability of the carbon 14 leaching rate are still not clear. It can be observed that the mean calculated carbon 14 leaching rate might be split into two groups: a first one with a R_O around 10^{-11} $m.day^{-1}$ and another one with a higher R_O close to 10^{-8} $m.day^{-1}$. These values must be considered with caution depending on the assumptions made for the graphite surface assessment. However, leaving aside the issue of the origin of the graphite, it can be noticed that these two groups correspond to two types of UNGG reactors with slightly different operational conditions.

The sleeve graphite (operational waste which represents a small part of the total inventory of carbon 14) seems to have a faster carbon 14 leaching rate. More investigation is required to clarify this particular behavior.

The impact of the nature of the leaching liquid (deionised, lime or soda water) on the carbon 14 leaching behaviour is unclear and has to be confirmed. Actually, many results are below the quantification limits of the method used for the carbon 14 measurement in the leaching liquid. One of the main challenges for carbon 14 leaching studies in graphite is the very slow release rate. To obtain significant results (above the quantification limit), the requirement is to use high masses of trepanned samples (which are not always available) and to use a suitable methodology of leaching liquid sampling and carbon 14 measurements.

Concerning the implications of these studies for others i-graphites, it is important to recall that the results obtained on the radionuclide behavior might depend on the history and on the background of i-graphites. In the case of French i-graphites, thanks to the radiological inventory assessment, it has been shown that most of the carbon 14 remaining in i-graphites comes from carbon 13 activation. The carbon 14 arising from nitrogen activation (supposed to be mainly located on the surface of i-graphites) was released during operation because of the temperature and the radiolytic corrosion. On the contrary, according to some publications about reactors such as Magnox reactors in the UK, it is assumed that carbon 14 remaining in i-graphites may arise mainly from nitrogen activation located on the surface of the graphite. As a consequence, it can be clearly assumed that carbon 14 behavior in disposal conditions might not be necessarily the same for both graphites depending on the origin (and location) of carbon 14. In the same way, some reactors such as G1 in France were air-cooled. It can also be assumed that in that case the carbon 14 might behave differently compared to the carbon 14 of the i-graphite from CO_2-cooled reactors. Because of the foregoing, the results obtained on the i-graphites studied in D5.1 cannot be directly and simply extended to other i-graphites.

8.2 *Extract from D5.1 (chapter 2): Reactors and material description (Petit et al., 2014)*

This annex is an extract from chapter 2 of D5.1 (parts 2.1 and 2.2). It gives an elemental review of the history and background behind the i-graphite material that was used for leaching tests. It focuses on two out of the nine French UNGG reactors: G2 and Saint-Laurent A2 (SLA2). The location of these three reactors in France is presented in Figure 11. More details on French UNGG reactors can be found in (Petit, 2009).

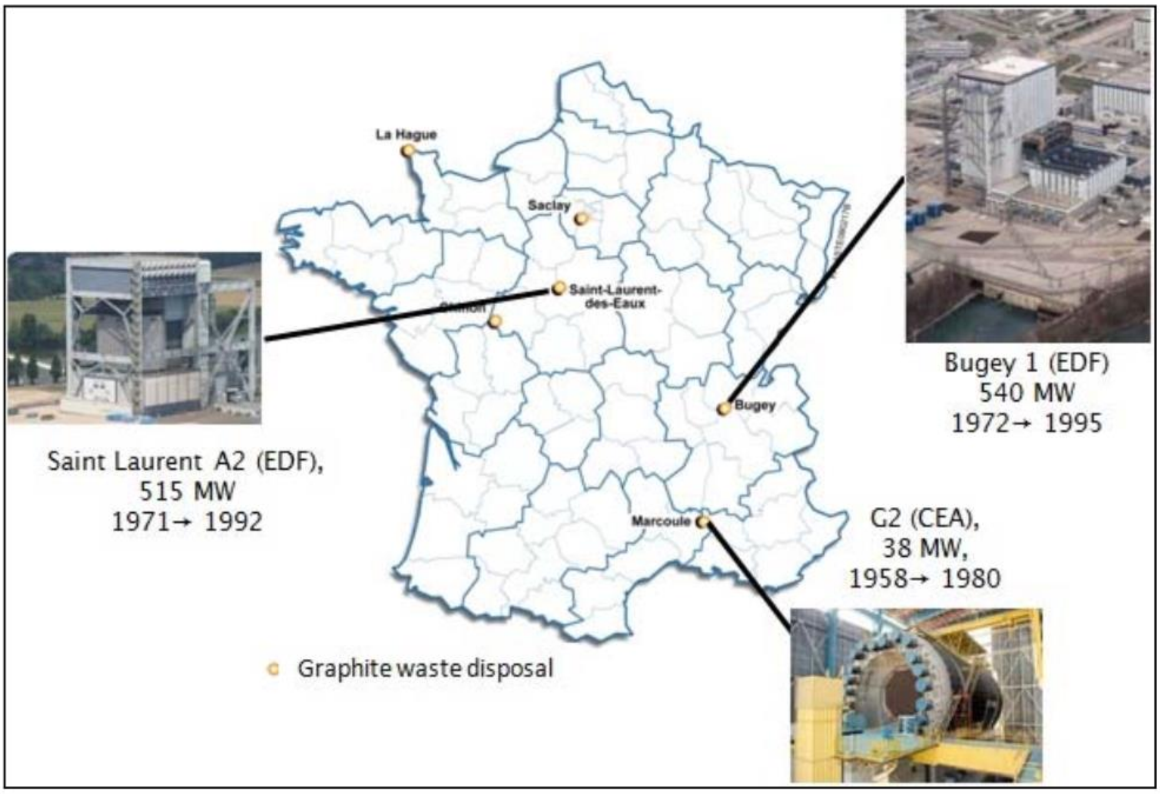

Figure 11. Location of G2, SLA2 and BUA1 reactors

8.2.1 G2 reactor

8.2.1.1 General description

The G2 reactor is a French UNGG reactor built and operated by the CEA on the Marcoule site (Gard, south-east of France). It was cooled by pressurized carbon dioxide and fuelled with metallic natural uranium. Its first divergence happened on July 1958 and shutdown on February 1980. The pressure vessel is made of pre-stressed concrete, which also acts as biological shielding. Its rated thermal power was around 250 MW. The G2 reactor reached the IAEA dismantling level II.

Table 6. Material properties of SLA2 and G2 graphite (before irradiation)

Properties	SLA2 moderator	Graphite G2 moderator	G2 reflector
Coke	Lima	Special A	Lockport L
Bulk density	1.68	1.71	1.68
Capture section (mbarn)	3.75	3.95	4.02
Ash content	98 ppm	106 to 125 ppm	136 to 156 ppm
Thermal expansion coefficient a (⊥) Thermal expansion coefficient a (//) Anisotropy ratio a (⊥) / a (//)	$3.8.10^{-6}$ C^{-1} $2.4.10^{-6}$ C^{-1} 1.6	 1.2 10^{-6} K^{-1} 2.3	 2.7 10^{-6} K^{-1} 1.3
Compressive strength (MPa)	42	27	34

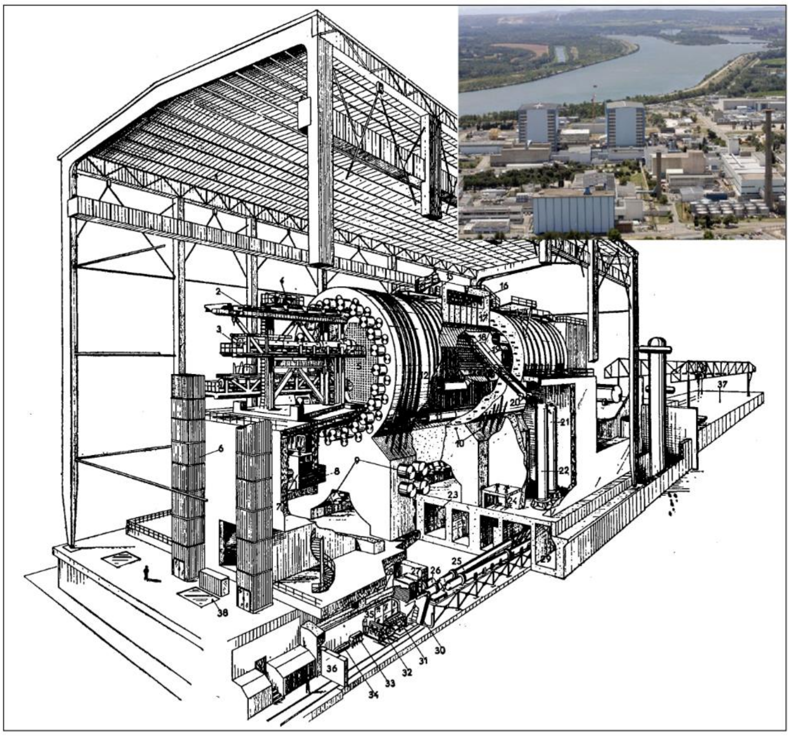

Figure 12. General cutaway view of the G2 reactor and aerial photography of the G2 and G3 reactor buildings in Marcoule (upper right in the backgroung)

The graphite stack of reactor G2 was made of “special” Grade A coke and Lockport L coke (see Table 6). The stack consists of 14,092 rectangular block shaped bricks with a square section of 200 mm sides and a maximum length of 1,500 mm. The bricks are laid out horizontally to form a horizontal prism 9.05 m long, 9.40 m high and 9.53 m wide perforated with 1200 channels. The reactor consists of three types of graphite located in four distinct zones (see Figure 13):

- Zone A: The active cylinder (moderator) of G2 consists of Special A coke (similar to British Grade A coke) impregnated once and purified, having a specific density generally stated as 1.71;
- Zone B: it is the internal reflector which is based on special “A” coke (similar to british Grade A graphite) that had undergone both impregnation and purification;
- Zone C: it is the external reflector which is based on Lockport L coke that has undergone both impregnation and purification;
- Zone D: The 80 cm thick graphite wall plays the role of a reflector on the back of the graphite block (opposite side to the loading face) to avoid the exposure of the back end concrete to fast neutrons. It consists of purified graphite based on non-impregnated Lockport L coke.

The graphite of the moderator and of the reflector was once impregnated and purified with a NaF conditioner.

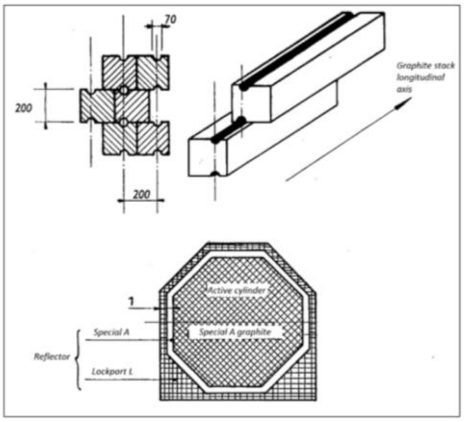

Figure 13. Graphite stack and graphite bricks of the G2 reactor

Carbon dioxide cooling gas pressure was 15 bars. The inlet gas temperature was 140 °C and the outlet temperature ranged from 300 to 390 °C depending on the location (center or periphery). The temperature of the graphite ranged in the same scale. The nuclear fuel consists of natural uranium with a magnesium-zirconium (0.7 % Zr) alloy cladding. Two coring campaigns were carried out on the shutdown G2 reactor. In 1988, a horizontal radial coring was carried out. Lastly, in 1989, a vertical radial coring was performed along the entire height of the stack.

8.2.1.2 Material used for leaching tests

The origin of the cores used for the leaching tests carried out in 1990 in a comparative study with PNL is identified as cores from the moderator or from the reflector cored during the 1988 campaign.

The series of leaching tests carried out in 2007 were performed on sample n°36 from the vertical coring (1989) in the lower half of the reactor. This sample was located in the moderator part of the reactor and its operating temperature was around 310 °C. It was certainly produced from Special A coke. These cores were 13 to 20 cm long and 6.3 cm in diameter in the case of sample from the vertical coring (Figure 14). It was therefore necessary to cut them up to prepare samples for the leach and impregnation experiments and microstructure characterizations.

Figure 14. G2 core

8.2.2 Saint Laurent A2 reactor (SLA2)

8.2.2.1 General description

The SLA2 reactor is a French UNGG reactor operated by EDF. It was commissioned in August 1971 and the final shutdown happened on May 1992. The pressure vessel is made of pre stressed concrete which also acts as biological shielding. It is an integrated type reactor where the heat exchangers and the entire primary circuit are in the same containment (see Figure 15). As for G2 reactor, SLA2 was CO_2-cooled. The coolant moved from the top to the bottom of the reactor at a pressure of 29 bars. The nuclear fuel was metallic natural uranium in a Mg-Zr alloy cladding. The thermal power was 1,700 MW with a gross electrical power of 530 MW and a net electrical power in nominal operation of 515 MW. The thermal neutron flux (10^{-5} eV to 0.5 eV) was up to 3.12×10^{13} $n.cm^{-2}.s^{-1}$ in the central zone of the graphite stack. The operating temperature of the graphite ranged from 250 to 460 °C.

In March 1980, because of the obstruction of a fuel channel by a metal plate, the loss of cooling in this fuel channel led to the melting of two fuel elements. Therefore the SLA2 reactor was shut down for 30 months (from March 1980 to September 1982) for decontamination and cleanup work.

The SLA2 graphite stack is cylinder-shaped with a vertical axis of 15.73 meters in diameter (13.43 meters of moderator surrounded by a 1.15 meters thick reflector). It is 10.2 meters high. The total mass of graphite is 2,440 tons including 1,580 tons of moderator and 860 tons of reflector (periphery of the stack). The elementary graphite blocks are prismatic bars with a hexagonal base whose distance between two opposite faces is 225 mm. The stack is made of 8 beds of 4,429 side-by-side juxtaposed bars.

The graphite of the Saint-Laurent A2 stack was manufactured by the Pechniney/SERS Company between May 1966 and November 1967. This graphite was made from Lima coke. It underwent one impregnation and was purified using MgF_2. Some of its characteristics are compared to those of the graphite of the G2 reactor in Table 6.

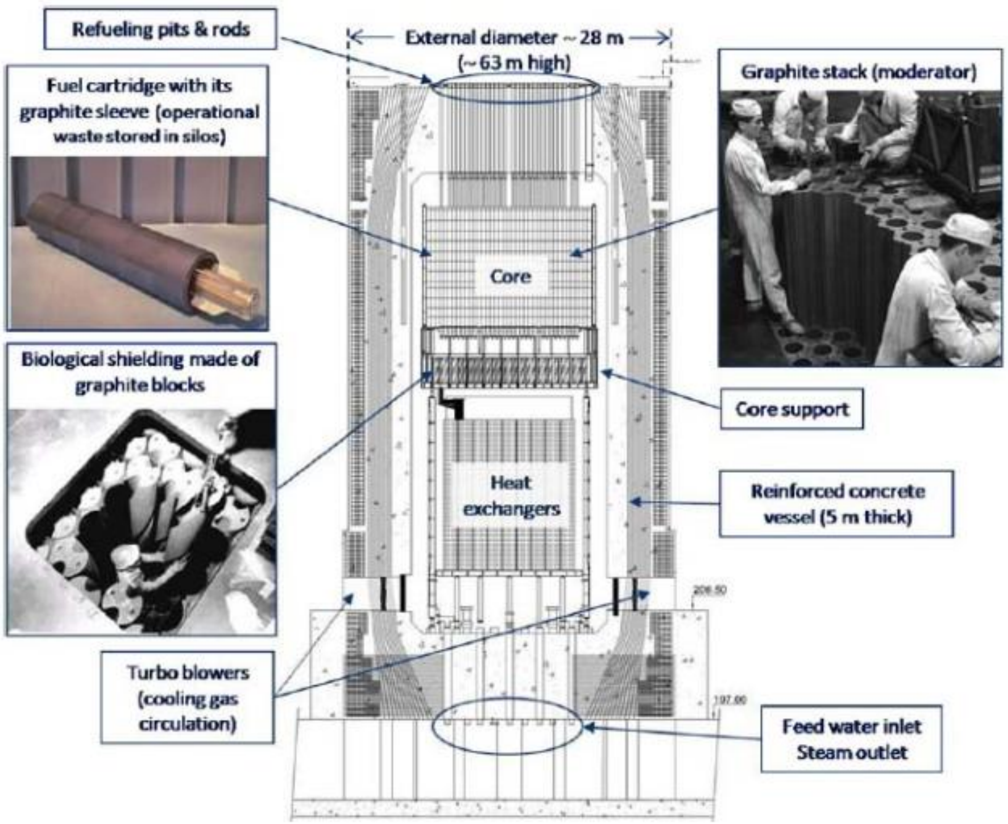

Figure 15. General cutaway view of an integrated UNGG reactor operated by EDF

8.2.2.2 Material used for leaching tests

After the reactor shutdown, EDF performed a coring operation in the fuel channels of the SLA2 graphite stack in 2005. Among the 180 cores, several were characterized from a mechanical and radiochemical viewpoint for the radionuclide inventory assessment and other samples were used for the reactor underwater dismantling studies. The SLA2 graphite cores for the experiment […] were taken from one single fuel channel. The sample used for the leaching tests is a mixture of these powdered cores in order to obtain a “mean” graphite stack sample that was submitted to the whole range of temperature (height) and dose rate (see Table 7). The initial samples were cylindrical in shape: 19 mm diameter and 50 mm high. In addition, it must be noted that three experiments were also carried out on graphite sleeves from the SLA reactors. The precise operating conditions for these sleeve is actually unknown (operational waste).

Table 7. SLA2 graphite samples used for leaching tests

Sample N°	**Height (mm)**	**Mass (g)**	**Contact dose rate in 2010 (µSv/h)**
SLA2-101	300	25.86	8
SLA2-107	3450	25.00	132
SLA2-112	5900	18.55	67
SLA2-115	7280	21.47	112
SLA2-118	8660	21.69	164