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Review of leaching data on irradiated graphite

Author(s): **Jérôme Comte (CEA), Lorraine McDermott (UoM), Laurent Petit (EDF), Laurence Petit (Andra)**

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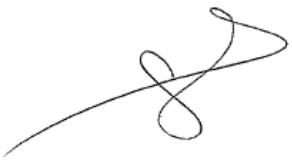
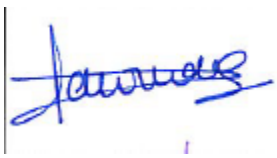
Review of leaching data on irradiated graphite

Executive summary

The focus of this deliverable report is on the information currently available for irradiated graphite material which has undergone a leaching experimental program for disposal purposes. This report aims at highlighting the previous reports carried out within this topic as well as research done as part of the CARBOWASTE program.

This report will evaluate the current isotopic inventory present within the irradiated graphite (i-graphite) as well as the interest in certain radionuclide release rates and their proposed mechanisms.

Revisions

Rev.	Date	Short description	Author	Internal Review	Task Leader	WP Leader
		First issue	Jérome Comte, Lorraine McDermott, Laurent Petit Laurence Petit 	Stéphan Schumacher, Andra  Christine Lamouroux, CEA 		B. Grambow, Subatech

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Executive Summary

Once current graphite moderated nuclear reactor operations cease there will be an estimated 250,000 tons of irradiated nuclear graphite waste worldwide. The long term disposal of irradiated nuclear graphite waste will have a significant impact on any future geological disposal facility. Proceeding forward with disposal of such large volumes of irradiated graphite (I-graphite) it is necessary to understand the nature and migration of isotopes present within the graphite structure. I-graphite has a combination of short and long term isotopes however this research focuses on Carbon 14 and Chlorine 36 for their ability to be of incorporated into the environment surrounding a repository, their long half-lives as well as their pontetial mobility in the geological medium.

Experiments have been carried out on French and UK irradiated graphite in order to establish the long term behaviour of Carbon 14 and Chlorine 36 in terms of migration, location and leachability. Future research objectives address differences in leachability to that of structural and reactor operational variation of the origin of each i-graphite material.

1 Introduction

Disposal behaviour is one of the main issues when considering graphite waste management scenarios. Leach tests are then commonly performed on irradiated graphite samples to characterise radionuclide release when graphite waste will be in contact with water. In irradiated graphite, the radiological inventory is almost exclusively based on activation products, i.e. impurities that initially existed in virgin graphite and were activated during reactor operation. In this regard, carbon 14 and chlorine 36 are of particular interest owing to their long half-lives and their potential biosphere impact:

- carbon 14 (5,730 y) is one of the main radionuclides present in i-graphite in terms of activity level viewpoint (up to 10^4 to 10^6 Bq / g). Its mobility under disposal conditions highly depends on its chemical form
- chlorine 36 (302,000 y) content in i-graphite is very low (some tens of Bq / g) but features a high mobility in cementitious materials commonly used in disposal and the geological environment

They are both weak β-emitters that do not present an external radiation hazard, but because of their ease of incorporation into living organism, it is very important to assess and understand their release rate and the associated mechanism in disposal condition.

The primary objective of this report is to provide a short synthesis of the main results obtained in the framework of the CARBOWASTE project on carbon 14 and chlorine 36 leaching behaviour.[1] These results were mainly obtained in WorkPackage 6 (WP6) devoted to "disposal behaviour of graphite and other carbonaceous wastes" but also in WP4 in which some studies regarding "treatment and purification" focused on i-graphite chemical treatment and leaching. A second objective is to put these results into perspective with the known literature on that topic in order to highlight the new and tangible results accomplished during the CARBOWASTE project.

It must be noted that due to CARBOWASTE member strategy on graphite waste management, the studies carried out in the framework of the CARBOWASTE project on disposal behaviour concern exclusively i-graphite from CO_2-cooled reactors that is to say from Magnox (UK) and UNGG (France) reactors. Operational waste (such as graphite sleeves) was not included for time reason in these studies. Some data on tritium and gamma emitters leaching are also available but will not be discussed thereafter.

[1] Other radionuclides, such as tritium and gamma emitters, have also been studied within CARBOWASTE but are not considered herein.

This report is divided into 4 main sections. Section 2 is dedicated to the description of the different graphite moderated reactors that were considered for leach tests within the CARBOWASTE project. Leach tests experimental conditions are detailed in Section 3 together with a comparative critical analysis of methodologies. The choice of different experimental procedures is also explained in the light of the desired outcome. Chlorine 36 and carbon 14 leaching behaviour is addressed in sections 4 and 5 respectively. Both sections aim at synthesizing the overall behaviour of these two radionuclides and at highlighting the influence of experimental parameters and graphite origin on the leaching behaviour. A phenomenological interpretation is each time proposed as understanding release processes is necessary for foreseeing long term behaviour. To do so, data obtained from other CARBOWASTE research topics such as graphite structural changes under irradiation in operating conditions and i-graphite water uptake (WP3) are considered. A specific focus is finally proposed on carbon 14 speciation (section 5.4) as it is determining for studying carbon 14 radiological impact in disposal. Such an analysis will be based on the few studies available in the literature as it has been scarcely considered within the framework of the CARBOWASTE project.

2 Reactors and Materials description

This chapter gives an elemental review of the history and background behind the i-graphite material that was predominately used for leaching tests during the CARBOWASTE project and whose results are detailed in sections 4 and 5. It focuses on French UNGG reactors G2, Saint-Laurent A2 and Bugey, as well as the British Experimental Pile ZerO (BEPO) and Magnox Wylfa reactor.

2.1 Saint-Laurent A2 Reactor

2.1.1 General description

The Saint-Laurent A2 reactor is a French UNGG reactor (Natural Uranium Graphite gas reactor). It was commissioned in August 1971 and finally shut down on May 25 1992. The pressure vessel is made of pre-stressed concrete which also acts as biological shielding. As for G2 reactor, SLA2 was CO_2-cooled. The coolant moved from the top to bottom of the reactor at a pressure of 29 bar within the free space between the graphite liners and the Mg-Zr alloy fuel claddings (Bastien, 1993). The thermal power was 1700 MW with a gross electrical power of 530 MWe and a net electrical power in nominal operation of 515 MWe (Bresard & Bonal, 2000). The thermal neutron flux (10^{-5} eV to 0.5 eV) in the core central zone and in the maximum flux plane was 3.12 10^{13} $n.cm^{-2}.s^{-1}$. The reactor was shut down between March 1980 and September 1982 following an incident which led to the melting of two fuel elements at the bottom of the "F5 M19 C14" channel (loss of cooling of the channel as a result of its obstruction by a metal plate, leading to overheating of the fuel elements) (Bastien, 1980).

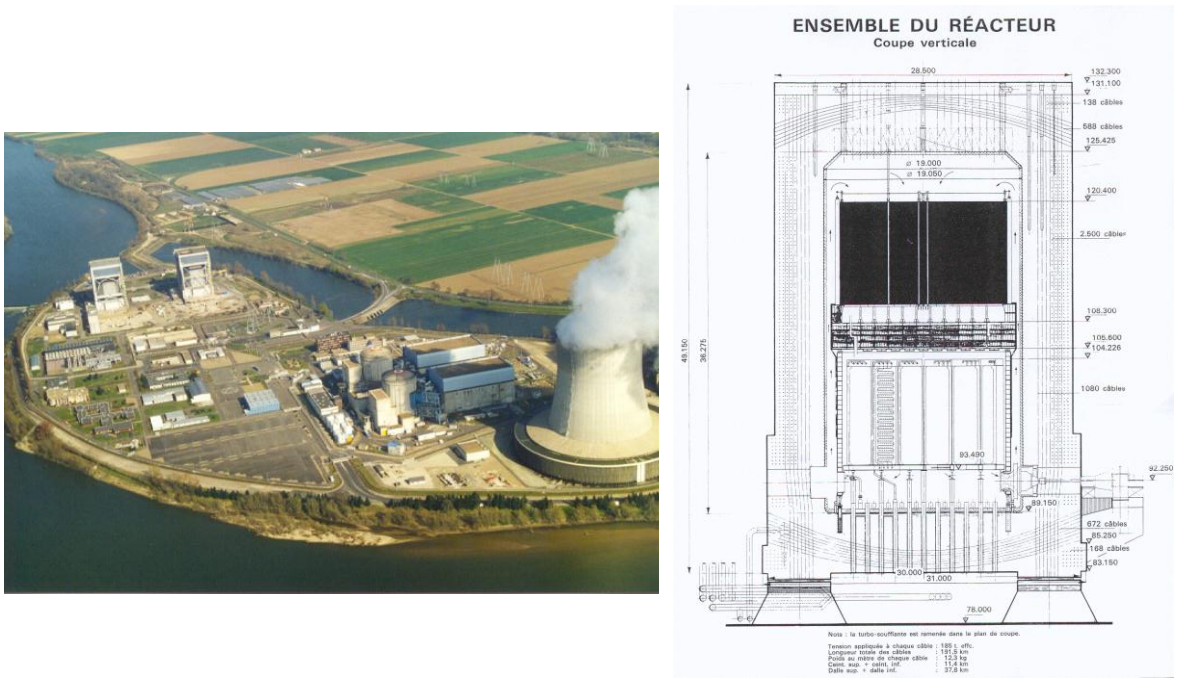


Figure 2-1 – Photograph of Saint-Laurent A1 and A2 reactors (left) and SLA2 graphite stack (right)

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 m thick reflector) and is 10.2 meters high (Figure 2-1). The total mass of graphite is 2440 metric tons including 1580 metric tons of moderator and 860 metric tons of reflector. The stack's network of graphite bricks is a hexagonal mesh with a pitch of 225.16 mm. The elementary graphite blocks are prismatic bars with a hexagonal base whose distance between two opposite faces is equivalent to the network mesh. The side-by-side juxtaposition of 4429 bars forms a bed, the SLA2 stack consisting of 8 superimposed beds (bed No. 1 is located at the bottom of the stack). Thus, the bars are superimposed and the stack may also be regarded as the juxtaposition of 4429 columns. The graphite stack comprises:

- The lateral reflector, consisting only of 828 solid columns surrounding the core,

- The moderator (or core) consisting of 3601 columns: 345 solid columns, 181 bored to 84 mm for the control rods and 3075 columns bored to 140 mm (basically for the fuel elements) (Bonal et al., 2006),

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, underwent impregnation and was purified using MgF_2. During its manufacture it was tested particularly with regard to effective cross-sections, density measurements and properties such as chemical composition, thermal expansion coefficients, mechanical strength, etc. The report (Yvars & Gaudez, 1968) covers the main elements measured over 164 operations of the production campaign, a summary of which is shown in Table 2-2.

Following the reactor shutdown, EDF performed a coring operation in the fuel channel on the St Laurent A2 graphite stack in 2005. Among the 180 core samples, several were characterised from a mechanical and radiochemical viewpoint. Other samples were also used for the reactor underwater dismantling studies.

2.1.2 Materials used for leach tests

The SLA2 graphite samples used for leach tests were taken from two channels: F10M16-C20 and F7M15-C19 located at a radius of 5 m and 2.95 m respectively from the reactor centre with variable sampling heights (variable neutron flux and irradiation temperature, see Table 2-1). Three samples per channel were chosen for the structural characterisation studies and the leaching tests.

Table 2-1 - SLA2 graphite samples chosen for the leaching tests

Channel	Well/Tube	Height (mm)	Sample No.	Température[#1] (°C)	Thermal neutron flux ($n.cm^{-2}.s^{-1}$)[#1]
F10M16	C20	2070	SLA2-44	435	$6.8x10^{12}$
F10M16	C20	7280	SLA2-55	310	$7.1x10^{12}$
F10M16	C20	8660	SLA2-58	270	$3.4x10^{12}$
F7M15	C19	2070	SLA2-124	455	$5.7x10^{12}$

Channel	Well/Tube	Height (mm)	Sample No.	Température[#1] (°C)	Thermal neutron flux (n.cm^{-2}.s^{-1})[#1]
F7M15	C19	7280	SLA2-135	310	5.8x10^{12}
F7M15	C19	8660	SLA2-138	270	2.7x10^{12}

#1 EDF-CIDEN data for temperature and neutron flux

The samples were initially cylindrical in shape (19 mm diameter and 50 mm high). Groove measurements required cutting up some samples into semi-circles about 10 mm thick. For the six samples chosen for the leaching tests, these semi-circles were used to determine the initial ^{36}Cl activity and to measure porosity (helium pycnometry and mercury porosimetry). The rest of the core, i.e. about 40 mm long, was used for continuous water impregnation tests. Figure 2-2 shows how the samples were divided up for the different analyses.

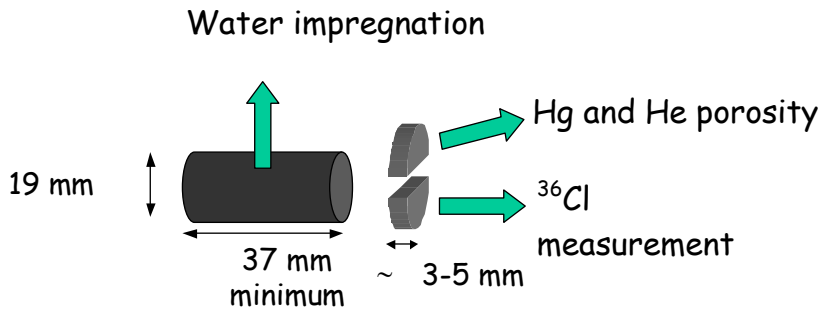


Figure 2-2 - SLA2 graphite core and its distribution for the different analyses

2.2 G2 reactor

2.2.1 General description

The G2 reactor is a French UNGG reactor. It was built on the CEA Marcoule site (Gard, south-east of France). Its first divergence was on 21st July 1958 and it was finally shut down on 1st February 1980. The pressure vessel of this reactor is made of pre-stressed concrete, which also acts as biological shielding. Its rated thermal power was 250-260 MW. Cooling was provided via pressurized CO_2 (15 bar).

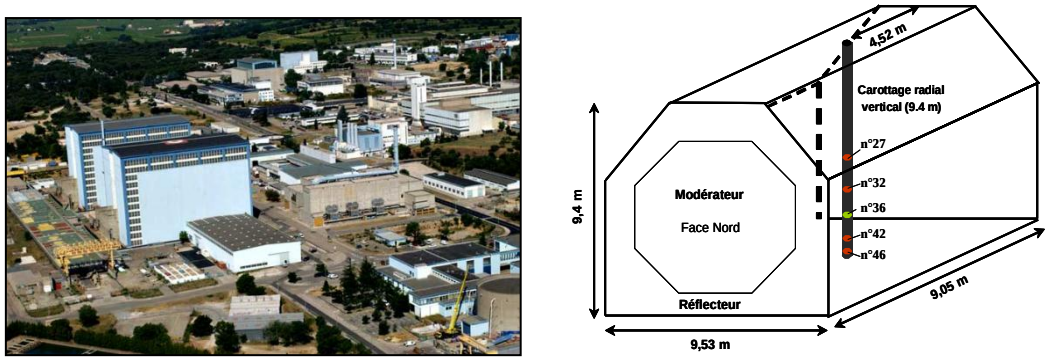


Figure 2-3 – Photograph of G2 and G3 reactors (left) and G2 stack (right).

The graphite stack of reactor G2 (Table 2-2) was based mainly on "special" Grade A coke and Lockport L coke, consists of 14,092 rectangular block shaped bricks with a square section of 200 mm sides and a maximum length of 1,500 mm. These 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 distributed in four distinct zones (Figure 2-3 and Figure 2-4):

- Zone A: The active cylinder of G2 consists of Special A coke (similar to English Grade A coke) impregnated once and purified, having a specific gravity generally stated as 1.71.

- Zone B: it is the internal reflector which is based on special "A" coke (similar to English 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.

Table 2-2 – Material properties of SLA2 and G2 non-irradiated graphite

	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	98.2 ppm	106 to 125 ppm	136 to 156 ppm
Coefficient of thermal expansion a (_) **Coefficient of thermal expansion a (//)** **Anisotropy ratio a (_) / a (//)**	$3.81.10^{-6}$ C^{-1} $2.41.10^{-6}$ C^{-1} 1.6	 $1.25\ 10^{-6}$ K^{-1} 2.3	 $2.68\ 10^{-6}$ K^{-1} 1.3
Compressive strength (Mpa)	42	27	33.9

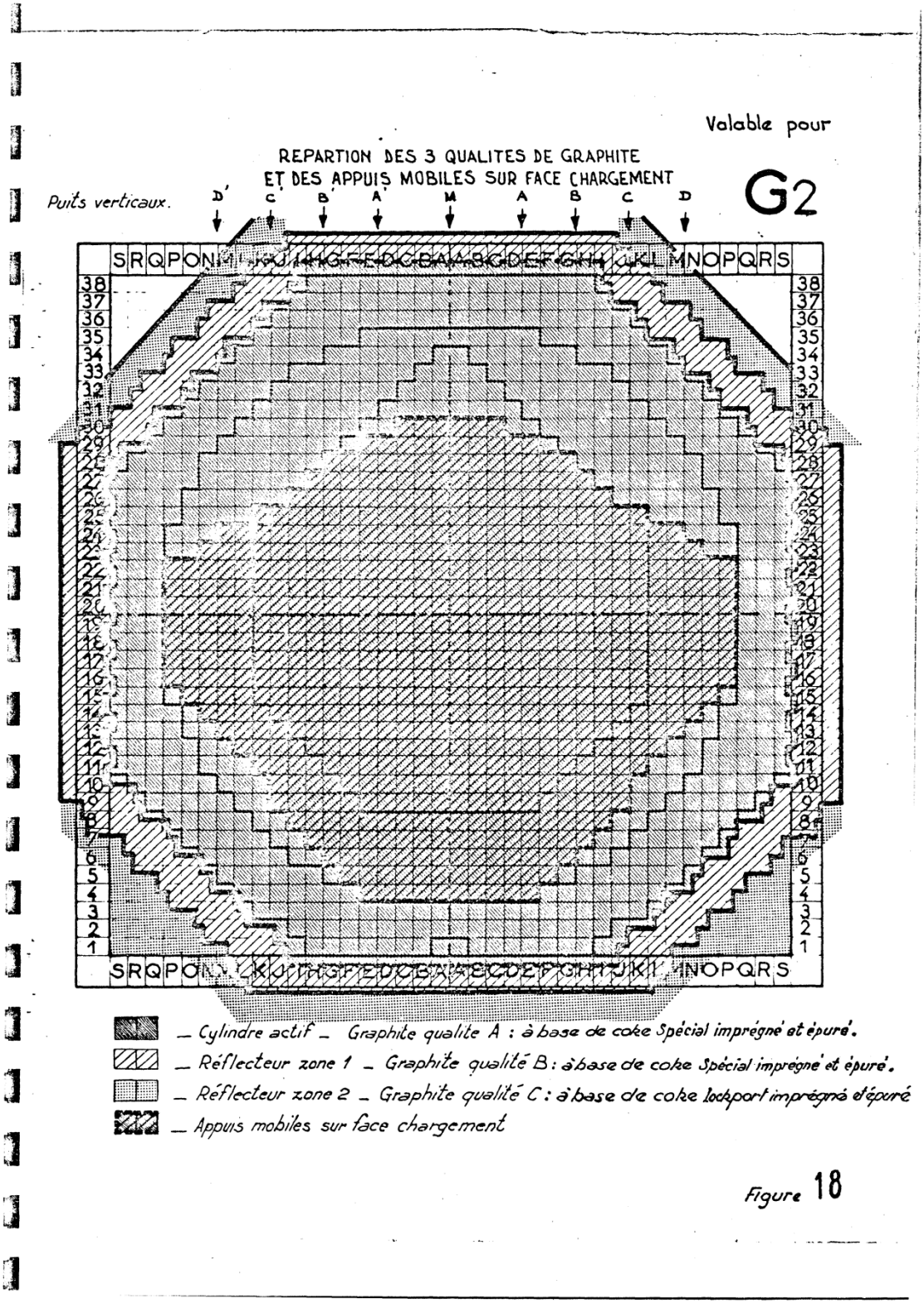


Figure 2-4 – G2 graphite stack

Cooling is provided by circulating carbon dioxide under a pressure of 15 bar. The gas inlet temperature was set at 140°C and the outlet temperature ranges from 300 to 390°C according to the zone (center or periphery). The temperature of the graphite ranges in the same range of values. The fuel consists of natural uranium surrounded by a magnesium-zirconium (0.7% Zr) alloy clad. During operation in the G2 reactor, many cores were taken of small samples, particularly to monitor the evolution of graphite under the combined effect of CO_2, irradiation and temperature.

Three coring campaigns were carried out on the G2 reactor. The first one was performed in 1980 along the channels. 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. Among these corings, only samples from the last operation were available and were chosen for leaching studies.

2.2.2 Materials used for leach tests

The active cylinder of G2 was comprised of graphite made from Special 1 coke impregnated once and cleaned with a NaF conditioner. The reflector was comprised of graphite made from Lockport L coke impregnated once and cleaned with a NaF conditioner.

In 2008, four core samples coming from the vertical coring in different places in the lower half of the reactor were chosen for leaching tests. Three of them were from the moderator (No. 27, 32 and 42) and one from the reflector (No. 46). Another sample (No. 36) – located between core sample No. 32 and 42 – was also used in 2004. These five core samples were more or less equidistant from each other but feature different coke, irradiation temperatures in reactor, etc.

Table 2-3 shows the sampling heights and the reactor operating temperature relative to the samples chosen for the impregnation and leaching tests.

Table 2-3 – Description of G2 samples used in leaching studies

Sample No.	Position	Presumed initial coke	Temperature (°C)
G2-27	Moderator	Special A coke	327
G2-32	Moderator	Special A coke	320
G2-36	Moderator	Special A coke	314
G2-42	Moderator	Special A coke	309
G2-46	Reflector	Lockport coke	<250

The cores collected in the G2 reactor were 20 cm long and 6.3 cm in diameter. It was therefore necessary to cut them up for the leaching and impregnation experiments and microstructure characterisations. Sub-samples were produced to conduct these leaching tests to study radionuclides behaviour, in particular two sub-samples located near the centre of the core samples as shown in Figure 2-5.

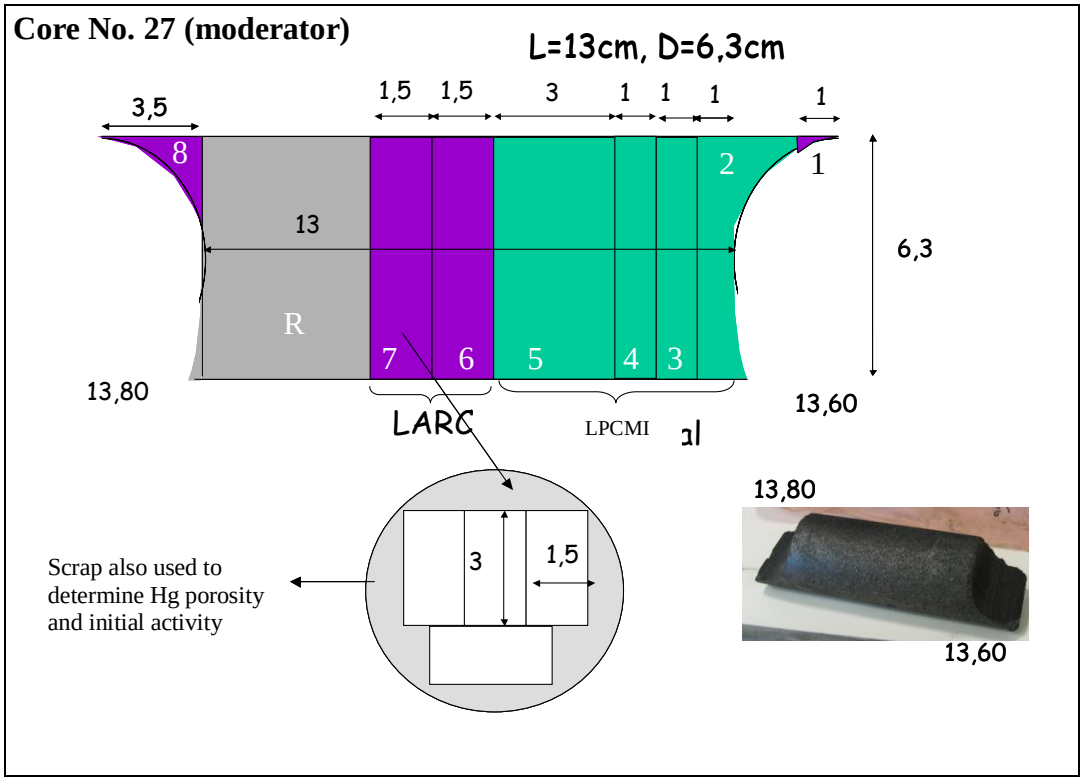


Figure 2-5 – Cutting diagram for G2-27 core.

2.3 Bugey

2.3.1 General description

Bugey 1 UNGG reactor diverged on December 7, 1971 and was finally shut down on May 27, 1994 after 12.18 years equivalent full power. The thermal power of the reactor was 1920 MW. The pressure vessel is made of prestressed concrete which also acts as biological shielding. The moderator consists of a stack of graphite bricks in twelve beds representing an active vertical cylinder with a height of 9 m and a diameter of 12.2 m.

Bugey graphite stack is made of coke Lima (petroleum coke) impregnated with coal tar pitch (d = 1, 685) and purified with MgF_2. The mass of the stack is more than 2000 tons of graphite.

The reactor was cooled with CO_2 at a pressure of 40 bar that entered by the top of the stack at 225 ° C and went out at 405°C. Thus the temperature of graphite varied from 230 to 580 ° C. The fuel used during operation is a 'Sicral F1' fuel introduced in graphite sleeves. Two types of fuel sleeves (Pechiney / SERS and Savoie-Acheson) have been used in the Bugey 1 reactor.

During operation, the graphite stack was subjected to several coring campaigns on the fuel channel (several hundreds of samples) to assess the evolution of the mechanical resistance of the reactor. Following its final shut down, new coring campaigns were performed in the fuel channel. Among the samples, 9 samples have been devoted to leaching studies for disposal purposes.

2.3.2 Materials used for leach tests

The samples were initially cylindrical in shape (16,5 mm diameter and 35-40 mm high). For the study of the behaviour of the main radionuclides of interest under disposal conditions, no particular specification on the sample has been made (height in stack or neutron flux) but the surface aspect was checked.

2.4 Conclusion on French UNGG samples

The first experiments on Bugey were performed with the samples available without taking account the history of the sample. Thanks to the feedback of Bugey leach tests, attention was paid within the CARBOWASTE project to the original location of the samples (flux, temperature…).

By choosing to study two reactors (G2 and SLA2) with several samples per reactor, a panel of representative and different samples was obtained. These samples feature different neutron flux or thermal history. In addition, they were characterised from a structural viewpoint (open/closed and total porosity and pore size distribution) which enabled to quantify the impact of the reactor conditions (neutron flux and thermal history) and to study the relationship between the graphite structure and the radionuclide release behaviour.

2.5 Overview of UK graphite

In addition to its role as moderator within British nuclear reactors, polycrystalline graphite is also a major structural component of the core, enabling access for control rods, coolant gas and fuel. Aging processes, exacerbated by fast neutron irradiation and radiolytic oxidation lead to distortion of the graphite components and property changes which ultimately reduce the material's effectiveness and can lead to component failure.
Despite much research into the material, graphite behaviour under irradiation conditions is not fully understood and has resulted in an overestimation of the extent of component failures in Magnox reactors, and a subsequent underestimation of component failures in the following generation Advanced Gas-cooled reactors (AGRs). Table 2-4 is taken from reference (Brocklehurst & Kelly, 1993) discussing dimensional change in irradiated nuclear graphite. It lists several properties of Pile Grade A (PGA) and Gilsocarbon and acts as a useful comparative summary of the material properties. For PGA the material used in the UK magnox reactor, two values are required, one to describe the property along the grain direction and another against.

Table 2-4 - Comparison of properties of PGA and Gilsocarbon graphite grades

Property	Units	Pile Grade A (PGA), ∥ and ⊥ to extrusion	Gilsocarbon
Density	g cm^{-3}	1.74	1.81
Open pore volume	cm^3 cm^{-3}	0.198	0.11
Closed pore volume	cm^3 cm^{-3}	0.01	0.086
Thermal expansion coefficient	K^{-1}	∥ 0.9 × 10-6 ⊥ 2.8 × 10-6	4.3 × 10-6

Property	Units	Pile Grade A (PGA), ‖ and ⊥ to extrusion	Gilsocarbon
Thermal conductivity	w m^{-1} K^{-1}	‖ 200 ⊥ 109	131
Young's modulus	GPa	‖ 11.7 ⊥ 5.4	10.85
Tensile strength	MPa	‖ 17 ⊥ 11	17.5
Flexural strength	MPa	‖ 19 ⊥ 12	23.00
Compressive strength	MPa	‖ 27 ⊥ 27	70.0
Poisson's ratio	none	~0.07	0.21
Electrical resistivity	μΩ cm^{-1}	‖ 620 ⊥ 1100	900
Diffusivity	none	13.6 × 10-3	3 × 10-3
Viscous flow coefficient	B0 m^2	‖ 712 × 10-16 ⊥147 × 10-16	6.5 × 10-15
Slip flow coefficient	K0 m	‖ 108 × 10-9 ⊥21 × 10-9	5.8 × 10-9

2.6 BEPO reactor

The British Experimental Pile Zero (BEPO) Energy Reactor was commissioned in 1948 and closed in 1968. BEPO was graphite moderated, air cooled and initially fuelled with natural uranium metal in aluminum cans. Two grades of enriched uranium fuel were used at a later date within this reactor. BEPO was initially used for the production of plutonium, but later this function was transferred to the Windscale piles with BEPO becoming a research reactor. BEPO's role as a material test reactor included isotope production, studying the irradiation behaviour of graphite and it was also used in studies for coolant compositions for the Magnox and AGR reactors. Figure 2-6 shows a photograph taken of the BEPO reactor, at Harwell.

Figure 2-6 – Photograph of the BEPO reactor

In 1975 a four inch cylindrical sample was trepanned from the BEPO core, through the control face of the pile, steel shielding, concrete bioshield and the 20 columns of graphite blocks (Wickam, 2002). From this core the samples used for analysis at The University of Manchester for the CARBOWASTE project were taken. Sampling was initially carried out in 1975 to provide radioisotope data on the graphite, steel and concrete, and to evaluate the Wigner energy release. It was retrieved using a diamond-tipped hole cutter using no coolant or lubricant. After retrieval the core was re-sealed and the reactor remains this way at Harwell to date (Wickam, 2002).

2.7 Wylfa reactor

Wylfa reactors were commission in 1971 and consist of two reactors with a combined capacity of 980 MW. Wylfa reactors were the largest and last of the magnox reactors to be built in the UK . Each Wylfa core has 6,156 vertical fuel channels and contains over 49,248 natural uranium magnox-clad fuel elements; these large graphite moderated reactors typically supply 23 GW h of electricity per day. The primary coolant used in carbon dioxide.

The graphite samples used in this research were trepanned from the fuel channel wall of reactor one channels 1413/02 and 1319/12 in April 2007. Figure 2-7 shows the location of these two sampling points. There are twelve graphite bricks per fuel column in reactor 1, numbered from the bottom of the core. Sample 1413/02 9U comes from an upper position in brick nine and sample 1319/12 8U comes from an upper position in brick eight. Table 2-5 details the irradiation history of these two samples. Sample 1413/02 was used for leaching experiments and sample 1319/12 for microstructural analysis.

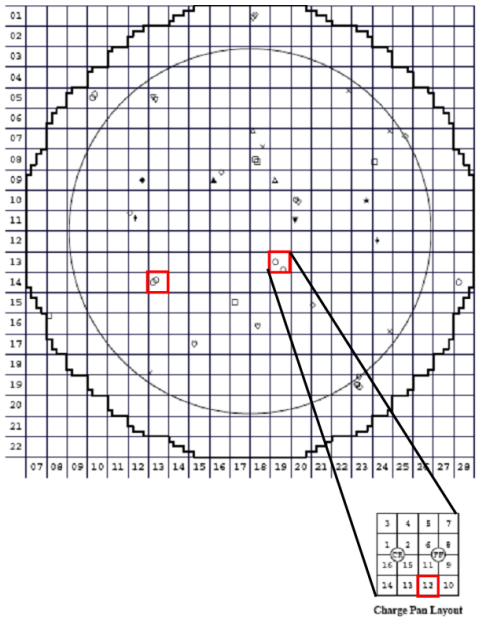


Figure 2-7 - Highlighted areas in red are the samples trepanned in 2007 from Wylfa reactor 1 and given to UoM for this research

Table 2-5 - Irradiation conditions of the Wylfa samples used in this study

Irradiation conditions	1413/02 9U	1319/12 8U
Irradition temperature (°C)	352	342
Adjacent fule dose (MWD/t)	34973	37319
DIDO equivalent dose at channel wall (10^{20} n/cm^2)	34.21	37.11

3 Experimental methodology

There are many possible options available when performing a leaching experiment on radioactive material. The leaching conditions used are often driven by repository environment or ground water systems. Sample history, size and availability also affect the number of experiments and repeats that can be performed. This gives rise to many different approaches to the experimental conditions and length of test. Various leaching parameters which are altered depending on the desired requirements:

- Comparison of sourced i-graphite
- Dynamic/semi-dynamic/static approaches
- Conditions employed – de-ionised water/locally sourced tap water/pH12/pH13
- Room temperature
- Length of test
- Isotopes determined – ^{3}H, ^{14}C, ^{36}Cl, gamma isotopes
- Varying the sampling time points for analysis
- Method of analysis – Liquid / Gas &/or Solid plus post leaching isotopic determination
- The three most commonly used methodologies are:
- IAEA recommendations (Hespe, 1971)
- Comparison methodology ANS-16.1(Encapsulated waste) (ANS, 1986)
- Diffusion process – CEA

This combined research report focuses on mainly the UK (IAEA) and French (CEA Diffusion) approaches. Each methodology has its own merits and reasoning behind its use.

The IAEA methodology centers on selecting the appropriate experimental methodology and always including a water standard which can be compared to other research programs in order to link up data. Experimental methodologies follow these standard formats:

- Dynamic – complete removal of leachant at each time point and fresh solution replaced
- Semi-dynamic – removal of portion of leachant which is replaced so the solution remains at a constant volume
- Static – at each time point a portion of leachant is removed and not replaced

Choosing to follow the IAEA semi-dynamic methodology is selecting the environmental standard which aims to give minimal damage and weight loss to i-graphite whilst determining what isotopes are removable under environmental conditions (limited ground water attack). Leachant is tested every 7 days until the isotopic removal falls to insignificant quantities justifying longer periods within the testing program, this makes this methodology one of the

few driven by release rates. This methodology utilizes cumulative fraction of isotopic released as a function of time and takes into account the sum of isotopic release taken to reach a steady state and beyond which not further significant release is exhibited. Following this; a trend in UK data analysis has emerged using incremental day leach rate (at 100 days) when comparing leaching data as this takes into account surface area, sample geometry and activity present per sample. Equation 3-1 details how leach rate has been calculated as recommended by the IAEA.

$$R_n = \frac{(a_n / A_n)}{(F/V)t_n}$$

Equation 3-1

R_n= Leach Rate ($cm.d^{-1}$)
a_n= Radioactivity released at renewal period (Bq)
A_o= Radioactivity present in specimen (Bq)
F= Exposed surface area (cm^2)
V= Volume of specimen (cm^3)
t_n= Duration of leachant renewal period (d)

"Measurement of the Leachability of Solidifed Low-Level Radioactive Wastes by a Short-Term Test Procedure" ANSI/ANS-16.1-1986. This methodology employs a process of waste samples immersed in leachants for a number of specific time periods after which the leachant is re-newed and analysed (dynamic approach). This methodology centers on producing a 'leachability index' which is the logarithm of the inverse of the effective diffusivity, often applied to leaching encapsulated waste. Initial sample preparation includes - demoulding, washing in 10% nitric acid, specific sample geometry & surface area determination. Total organic carbon (TOC) and pH determination. Leach test require samples to be suspended in a nylon mesh basket with a 4 cm cubed sample in 960 mls of de-ionised water, temperature 17.5 – 27.5° C with the experimental program lasting either 5 or 90 days. The pH is monitored following completion of test and the sample is examined for surface cracking.

The CEA approach to leaching experiments focuses on water solubility and the diffusion mechanism behind isotopic release. This approach utilizes a dynamic approach similar to the ANS-16.1 method without a pre acidic wash. The main aims behind this methodology are:

- Kinetics determination
- Speciation determination of the isotopes released
- Leaching rate
- Leaching in *repository or under dismantling* conditions

Factors that are considered prior to analysis include:

- Origin of the sample
- Microstructure characterisation (density, open porosity)
- Radionuclides inventory (initial and final)

- Leaching solution analysis
- Gas phase analysis
- Data from literature
- Mechanical release of radionuclides (diffusion, surface effect, ionic exchange)
- Chemical and radiological phenomena (flux, corrosion)

Many of the considerations on this list are also detailed on other leaching/environmental release methodologies. The most recent trend incorporated by the analysis carried out at CEA is *in situ* gas analysis.

CEA Experimental parameters were optimized for chlorine 36 measurements in the leaching solution (Table 3-1). The sampling sequences were calculated based on the assumption that the labile fraction of activity for ^{36}Cl follows a diffusion law so as to obtain closer timeframes in the first part of the leach test. After stabilization of water uptake and chlorine release, experiments are continued in order to determine the long-term kinetics.

Table 3-1 - Experimental conditions utilised in CEA for chlorine 36 leaching tests

Conditions	"Balance" tests	"Reactor" tests
Leachate	Deionised water	Deionised water
Leachate volume	150 ml	150 ml
Temperature	Ambient	21°C
Reactor	Unrinsed glass	Prewashed glass
Reactor internal volume	250 ml	430 ml
Atmosphere	Non-sealed air	Sealed and flushed by inert gas (N_2) after each renewal
Sample type	Cube Mass # 12g (L*l*h =15*15*30 in mm)	Cylindrical lamella Mass # 80g (diam = 63 mm * 15 mm)
Sample A/V	#3.3	# 2
Leachate A/V	#0.15	#0.6
Duration	211 days	610 days
Renewal	Partial on first sequences (16 days) more complete (16 days to 211 days)	Complete at each sequence
Number of sequences	20	20
Sample time points	30 min, 1h, 4h, 7h, 24h, 30h, 48h, 54h, 3d, 4d, 7d, 10d, 16d, 21d, 35d, 50d, 63d, 154d, 211d	1h, 6h, 1d, 2d, 3d, 6d, 7d, 9d, 13d, 15d, 17d ,27d, 31d, 45d, 59d, 76d, 90d, 181d, 455d, 610d
Analysis	^{3}H, ^{14}C, ^{36}Cl, gamma spec, ion chromatography	^{3}H, ^{14}C, ^{36}Cl, gamma spec, ion chromatography, TOC, pH

The state of the art made before starting experiments showed that the chemistry of the leachate water (UP water or water saturated with $Ca(OH)_2$) has no influence on chlorine 36 release so most of leaching tests were performed in ultra pure water. To complete results, leach tests on G2 samples were performed in UP water in a leaktight reactor vessel in an inert atmosphere on a greater amount of graphite that allowed to made dynamic leaching test.

Unlike the IAEA report which uses BET[2] surface area, the CEA method uses the geometrical surface area and graphite porosity to calculate the diffusion coefficient of the leached radionuclides. To study a potential release controlled by a diffusion process of chlorine 36, tests are performed on blocks to have the surface and the volume of sample. Diffusion calculations are performed by adjusting the value of the diffusion coefficients to reproduce the experimental data of the leaching tests according to Equation 3-2.

$$F = 2\frac{S}{V}\sqrt{\frac{D_a t}{\pi}}$$ **Equation 3-2**

F=Leach fraction (-)
S=Sample geometric area (m^2)
V=Sample geometric volume (m^3)
t=time(s)
*Da=Diffusion coefficient Da*θ=De where θ : graphite porosity*
De =Effective diffusion coefficient (m^2/s)

The analytical procedure used at the CEA is detailed in reference (Comte & Guy, 2010b).

[2] Brunauer-Emmett-Teller

4 Chlorine 36 leaching results

4.1 Review of available data

4.1.1 Overview of chlorine 36 leaching studies in graphite waste

Chlorine 36 mainly arises in graphite waste from stable chlore 35 activation. Most of chlorine 36 leaching studies have been performed on graphite samples trepanned in French UNGG reactors belonging to EDF (Bugey, Saint Laurent des Eaux A2) and CEA (G2 reactor in Marcoule). The only exception concerns the American Hanford reactor (light water cooled reactor). Overall, more than 60 leaching studies on chlorine 36 have been carried out for more than 20 years, mainly in CEA labs. This French specificity may be related to:

- The chlorine 36 issue which is of large concern in France for graphite waste disposal but which has been scarcely studied abroad
- The fact that both chlorine 36 inventory and leaching behaviour (detection limits) are hard to characterise. Specific methodologies have thus been developed (see (Narkunas et al., 2012) and CEA FR 2 940 470 patent).

The first chlorine 36 leaching studies were carried out in the late 80s (Comte & Petit, 2011). CEA and PNL performed at the same time leaching tests on G2 and Hanford graphite pile samples. Despite differences in the experimental procedure they both found a high variability in ^{36}Cl leaching rates - ranging from few % to more than 60% - together with high release kinetics (Figure 4-1). Yet chlorine 36 total activities were measured on graphite cutting loss and then extrapolated to all the samples set. No interpretation was then possible. Indeed, it has been shown since then that chlorine 36 distribution is highly heterogeneous within the same graphite core. Therefore it is necessary to assess each sample activity individually by measuring its residual activity after leaching and drawing up the overall activity balance.

Ten years later, CEA launched a new leaching campaign on SLA2 (Saint Laurent des Eaux A2) sleeve samples. These tests followed the Andra leaching standards, namely hermetic vessel, industrial water, full renewal (dynamic approach) of the leaching solution. The purpose was to clarify graphite behaviour under disposal conditions. Surprisingly enough, trends observed on G2 and Hanford pile samples were not confirmed. Chlorine 36 leaching kinetics were found to be far slower, without establishing stabilization over time. However, fuel retrieval conditions from SLA2 sleeves were not known. It was assumed that fuel chopping could have been made underwater which means that part of chlorine 36 inventory would have been already leached.

From 2001 to 2003 new leaching tests were performed on about ten Bugey pile samples. The aim was also to characterise the behaviour of the main radionuclides of interest under disposal conditions (^{36}Cl, ^{14}C, ^{3}H). These tests were carried out in both pure water and lime water under inert atmosphere. The high variability of chlorine 36 leaching rates was confirmed while chlorine 36 was found to be released in two stages (Figure 4-2): a first labile fraction released quickly (<50 days) followed by a non-labile fraction with slow release kinetics. The

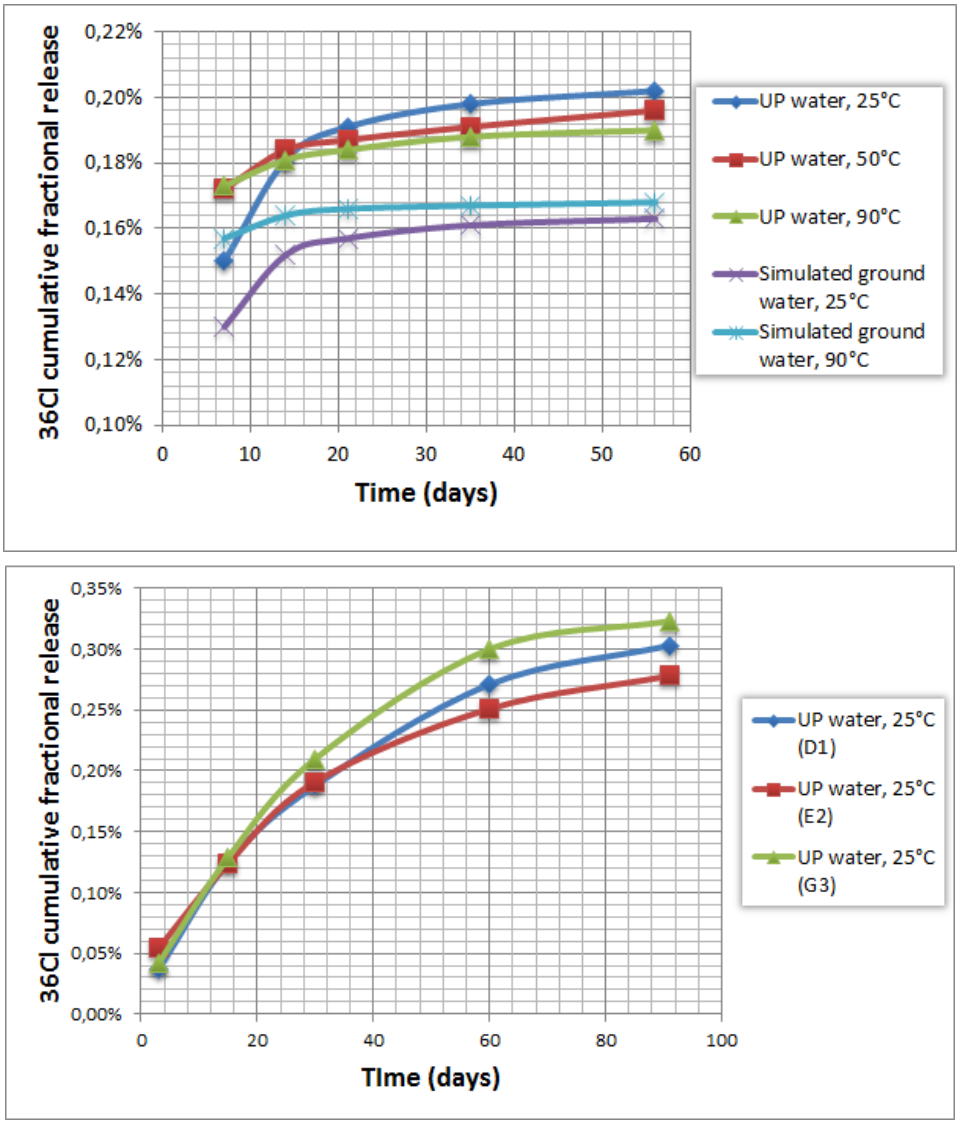


Figure 4-1 – Cumulative chlorine 36 released fraction for Hanford graphite samples. PNL results (up) and CEA results (down)

labile fraction released kinetics where found to be proportional to the square root of time which means that it follows a diffusion process through graphite porosity. No conclusion was drawn on the impact of the leachant composition on chlorine 36 release.

Accordingly new experiments were carried out in 2004 on a single G2 pile sample weighting several hundred grams. It was cut into slices to produce a structurally and historically homogenous samples subset and thus to avoid interpretation issues arisen so far. The fast chlorine 36 release kinetics was confirmed. Similar results were measured for each set of parameters (3 tests/leaching medium) which proves test consistency.

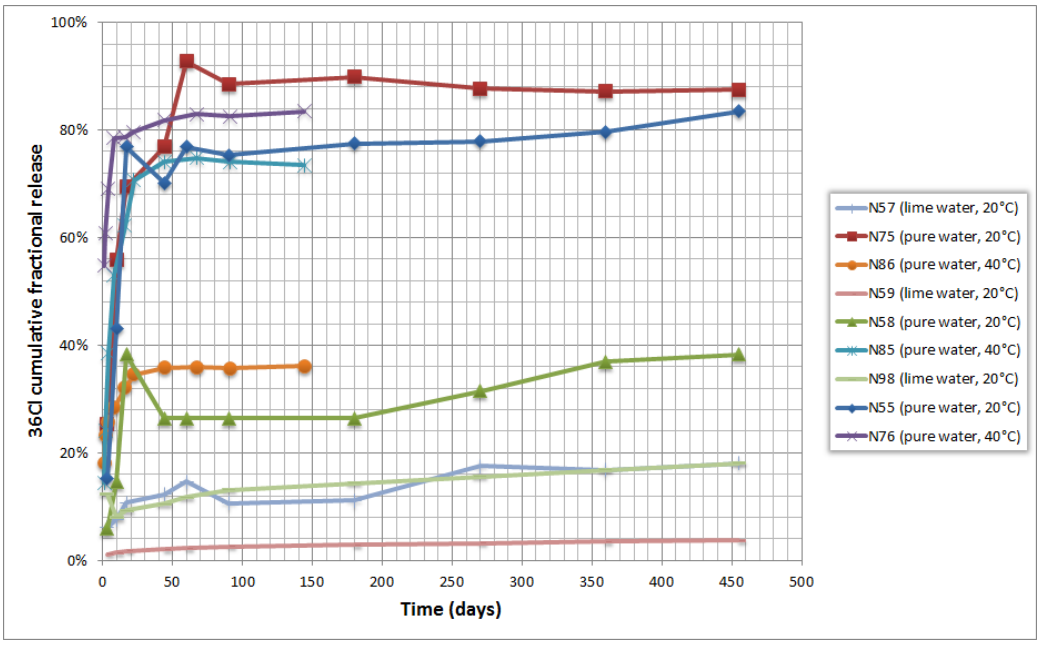


Figure 4-2 – Cumulative ^{36}Cl released fractions measured for Bugey graphite blocks (2001-2003)

In 2006, the graphite waste management issue started over in France. A new leaching campaign was initiated accordingly in 2008. New samples were trepanned from G2 and SLA2 piles. They were specifically selected to focus on parameters such as tar pitch nature, irradiation and temperature background, and diffusion processes. In order to make phenomenological interpretations easier, the experimental procedure was completed with microstructural analysis (Ammar & Rouzaud, 2010; Comte et al., 2010; Comte et Gosmain, 2012) and water uptake studies on both virgin and irradiated graphite samples (Comte & Guy, 2010a). Results are detailed in a specific CARBOWASTE report (Comte & Guy, 2010b) and illustrated in Figure 4-3 for G2 graphite samples.

4.1.2 Overview of chlorine 36 leaching behaviour

In spite of differences in the experimental protocol, all leaching studies on graphite piles show that chlorine 36 is released in 2 stages:

- The first stage shows very rapid chlorine 36 release kinetics (labile fraction) proportional to the square root of time which is a feature of a diffusion driven release process through graphite porosity
- The second stage shows slow chlorine 36 release kinetics (non-labile fraction)

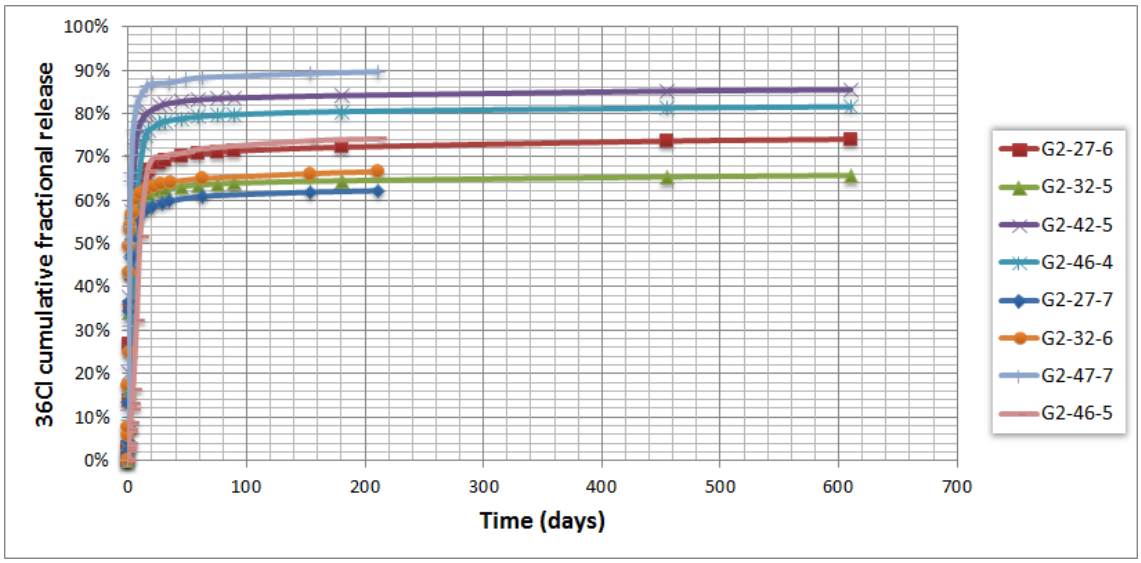


Figure 4-3 – Chlorine 36 cumulative fractional release as a function of time for G2 graphite samples (moderator samples for cores n° 27, 32, 42 – reflector sample for core n° 46). Tests performed with pure water, under air (end after 210 days) or inert atmosphere (end after 610 days)

On the whole, chlorine 36 release rates vary widely ranging from few % to 90% of the initial inventory. To provide a better understanding of chlorine 36 release phenomenology, several experimental parameters were tested. Results are summarized in section 4.2 while section 4.3 provides an interpretation of chlorine 36 release processes.

Most of the following studies focus on chlorine 36 labile fraction. Studies of the chlorine 36 non labile fraction are underway in France since 2011. Results should be available in 2013.

4.2 Results analysis

4.2.1 Impact of leaching conditions on chlorine 36 release

4.2.1.1 Impact of the leachant chemical composition

The influence of the leachant chemical composition on chlorine 36 releases has been considered from the very first experiments in 1990. Several leaching media were used, from the simplest (deionized water, with or without oxygen) to the most complex simulating disposal conditions (NaOH pH=13 or lime water pH=11 to 12.5). Other media were also studied like ‘‘industrial water” and ground water.

On the whole, most of leaching tests do not allow us to conclude as to the possible impact of the leachant chemical composition because of different experimental procedures and samples characteristics. Only one leaching tests series is relevant in this regard. It is based on a G2 core that was cut into slices to produce a structurally and historically homogeneous sample subset (2004 leaching campaign). In this case, Figure 4-4 clearly displays that there is no impact of the leaching chemical composition on chlorine 36 labile fraction release. Many

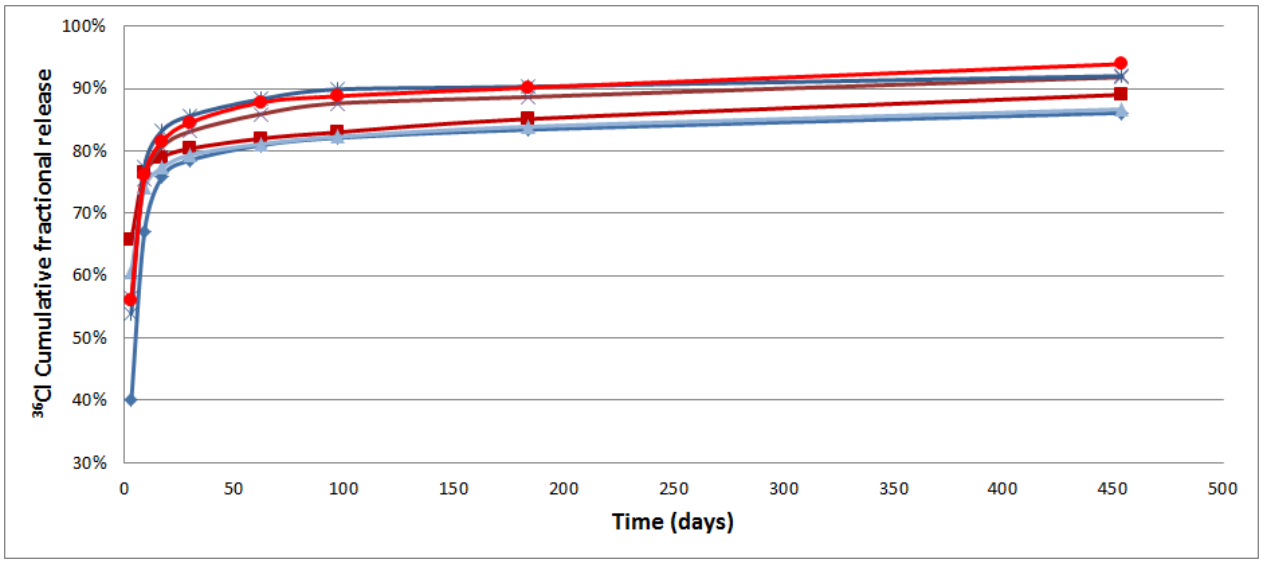


Figure 4-4 – Cumulative chlorine 36 released fractions measured for G2 pile samples (sample weight ranges from 72 to 90 g, hermetic vessel, argon atmosphere). Blue plots for water, red plots for lime water (pH=12.5)

experiments were therefore carried out in water instead of alkaline media afterwards to make interpretations easier.

4.2.1.2 Impact of the S/V ratio[3]

Leaching experiments on both SLA2 sleeve (1997-1999) and Bugey moderator (2001-2003) samples have proved that chlorine 36 labile fraction release is a diffusion driven process through the graphite's porosity. Diffusion can be described in a simplified manner by Equation 3-2 where the released fraction is proportional:

- to the square root of time. Diffusion can thus be easily identified by plotting the released fraction as a function of $\sqrt{t}$
- to the sample leached surface (S/V ratio). This is shown in Figure 4-5 where SLA2 sleeves crushed samples lead to higher leaching rates than graphite blocks.

In contrast, this does not explain the chlorine 36 leaching rate variability.

[3] Geometrical surface / volume ratio

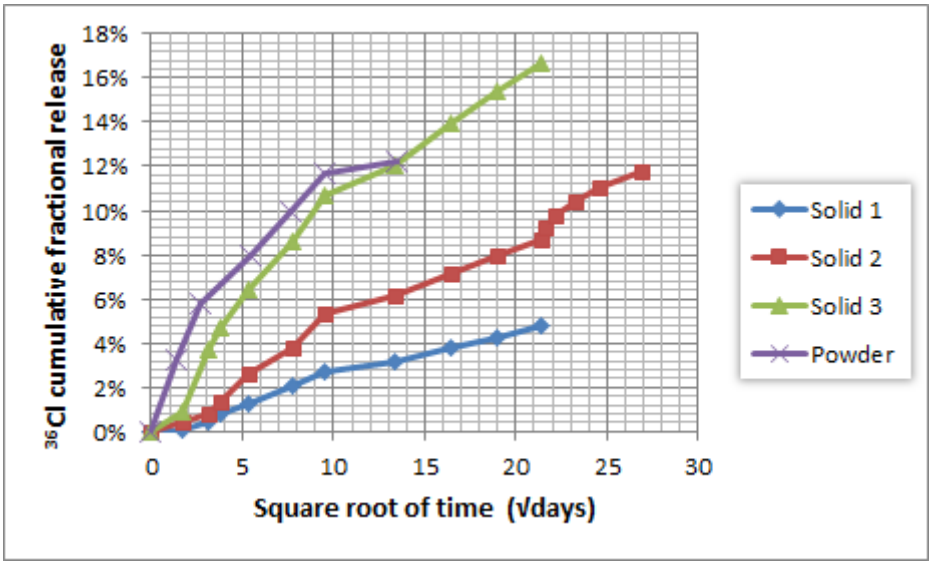


Figure 4-5 – Cumulative chlorine 36 leached fraction as a function of the square root of time for SLA2 sleeve samples (crushed sample vs. massive samples, pH=8.2)

4.2.2 Impact of graphite samples characteristics

The origin (coke, manufacture process…) and the thermal and neutron irradiation background make each i-graphite sample unique. It is thus of importance to consider these parameters when analysing leaching tests results.

4.2.2.1 Impact of chlorine 36 initial activity

As chlorine 36 activity is highly heterogeneous from one sample to another, radiological measurements must be performed on the samples that were effectively leached. Such measurements are based on destructive radiochemical techniques using liquid scintillation counting which means that graphite samples must be partially destroyed to determine chlorine 36 accurately. Therefore, chlorine 36 initial activities are always determined at the end of leach tests by adding up chlorine 36 released amounts and the remaining activity in the leached sample.

The major drawback of such a methodology is that chlorine 36 activity is not accurately known when leach tests are being carried out so that the sample activity can finally turn out to be too low to provide reliable measurements.

The impact of chlorine 36 initial activity on the release rate was analyzed for samples featuring similar leaching solutions, locations in reactor and irradiation history. Results are displayed in Figure 4-6 for 3 French reactors (G2, Bugey and SLA2). The broad spread of experimental measurements does not indicate any correlation between the chlorine 36 initial activity and its release rate.

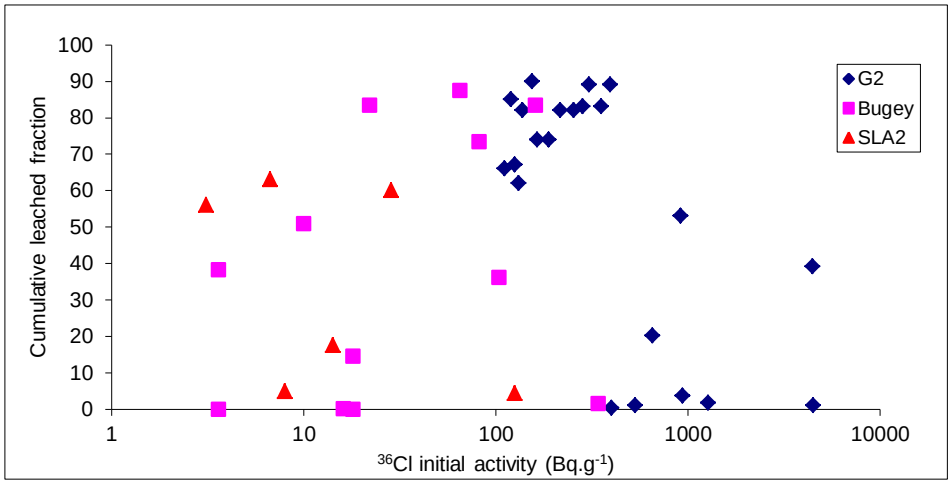


Figure 4-6 – Chlorine 36 leaching rates as a function of samples initial activity in Bq.g^{-1}(logarithmic scale)

4.2.2.2 Impact of samples location in reactor piles

Graphite samples location in reactor is closely related to their thermal and neutron irradiation background. It may also affect radionuclides location and chemical form in graphite and thus their leaching behaviour.

A clear correlation has been indeed observed between chlorine 36 labile fraction release rate and irradiation temperatures in the reactor, regardless of the experimental protocol the trend of irradiation temperature remains. This correlation was first noticed on Bugey graphite pile samples and was confirmed afterwards on G2 and SLA2 graphite samples (see Figure 4-7 and Figure 4-8). For Bugey samples, only the core height in the reactor is available (Figure 4-8). Corresponding temperatures are unknown.

Overall, high release rates are observed for samples that were irradiated at low temperatures whereas high irradiation temperatures lead to low release rates. Such a trend can explain the high variability in chlorine 36 release rates. A possible interpretation is thus proposed in section 4.3.4. In contrast, the impact of the neutron history has not been studied yet.

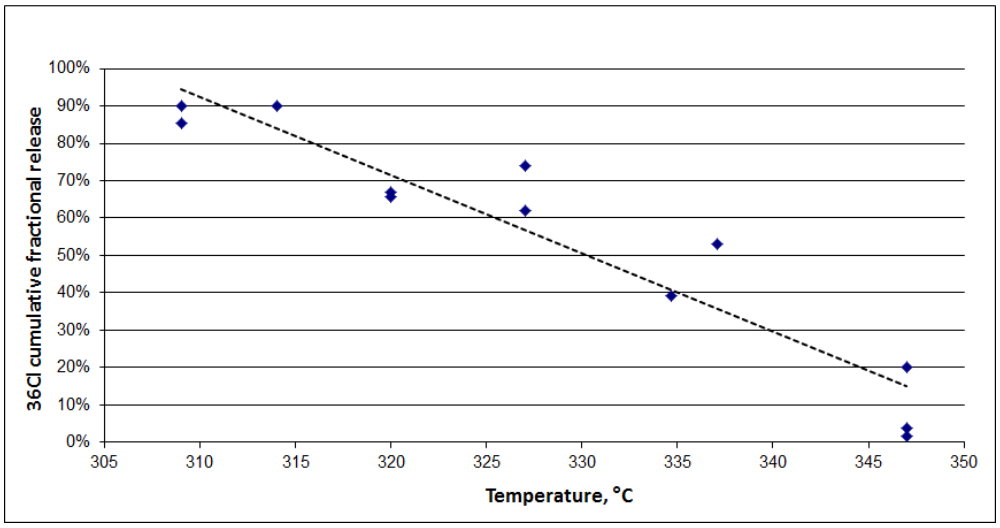


Figure 4-7 – Chlorine 36 cumulative fractional release as a function of the reactor irradiation temperatures for G2 pile samples.

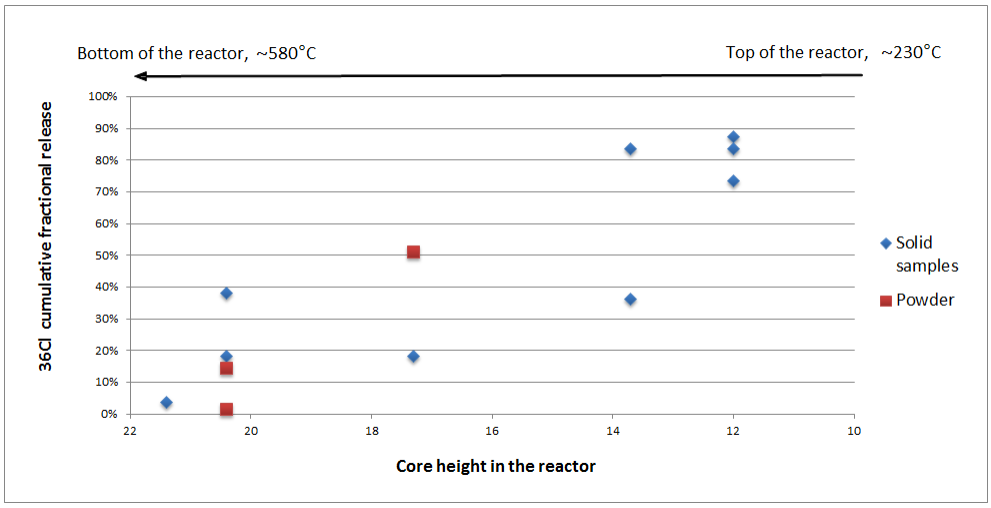


Figure 4-8 - Chlorine 36 cumulative fractional release as a function of core height in the reactor for Bugey graphite samples.

4.2.2.3 Influence of the coke nature

Most of leaching tests campaigns were performed on graphite pile samples feature different cokes and purification processes that directly affect their impurities content and thermal and irradiation behaviour. In Table 4-1, several G2, SLA2 and Bugey unirradiated graphite properties are displayed. In particular a correlation between the coke nature and graphite thermal properties, with reference to structural evolution under reactor operating conditions, is indeed suggested. Similarly a correlation between the coke nature and chlorine 36 inventories is highlighted in Table 4-2.

Table 4-1 – G2, SLA2 and Bugey 1 non irradiated graphite properties.

	G2 moderator	G2 reflector	SLA2 moderator	Bugey moderator
Coke	Spécial A	Lockport L	Lima	Lima
Purification gas	NaF	NaF	MgF2	MgF2
Neutron cross section, mbarn	3,95	4,02	3,75	3,74
Density, g.cm^{-3}	1,71	1,68	1,68	1,685
Thermal expansion coefficient α(⊥)	1,25 .10-6 K^{-1}	2,68.10-6 K^{-1}	3,81.10-6 C^{-1}	4,06.10-6 K^{-1}
Thermal expansion coefficient α(//)			2,41.10-6 C^{-1}	2,49.10-6 K^{-1}
Anisotropy ratio α(⊥)/α(//))	2,3	1,3	1,6	1,63
Compression (//), MPa	27	33,9	42	40,6
Ashes content, ppm	106 à 125	136 à156	98,2	98

However as no correlation was found between chlorine 36 initial activity and its release in solution (see section 4.2.2.1), the impact of graphite coke on chlorine 36 release is unclear. Moreover, none of leaching tests series performed so far were suitable for studying the coke influence exclusively as the samples thermal and irradiation backgrounds were each time different. Therefore, although a relation between graphite coke and chlorine 36 leaching behaviour makes sense; it has thus never been clearly proven.

Table 4-2 - Mean chlorine 36 mass activity calculated by the identification calculation-measurement method for different type of graphite in UNGG reactors

UNGG reactor	Graphite mass pile (t)	Specific power (W_{th} / g U)	Coke used for graphite manufacturing	Mean ^{36}Cl mass activity (Bq/g)
Chinon A3	2,530	3.2	Lockport L (74 %) Lockport M (26 %)	2.1
Saint-Laurent A1	2,570	3.7	Lockport M	1.7
Saint-Laurent A2	2,440	3.8	Lima	18.2
Bugey 1	2,060	5.7	Lima	25.5

4.2.2.4 Influence of graphite samples use in reactor

Graphite was used in UNGG reactors for several purposes:

- As a moderator. It was the main part of the reactor core
- As a reflector. It was then located on the core periphery to reduce radiation loss
- As a biological shielding. It was sometimes located below the reactor pile to reduce metallic internals activation
- As sleeves to maintain fuel cartridges

No chlorine 36 leaching experiment have been performed on biological shielding samples while there is only one reference available on graphite sleeves leaching (Saint Laurent reactor). In the latter, as for graphite piles, chlorine release was found to be proportional to the square root of time. This means that chlorine release follows a diffusion driven process through graphite porosity. In contrast, no stabilization was observed beyond 400 days of leaching (see Figure 4-9) so that chlorine 36 labile and non-labile fractions cannot be distinguished. It is indeed assumed that fuel chopping has been carried out underwater and thus that the labile fraction would then have been leached.

Overall, available data is too scarce to allow concluding remarks on the influence of irradiation damage on graphite used in different sections of a reactor. Yet it should be noted in this regard that most of chlorine 36 leaching studies have focused on graphite piles (moderator and reflector) which make up the main part of graphite waste to be disposed of.

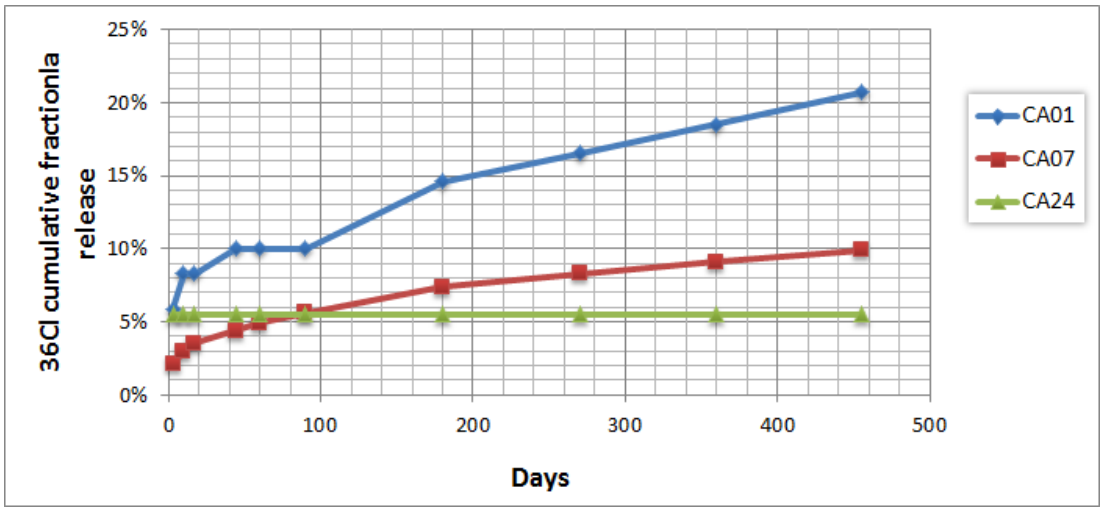


Figure 4-9 – Chlorine 36 cumulative fractional release as a function of time for Saint Laurent des Eaux A2 graphite sleeves samples. "CA24" sample measurements are below detection limits.

4.3 Phenomenological interpretation of chlorine 36 release in graphite

In this previous section, chlorine 36 was found to be released in two stages: a first fast release phase followed by a near stabilization with low release kinetics. The variable leach rate does not seem to be related to the chlorine 36 initial activities nor the leachant nor the leaching temperature. In contrast, a correlation between chlorine 36 leach rate and the irradiation temperature was pointed out.

In the following, we propose to study several phenomenological assumptions that could explain chlorine 36 leaching behaviour;

- **Water uptake** kinetics through graphite pores. Water penetration could be indeed a limiting factor to chlorine release as graphite is hydrophobic
- **Chlorine diffusion** through graphite porosity
- **Chlorine chemical forms** in graphite, featuring different solubility
- **Chlorine location** within the graphite matrix both in the open porosity and in areas where water cannot easily penetrate
- **Chlorine thermal behaviour** under reactor operating conditions

4.3.1 Impact of water uptake on chlorine 36 release

Water uptake in graphite has been studied on both unirradiated and irradiated graphite samples. Results are collected in CARBOWASTE report (Comte & Guy, 2010a). They show that water uptake kinetics are rather low in virgin graphite samples while they are faster in irradiated graphite samples as 50-70 % of the open porosity is filled within a few days.

Chlorine 36 leaching rate has been compared to water penetration within graphite open porosity in order to know whether water uptake may delay chlorine 36 release. Both G2 and SLA2 graphite samples were tested. Results are shown in Figure 4-10:

- In phase 1, water uptake is faster than chlorine 36 leaching. The biggest graphite pores are being filled up with water. This phase is very short (a few hours). A low amount of chlorine 36 is released
- In phase 2, most of chlorine 36 is leached while water uptake in graphite hardly increases. This phase lasts 30 to 60 days. Chlorine 36 “labile” fraction is almost entirely released
- During the last phase (phase 3) the smallest graphite pores are being filled with water while chlorine 36 leaching is close to zero

Overall, there is no linear correlation between water uptake in graphite pores and chlorine 36 leaching rate which means that water uptake does not limit chlorine 36 release.

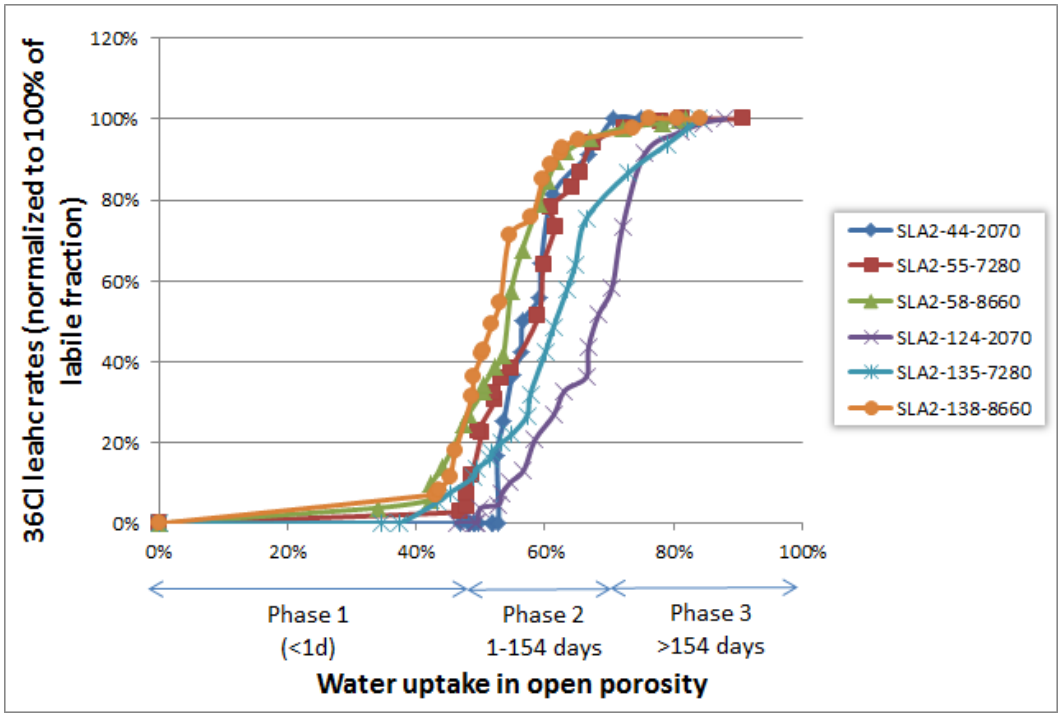


Figure 4-10 - Correlation between ^{36}Cl labile fraction leach rate and water uptake in graphite open porosity for SLA2 samples. To make comparison easier, leach rates are normalized to 100% of ^{36}Cl labile fraction.

4.3.2 Diffusion of chlorine 36 labile fraction in graphite porosity

Diffusion tests[4] have been carried out in order to check whether chlorine release might be a diffusion driven process. Results have been compared to diffusion coefficients fitted on leaching plots.

Diffusion tests were performed on virgin graphite samples by monitoring chlorine 36 transfer kinetics through the samples. Chlorine 36 effective diffusion coefficient was found to be about $4.E^{-12}$ $m^2.s^{-1}$ for G2 graphite moderator samples.

Chlorine 36 diffusion coefficient was also fitted on leaching data by plotting chlorine 36 leaching rate as a function of the square root of time. Results are shown in Figure 4-11 for G2 graphite samples. Diffusion coefficients are collected in Table 4-3 for G2 and SLA2 samples.

[4] As a reminder, Da=Diffusion coefficient Da= θ *De where θ is the graphite porosity and De is the effective diffusion coefficient

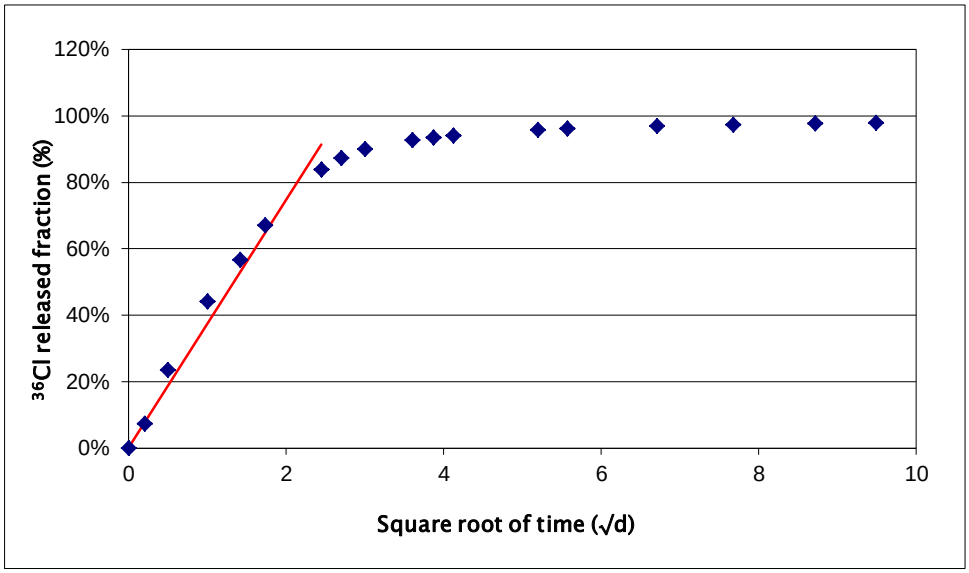


Figure 4-11 – Comparison of ^{36}Cl release with a diffusion model for a G2 graphite sample (G2-42). Experimental dots are in blue while calculated dots are plotted in red. The overall release is normalized to 100% of ^{36}Cl labile fraction

In Table 4-3 apparent diffusion coefficients (Da) for G2 moderator samples are close ([1.3E^{-11} – 4.6.E^{-11}] m^2.s^{-1}). The mean value is 3.E^{-11} m^2.s^{-1} which accounts for an effective diffusion coefficient (De) of 6.E^{-12} m^2.s^{-1}. These values are consistent with diffusion coefficient measured on G2 virgin graphite samples (De = 4.E^{-12} m^2.s^{-1} i.e. Da=2E^{-11} m^2.s^{-1} when the open porosity is about 20%).

Table 4-3 - Chlorine 36 mean diffusion coefficients fitted from leaching tests on G2 and SLA2 graphite samples (Da and De stand for apparent and effective diffusion coefficients respectively).

Reactor	Graphite origin	Coke	Mean Da (m^2.s^{-1})	Mean De (m^2.s^{-1})
G2	Moderator	« Spécial »	3.E^{-11}	6.E^{-12}
G2	Reflector	« Lockport »	9.E^{-12}	2.E^{-12}
SLA2	Moderator	« Lima »	3.E^{-12}	6,5.E^{-13}

G2 reflector samples feature a lower and more scattered apparent diffusion coefficients than moderator samples with a mean value of 9.E^{-12} m^2.s^{-1}.

Eventually SLA2 graphite moderator samples show a mean apparent diffusion coefficient of 3.E^{-12} m^2.s^{-1} which is lower by a factor 10 than the apparent diffusion coefficient measured for G2 moderator samples. The difference in porosity may explain this trend as there are far more small pores (10 to 100 nm) in SLA2 moderator samples than in G2 moderator samples.

Overall, the consistency between fitted and measured diffusion coefficients confirms that chlorine 36 labile fraction release is a diffusion-driven process through graphite porosity. Results also confirm chlorine 36 high mobility which explains high leaching kinetics while the variability in leach rates remains unclear. Eventually results suggest that diffusion coefficients may depend on the coke used for graphite manufacture, on irradiated graphite structure and thus maybe on its nanoporosity.

4.3.3 Impact of chlorine speciation and location in graphite

It can be assumed that chlorine 36 two-step release process may be related to two different/complementary effects;

- Chlorine 36 may be located in different areas within the graphite. The labile fraction may thus be located in graphite open porosity while the non-labile fraction may be located in areas where water hardly penetrates. Such a distribution may differ depending on samples thermal and irradiation backgrounds
- Chlorine 36 may also feature different chemical forms in line with different water solubility effects i.e. high solubility for the labile fraction and low solubility for the non-labile fraction

The occurrence of two different chlorine chemical forms has been suggested by XPS and XAFS measurements[5] on virgin graphite samples (Vaudey et al., 2009; Vaudey et al. 2010);

- A very low amount of inorganic chlorine (oxychlorine species ClO_x^-)
- A major part of organic chlorine covalently bound to the graphite matrix (C-Cl bonds)

The occurrence of metallic chloride species has not been detected.

Similar measurements could not be performed on irradiated material for both equipment availability and detection limits issues. Moreover, results on virgin graphite samples cannot be directly transposed to irradiated graphite because of strong modifications during reactor operation. Chlorine 36 speciation in i-graphite is thus still unclear.

Since 2011 specific tests have been undertaken in France in order to characterise chlorine non labile fraction speciation and location. To do so, G2 and SLA2 samples that have been already leached once i.e. whose chlorine labile fraction has been already released are used for this experiment. Several leaching media were considered;

- Alkaline water (pH=13) simulating water percolating through cementitious materials under disposal conditions
- Oxidative media (H_2O_2) in order to promote reduced and hydrolysable species release (organic species)

[5] XPS: X-ray photoelectron spectroscopy; XAFS: X-ray Absorption Fine Structure

- Pure water (pH=7) together with ultrasonic sound to promote graphite de-structuring effects and water penetration

Experiments are still underway. Results should be available in 2013.

As for chlorine location, Secondary Ions Mass Spectrometry (SIMS) measurements have been carried out on irradiated G2 and SLA2 samples (Comte et al., 2012). However chlorine 36 concentration was so low (in the order of 10 $Bq.g^{-1}$, ie. 8 $ng.g^{-1}$) that it was not possible to be studied, even qualitatively. As a result, only chlorine 35 distribution was studied. Figure 4-12 shows:

- A surface pollution in chlorine (chlorine in the air, cutting tool pollution, vial pollution…)
- A strong decrease of chlorine concentration after removal of a small sample thickness (few nm)

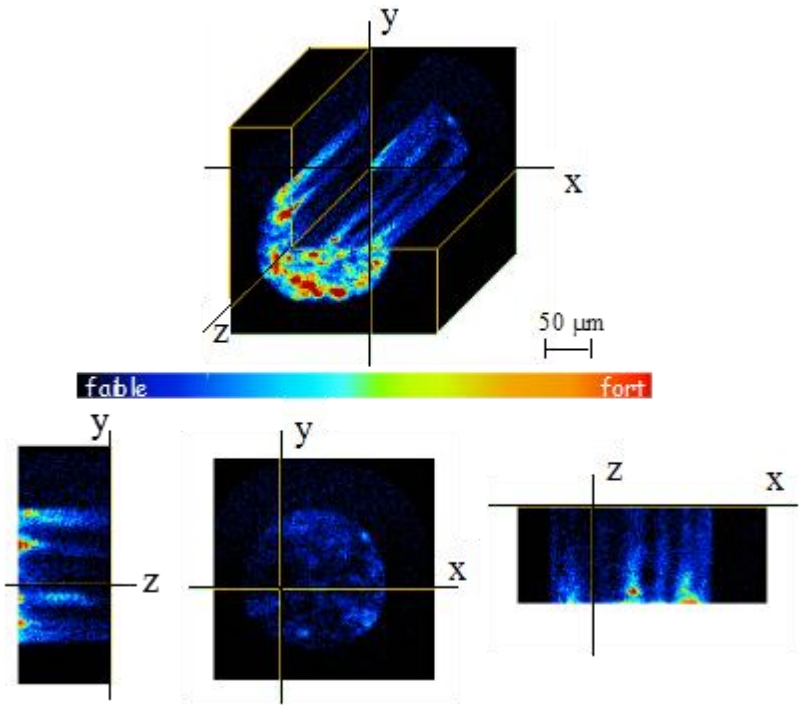
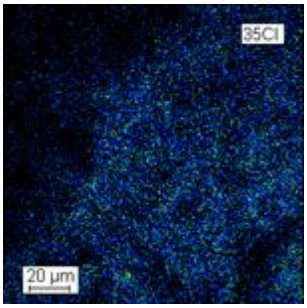
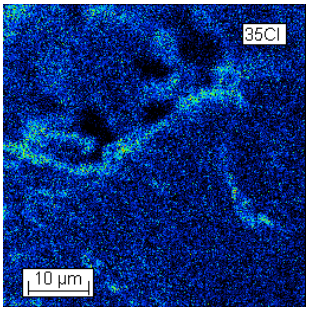


Figure 4-12 –3D chlorine 35 mapping in a SLA2 irradiated graphite sample

After removal of a surface layer (Figure 4-13), for G2 samples, chlorine is found to be homogeneously spread with some small spots. In contrast, for SLA2 samples, there are more chlorine 35 spots but they tend to disappear when going deeper into the graphite matrix.

Eventually, SIMS measurements also confirm that there is no clear correlation between metal impurities and chlorine distribution which means that chlorine should not be as metallic chloride species.





SLA2 irradiated graphite sample *G2 irradiated graphite sample*

Figure 4-13 – SIMS pictures of chlorine 35 in G2 and SLA2 irradiated graphite samples after removal of a surface layer

4.3.4 Impact of chlorine thermal behaviour in reactor

The impact of graphite sample location in the reactor (in relation with the thermal background) on chlorine 36 leaching rate has been clearly demonstrated on three French UNGG reactors Bugey 1, SLA2 and G2. As shown in section 4.2.2.2, chlorine 36 leaching rate is indeed higher when graphite samples were irradiated at low temperature than when they were irradiated at high temperature.

IPNL studies (Vaudey et al, 2009; Vaudey et al., 2010) on virgin nuclear graphite samples provide some explanation. Indeed, thermal annealing and thermal desorption experiments on virgin (^{35}Cl) and ion-implanted (^{37}Cl) samples have shown that chlorine release starts at low temperature, around 200°C-300°C, that is to say in the range of reactor operating temperatures.

As a consequence a large amount of chlorine that initially existed in virgin nuclear graphite must have been released in the reactor coolant, the release level being correlated to the irradiation temperature. In the reactor warmest areas, the chlorine labile fraction must have been more released than in the coolest areas, which may explain that the residual chlorine 36 labile fraction measured during leaching experiments also being lower.

It has also been suggested that chlorine labile fraction may be related to graphite structural evolution under reactor operating conditions. Indeed, temperature and neutron flux have an opposite effect on graphite structure (Ammar & Rouzaud, 2011; Vaudey et al., 2009): while graphite structure is altered by irradiation which promotes structural defects generation, temperature features a structural recovering effect by promoting defects recombination. Such a structural recovering has been evidenced for graphite samples trepanned from the reactor warmest areas whose structure is far less disturbed than for samples coming from cooler areas (Comte & Gosmain, 2010; Comte & Gosmain, 2012).

Chlorine 36 could thus have been trapped within graphite matrix due to the recovering process which could explain that the resulting labile fraction in leaching tests is lower in highly-restructured areas. However, this assumption has not been confirmed experimentally. Moreover such an effect should logically be also observed for other radionuclides but it does not in practice. There is thus no clear correlation between chlorine leach rates and graphite structure.

Eventually, it is interest to highlight the range of temperatures related to chlorine 36 leach rates variability. For G2 samples, Figure 4-7 shows that chlorine 36 leach rates range from a few % to more than 90% over 40°C (310-350°C). For Bugey samples, Figure 4-8 shows that the same range of chlorine 36 leach rates is found over more than 200°C. Similar results were also found for SLA2 graphite samples. An interesting study would be check whether such a range of temperature matches with the graphite coke (see section 4.2.2.3) although such data are not available. Currently, no explanation is thus provided.

5 Carbon 14 leaching results

5.1 Review of available data

The carbon 14 issue in i-graphite waste is overall much more documented than that of chlorine 36 as it is the main long-lived radionuclide in terms of activity in most of graphite reactors. However, as for chlorine 36, specific leaching studies were really stepped up during the 1980's where many research groups concentrated their efforts on radioisotope release and mechanism.

Several reviews have already been published on carbon 14 leaching in irradiated graphite (Wickam & Marsden, 2006; Marsden et al., 2002). We thus propose below a brief updated overview of the major results concerning carbon 14 release and speciation in graphite waste. All references and main leaching parameters are compiled in Table 5-1.

In 1984, White et al. (White et al., 1984) examined the management options for irradiated graphite arising from the decommissioning of UK reactors. Leaching tests were performed on Magnox CEGB samples roughly following IAEA standards. Various leaching media simulating possible disposal environments were considered as well as a control test in demineralized water. Whatever the leaching media, carbon 14 release was always found to be low (c. 0.1% over 100 days) and to occur in two stages, with a first rapid release (c.10 days) followed by a near-stabilization (Figure 5-1).

In 1988, Gray and Morgan (Gray & Morgan, 1988) studied carbon 14 and chlorine 36 leach rates in Hanford reactor graphite samples. Various leaching media (groundwater, deionized water) and temperature (25°C, 90°C) were tested. Very low carbon 14 leach rates were found as well. They proceeded thereafter with a comparative work with French G2 graphite (Gray & Morgan, 1989). Carbon 14 release rate was also found to be very low although slightly higher than that for Hanford graphite (0.85% max. over 90 days).

Since the late 1980's, several leaching campaigns have been launched in France on G2, SLA2 and Bugey 1 UNGG reactors (Figure 5-2). Although these tests primarily aimed at studying chlorine 36, carbon 14 release data was also collected. Results are shown in Table 5-1 and were detailed in a CARBOWASTE report (Comte & Petit, 2011). Overall, several tens of leaching tests were carried out in various experimental conditions (temperature, coke, sample location in reactor…) but interpretation were made difficult as lots of measurements were below detection limits. As for White et al. carbon 14 was often found to be released in two stages.

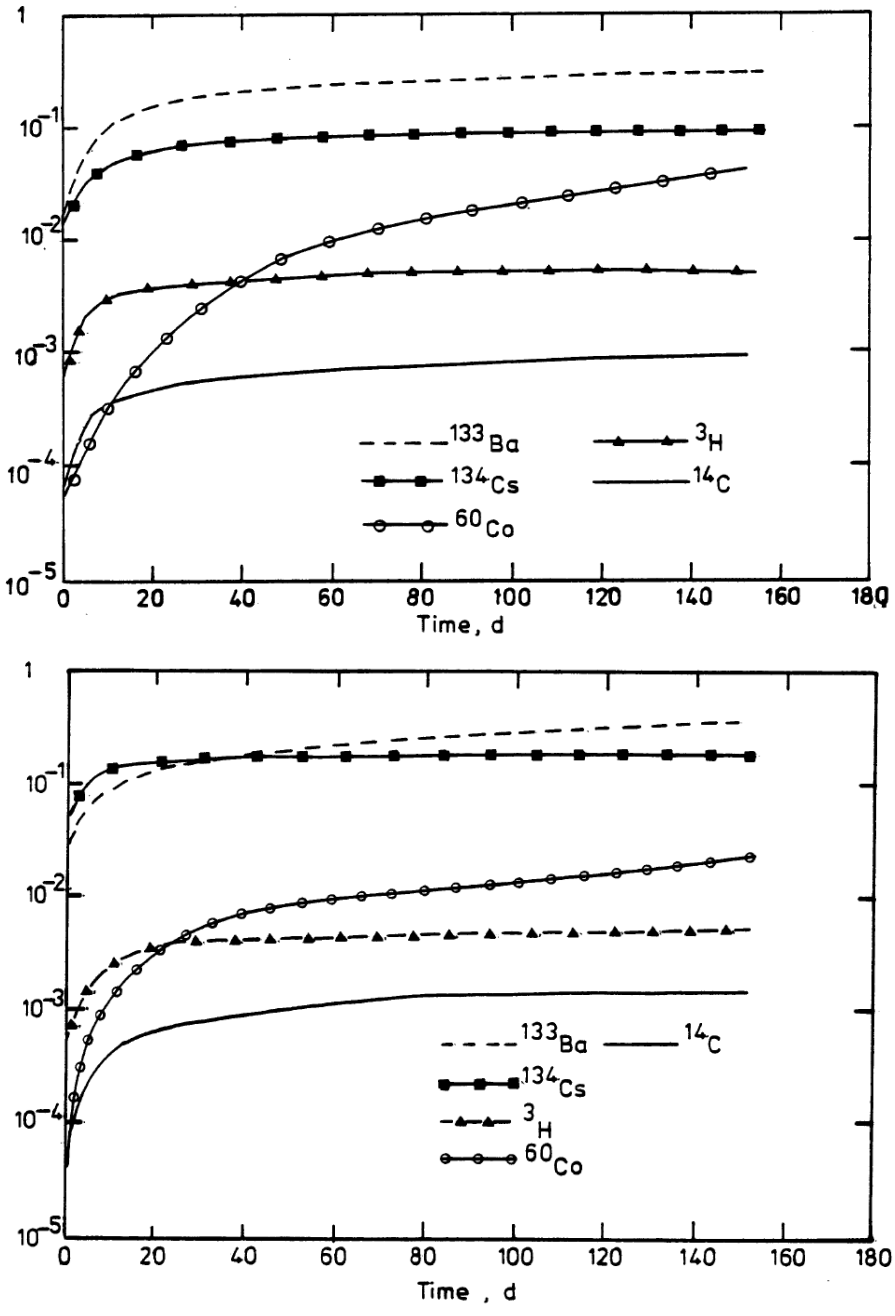


Figure 5-1 – Cumulative fraction of activity leached in demineralised water (top panel) and simulated ground water (bottom panel), 1bar, 25 °C (White et al., 1984)

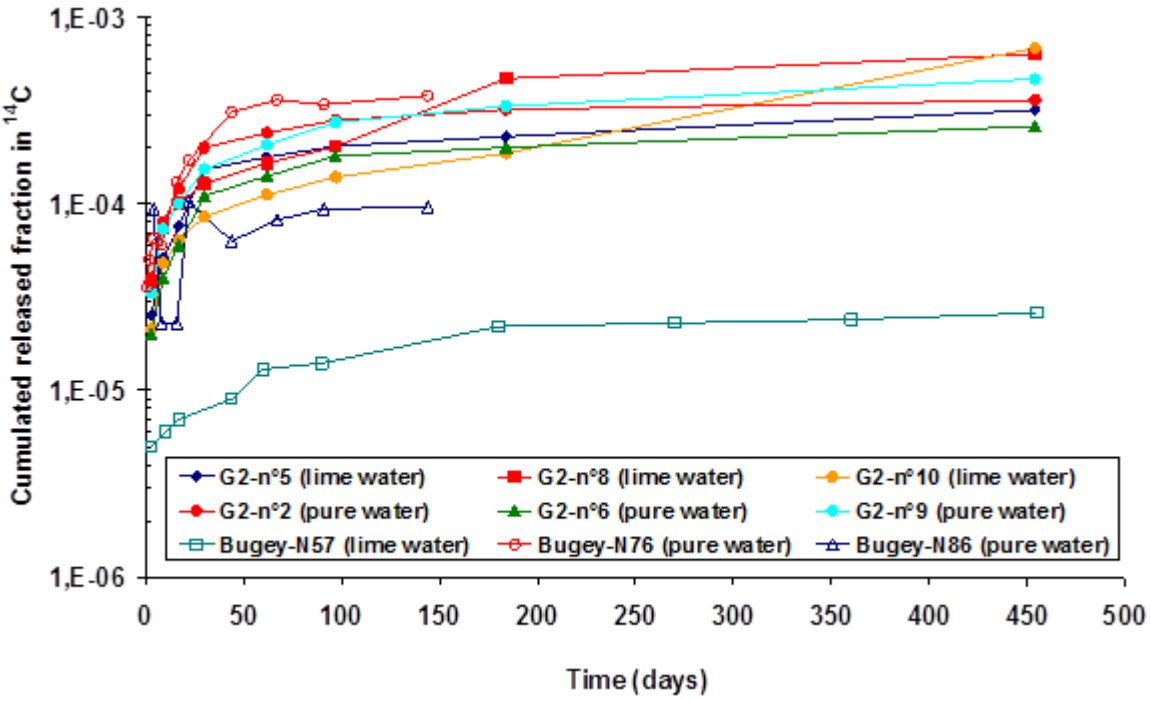


Figure 5-2 – Carbon 14 cumulative leached fraction as a function of time for graphite samples from G2 and Bugey reactors (Comte & Petit, 2011).

More recently, within the framework of the CARBOWASTE program, leach tests on UK irradiated British Experimental Pile Zero (BEPO) and Magnox Wylfa graphite were undertaken according to IAEA standards for semi-dynamic leach test (McDermott, 2012). As these tests primarily aimed at removing tritium and carbon 14, oxidizing and various acidic environments were tested and proved to be effective in increasing tritium and carbon 14 mobility. Yet, tests in pure water and alkaline solution (pH=13) were also made as control tests and will be of interest in the following analysis. Although carbon 14 leach rate remains limited, it is often one order of magnitude higher than in other leaching studies (c. few %) which may be partly related to the occurrence of some interferences with other radionuclides when quantifying the released activity by liquid scintillation counting. It is also of interest to observe that all carbon 14 leaching plots feature a first quick release whereas hardly any carbon 14 is released afterwards.

Few other references were also found concerning Spanish (Vandellos I reactor, (de la Huebra et al., 1994; Pina et al., 2013)) and Japanese (Tokai 1 reactor (Takahashi, 1999)) graphite.

Spanish results are of particular interest as they focus on graphite sleeves whereas most of previously-mentioned studies deal with graphite moderator samples. In this regard, a specific analysis of graphite sleeves leaching results is proposed in section 5.2.2.2.

Japanese leaching studies were performed at the end of the 90's on graphite trepanned from Tokai I Magnox reactor. An alkaline $H_2SO_4/KMnO_4$ solution was used as a leachant in order to accelerate carbon 14 release, however over 90% of the carbon 14 activity remained

in the graphite with a leach rate of 10^{-5} reported for 720 days. Yet these results will not be further analyzed as experimental conditions are unclear and poorly detailed.

Finally, carbon 14 speciation started to be characterised in leach studies from the end of 2000's as detection limits issues and applied experimental conditions previously prevented from monitoring carbon 14 species. Carbon 14 chemical form can drastically affect the dose impact under disposal conditions. Indeed, whereas inorganic forms (CO_2, CO_3^{2-}, HCO_3^-) are strongly trapped in cementitious materials, organic species and carbon monoxide are much more mobile, all the more so since they can be released as gaseous species. Currently, few references[6] on carbon 14 speciation in the gaseous phase are available in the literature (Handy, 2006; Baston et al., 2006; Marshall et al., 2011). Detailed analysis of such references is proposed in section 5.4. The major part of carbon-14 is released in solution while less than 0.01 % of the initial carbon 14 inventory is found in the gas phase. These references are also consistent with previously-mentioned studies where carbon 14 release is always found to be low.

Overall, regardless sample history, geometry and leaching methodology, all leaching studies show similarities in carbon 14 leaching behaviour. Carbon 14 release in solution is indeed always found to be low, often below detection limits. This made results analysis difficult and it is often even impossible to identify any global trend in carbon 14 release behaviour. This implies to perform long leaching studies or to use larger samples in order to increase carbon 14 concentration in the leaching solution. When results are significant, a sharp initial release is often observed followed by a near stabilization. It suggests that there may be 2 separate forms of carbon 14 i.e. leachable and non-leachable. In this regard, an attempt to interpret such behaviour is proposed in section 5.3.2. Eventually, it is of importance to underline that most of available data focus on carbon 14 release in solution whereas the gas phase should also be monitored, in particular when acidic conditions are considered. The lack of gas phase measurements may also limits reliable interpretations. Conversely, to date carbon 14 speciation studies have focused on the gaseous phase whereas most of carbon 14 is released in solution. Carbon 14 speciation in solution should thus be investigated as well in future studies.

[6] Another study should be available by the end of 2012 (Vendé, 2012).

Table 5-1 – Summary of main carbon 14 leaching studies (RT: room temperature, UP: ultra pure)

Graphite origin	Technology[7]	Duration	Leachant	Gaseous phase	Graphite form	Speciation	Cumulative release	Reference
CEGB	Magnox	100 days	Simulated groundwater (25°C)	Unknown	Solid	Not studied	2-steps release, 0.14%	White et al., 1984
CEGB	Magnox	100 days	Demineralised water, 20-23°C	Unknown	Solid	Not studied	2 steps release, 0.088%	White et al., 1984
Hanford moderator	LWGR	56 days	Water and simulated ground water, 25/50/90 °C	Hermetic vessel, air atmosphere	Solid (40 g)	Not studied	From 0.004 to 0.050 %	Gray & Morgan, 1988
G2 moderator	UNGG	90 days	Water, 20°C	Hermetic vessel, air atmosphere	Solid (40 g)	Not studied	From 0.26 to 0.85 %	Gray & Morgan, 1989
G2 moderator	UNGG	90 days	UP Water, 20°C	Hermetic vessel, air atmosphere	Solid (~630 g)	Not studied	Up to 0.003%	Comte & Petit, 2011
G2 moderator	UNGG	455 days	UP Water, 20°C	Hermetic vessel, inert gas purge (Ar, N_2)	Solid (~90g)	Not studied	< 0.05%	Comte & Petit, 2011
G2 moderator	UNGG	455 days	Lime water, 20°C	Hermetic vessel, inert gas purge (Ar, N_2)	Solid (~90g)	Not studied	Up to 0.07%	Comte & Petit, 2011
Bugey moderator	UNGG	181 days	UP Water, 20°C	Hermetic vessel	Powder (~2g)	Not studied	< 0.1%	Comte & Petit, 2011

[7] UNGG : Natural Uranium Graphite Gas reactor, ie fueled with natural uranium metal and cooled with CO_2– LWGR : Light-Water-cooled Graphite-moderated Reactor

Graphite origin	Technology[7]	Duration	Leachant	Gaseous phase	Graphite form	Speciation	Cumulative release	Reference
Bugey moderator	UNGG	455 days	UP Water, 20°C	Hermetic vessel, inert gas purge (Ar, N_2)	Solid (~10g)	Not studied	<0.01%	Comte & Petit, 2011
Bugey moderator	UNGG	144 days	UP Water, 40 °C	Hermetic vessel, inert gas purge (Ar, N_2)	Solid (~10g)	Not studied	Up to 0.034%	Comte & Petit, 2011
Bugey moderator	UNGG	455 days	Lime water, 20°C	Hermetic vessel, inert gas purge (Ar, N_2)	Solid (~10g)	Not studied	<0.005%	Comte & Petit, 2011
SLA2 sleeve	UNGG	455 days	Industrial water pH=7.2	Hermetic vessel, air atmosphere	Solid (<10g)	Not studied	~ 1%, up to 6.3%	Comte & Petit, 2011
BEPO moderator	Air cooled pile	190 days	Deionised water & pH=13, RT	Under air	Both solid & powder samples (0.5g)	Not studied	Up to 4.6% of 14C released	McDermott, 2012
Wylfa moderator	Magnox	190 days	Deionised water & pH=13, RT	Under air	Granulated samples (0.5g)	Not studied	Up to 2.5% of 14C released	McDermott, 2012
Vandellos I sleeve	UNGG	~380 days	Distilled water, 40°C	Hermetic vessel Partial nitrogen flushing	Solid (~700g)	Not studied but almost no ^{14}C gaseous species detected	Up to 0.11% of 14C released	De la Huebra et al., 1994
Tokai I moderator	Magnox	720 days	Alkaline H2SO4/KMnO4 solution, T unknown	Unknown	unknown	Not studied	~0.005%	Takahashi, 1999

Graphite origin	Technology[7]	Duration	Leachant	Gaseous phase	Graphite form	Speciation	Cumulative release	Reference
WAGR moderator	AGR	224 days	$Ca(OH)_2$, pH=13, RT	Hermetic vessel, inert gas purge (Ar, N_2)	Both solid & powder samples (2g)	^{14}C mainly released in solution (0.86%)	<1% of ^{14}C released	Handy, 2006
WAGR moderator	AGR	15 days	NaOH, pH=13, RT	Hermetic vessel, CO_2 and H_2O removal from air flushing	Crushed sample (9g)	Very low amount of gaseous ^{14}C species	Initial ^{14}C activity not measured	Baston et al., 2006
BEPO moderator	Air cooled pile	431 days	Sodium hydroxide pH=13, RT	Hermetic vessel, CO_2 and H_2O removal from air flushing	Solid (59 g)	^{14}C mainly released in solution (95%, Ie. 0.1%)	2-step release, c.0.1% of ^{14}C released	Marshall et al., 2011

5.2 Results analysis

5.2.1 Impact of leaching conditions

5.2.1.1 Leachant chemical composition (water vs. pH=13)

The leachant chemical composition is of great importance for carbon 14 leaching studies as it can affect carbon 14 solubility and its distribution between the gaseous phase and the solution. Most of available references have focused on water and alkaline environments to simulate disposal conditions although some aggressive conditions have been also tested in CARBOWASTE report T-4.3.3-b (McDermott, 2012) for treatment purposes.

In the first PNL tests on Hanford graphite block samples, the impact of the leachant chemical composition was tested comparing carbon 14 leach rates in pure water and simulated ground water. As shown in Figure 5-3, leach rates were found to be slightly higher in water (3 times higher at 25°C) but tests were performed under air resulting in some dissolved oxygen in the leaching solution. Then, as the solution salinity is higher in ground water, the oxygen solubility in the leaching solution decreases which could explain that the amount of released carbon 14 is lower (if it is assumed that carbon 14 release relies on an oxidation process).

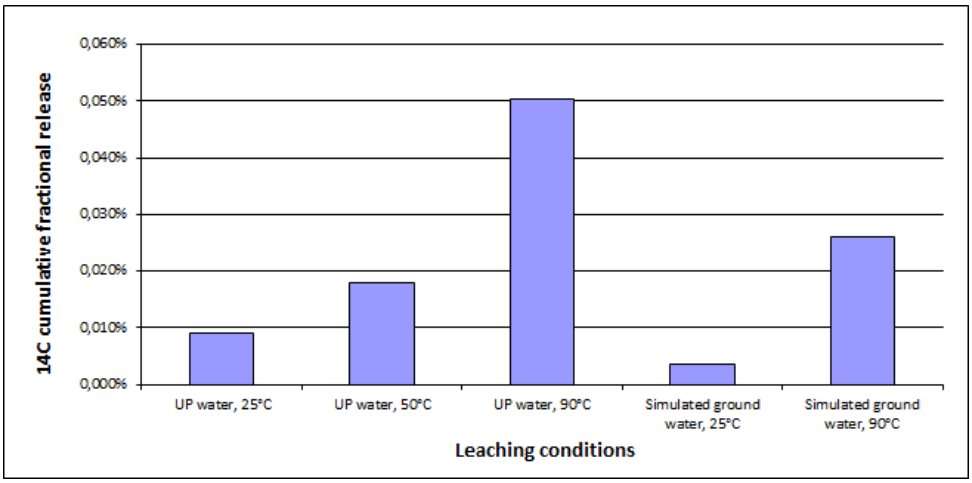


Figure 5-3 – Carbon 14 behaviour in Hanford graphite samples – influence of temperature and of the leachant composition.

The effect of temperature is more significant. Carbon 14 release increases with temperature in both water and ground water media. Such an effect cannot be related to the amount of dissolved oxygen as gas solubility decreases with temperature. In contrast, it might be related to the increase in graphite corrosion kinetics.

In 2004, tests were performed on French G2 graphite samples under similar experimental conditions (core n°36) with the exception of the leaching media for which both water and lime water were used. Experiments were carried out in a sealed reactor under argon to avoid the problems faced for PNL leach tests. The carbon 14 released fraction was found to be

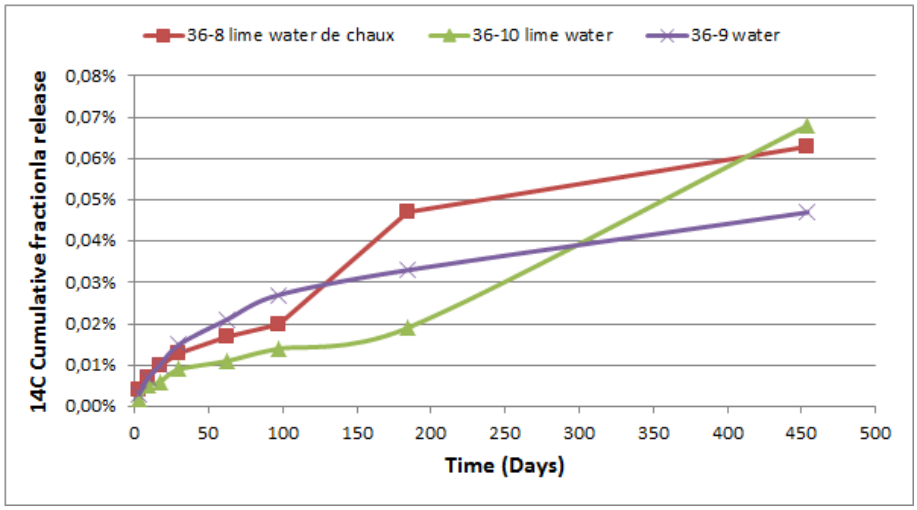


Figure 5-4 – Carbon 14 cumulative fractional release as a function of time for different leaching solutions on G2 graphite samples (core n° 36)

below detection limits for 3 tests out of 6, in both water and lime water. For the 3 other vessels, no significant difference was found between the two leaching media (see Figure 5-4).

The leachant composition effect was also found to be unclear in the recent report (McDermott, 2012). For BEPO samples, the carbon 14 leach rate for pH=13 was higher than pure water but the opposite trend was measured for Wylfa Magnox graphite (see Table 5-2).

Table 5-2 – Comparative carbon 14 cumulative leach rates under water and alkaline conditions (McDermott, 2012)

Reactor	Leachant	Sample	Duration, days	^{14}C cumulative fractional release
BEPO (channel 16)	water	powder	190	1.2%
BEPO (channel 16)	pH=13	powder	190	3.5%
Wylfa	water	solid	190	2.5%
Wylfa	pH=13	solid	190	1.1%

Overall, there is no clear effect of the alkaline environment on carbon 14 release. There are often minor differences with pure water, one media showing alternatively a slightly higher or lower leach rate than the other. However, as the alkaline environment may induce a different chemical behaviour of carbon 14 species than pure water (gas/solution distribution, precipitation…) experimental conditions should be chosen as close as possible to the real disposal environment.

5.2.1.2 S/V ratio[8]

The influence of the S/V ratio has been well characterised in reference (McDermott, 2012) which is the most relevant study in this regard. Samples have been powdered to maximize the surface available to the leachant and contrasted against solid samples. Results are shown in Figure 5-5 for BEPO samples in water where the surface area has clearly promoted carbon 14 release. Similar results have been obtained in alkaline solution. For those samples, BET surface area was 55.0 m^2/g for powder vs. only 0.8 m^2/g for the solid sample. Interestingly, a steady state release seems to be rapidly reached which means that increasing the surface available to the leachant allows releasing an initial carbon 14 fraction that is hard to access. In this regard, it would be of interest to increase graphite destructuration (e.g. with ultrasonic sound) to see whether carbon 14 availability increases (problem of accessibility in the graphite matrix) or not (problem of solubility).

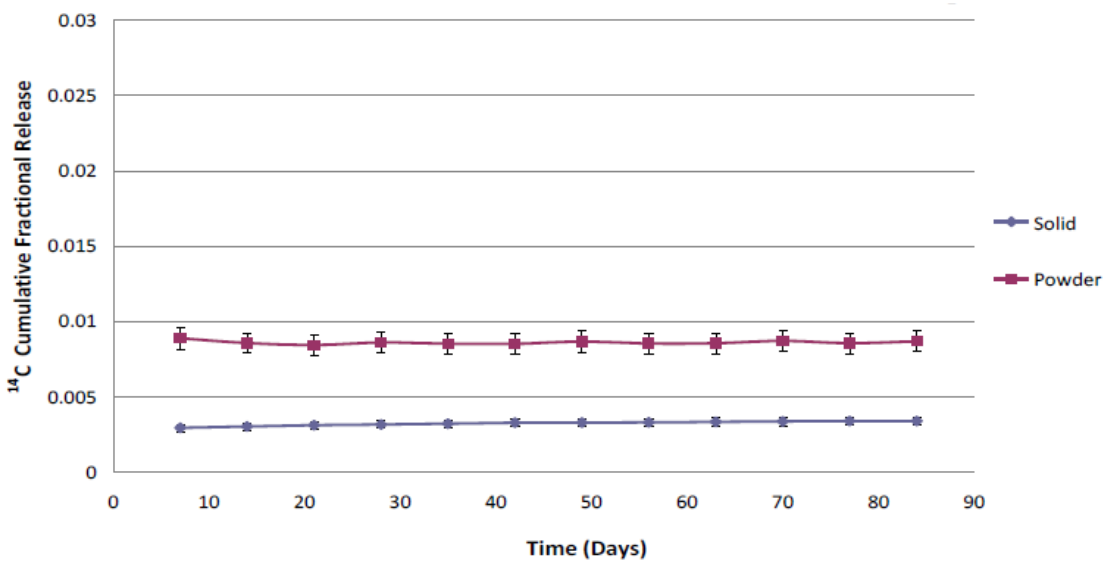


Figure 5-5 – BEPO (channel 16) carbon 14 release under water conditions (McDermott, 2012). Data have been corrected for the sample weight.

5.2.2 Impact of graphite properties

5.2.2.1 Carbon 14 initial activity

Carbon 14 measurements in leaching solutions are often close or even below detection limits, all the more so since experiments are made with dynamic conditions (full leachant renewal). As a result, the overall leach rate is often low and calculated by adding up detection limit values. As detection limits are similar from one test to another, carbon 14 leach rates often depend on the sample mass and of their initial carbon 14 activity. It is thus rather difficult to conclude on the influence of the initial activity on carbon 14 release rate. In this manner most

[8] Geometrical surface / volume ratio

of carbon 14 release data collected on French graphite samples are below detection limits. Figure 5-6 shows, based on the few significant values, that there is no clear correlation between carbon 14 release and carbon 14 initial activity.

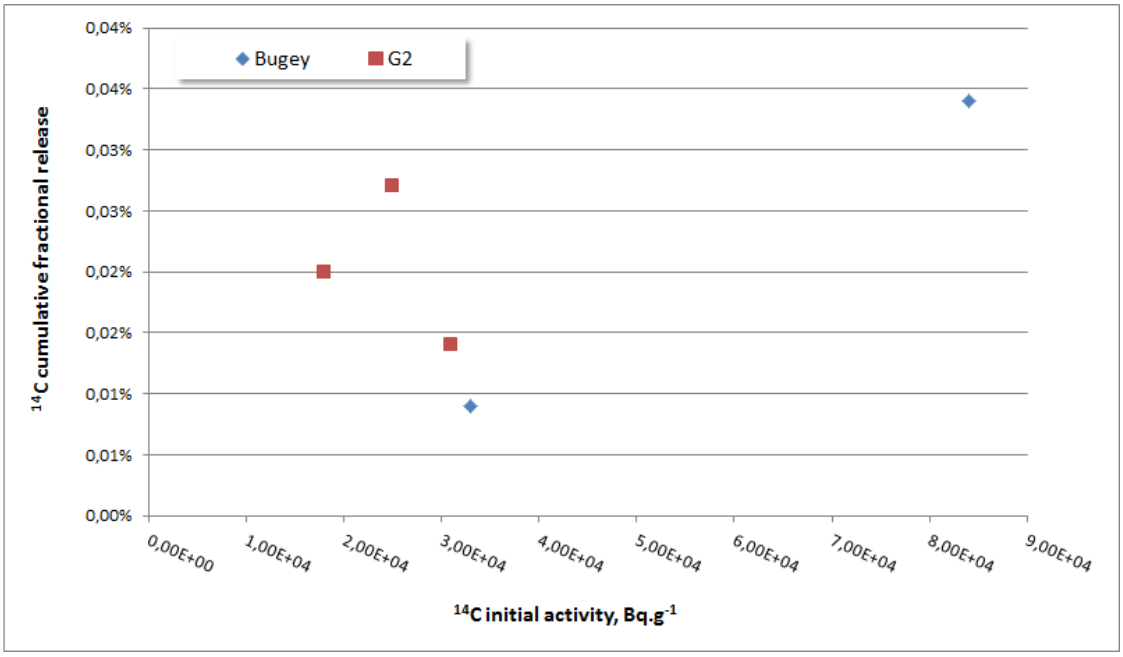


Figure 5-6 – Carbon 14 cumulative fractional release as a function of samples initial activity for French graphite samples.

5.2.2.2 Sample function in reactor

Most of available data on carbon 14 leaching are based on graphite moderator samples. Few studies deal with other graphite components. To our knowledge two studies are available on graphite sleeve samples for Vandellos I (de la Huebra, 1994) and Saint Laurent des Eaux A2 UNGG reactors (Comte & Petit, 2011).

Spanish studies are of particular interest as they are based on massive samples (c. 700g) trepanned from three different sleeves with different backgrounds. In this manner, two sleeves out of three stayed several months underwater during fuel retrieval. Leach tests were performed in distilled water with a hermetic vessel. Carbon 14 was analyzed both in the leaching solution and in the gas phase. On the whole, whatever the sleeve sample considered, the carbon 14 leach fraction is always low (max. 0,11% over 1 year). Carbon 14 is mainly released in solution and is hardly detected in the gas phase. Recently new leaching tests were performed on Vandellos sleeve powder samples (Pina et al., 2012). No carbon 14 was detected in solution after a few days of leaching.

French results measured on SLA2 sleeve samples also give low carbon 14 leach rates although one order of magnitude higher than Vandellos sleeve samples, from 1 to 7% (see

Figure 5-7). Contrary to many other tests, carbon 14 leach values are significant and well above detection limits. In this context, carbon 14 release appears to be rather fast over the first hundred days and then decreases to reach a near equilibrium. In this regard, measurements after 100 days are below detection limits.

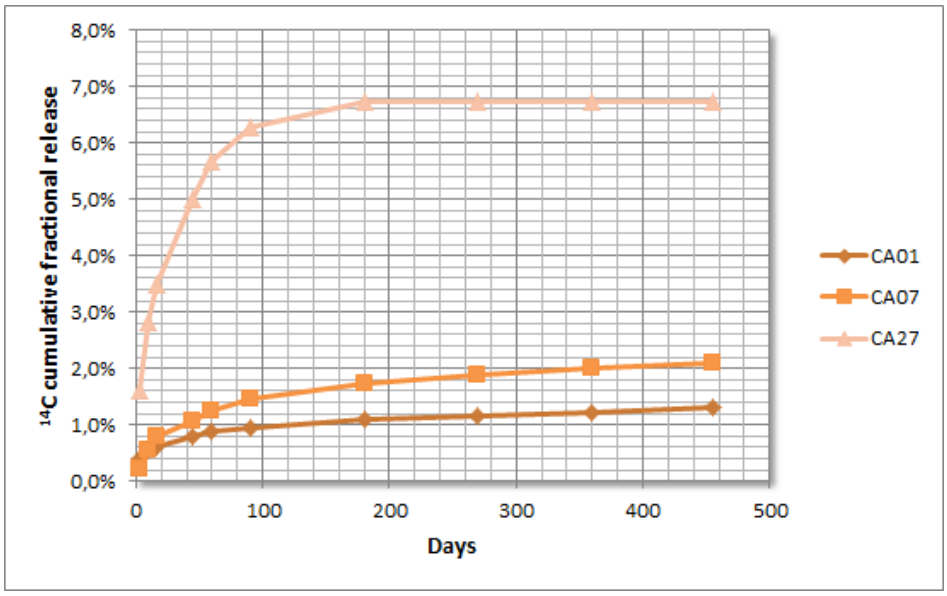


Figure 5-7 - Carbon 14 cumulative fractional release as a function of time for 3 SLA2 sleeve samples.

5.3 Phenomenological analysis

5.3.1 Water uptake

Water uptake in graphite has been studied on both unirradiated and irradiated samples for G2 and SLA2 French reactors. Results are collected in a CARBOWASTE report (Comte & Guy, 2010a). They show that water uptake kinetics are rather low in virgin graphite samples while they are faster in irradiated graphite samples as 50 to 70 % of the open porosity is filled up within a few days (Figure 5-8). Water uptake should thus not limit carbon 14 release.

5.3.2 Carbon 14 origin and location

The source of radionuclides in graphite is a combination of the activation of:

- Original impurities in graphite that may initially exist in graphite precursors or introduced during graphite manufacture
- Impurities arising from general reactor operations, such as coolant contamination

Carbon 14 is a β-emitter which is produced by three nuclear reactions as shown in Table 5-3. Although the $^{14}N(n,p)^{14}C$ reaction features the highest neutron cross section, calculations have proved that the remaining amount of carbon 14 after reactor shutdown mainly arises from carbon 13 activation (Narkunas et al., 2012). These two routes of production may affect

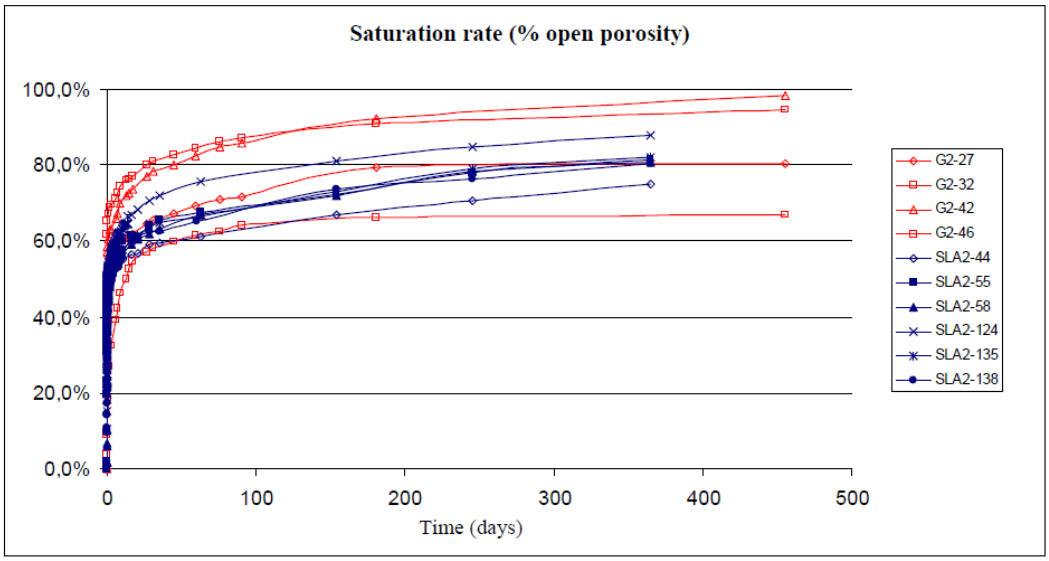


Figure 5-8 – Water uptake for G2 and SLA2 irradiated graphite samples

carbon 14 location and behaviour in i-graphite. It is thus assumed that carbon 14 arising from nitrogen 14 activation is mainly located onto graphite surface as most of nitrogen 14 impurities may be brought by the coolant. Conversely most of carbon 13 impurities being located in graphite bulk, carbon 14 produced by carbon 13 activation should be trapped in the bulk[9].

Such assumptions are supported by several studies on carbon 14 leaching which have evidenced that carbon 14 is released in two stages. In such studies release plots exhibit a sharp initial rise in the first days before approaching equilibrium values. It has been suggested that these two stages may be related to two different forms of carbon 14:

- The first fraction may be related to carbon 14 arising from nitrogen 14 activation, located onto the surface and loosely bound to the graphite matrix
- The remaining carbon 14 fraction would then be trapped in the bulk in line with low leach rates

[9] Carbon 14 located in graphite bulk may also partly come from nitrogen 14 graphite impurities.

Table 5-3 – Ways of production of carbon 14.

Reaction	Neutron cross section (barn)	Natural abundance of the isotope (%)
$^{14}N(n,p)^{14}C$	1.8	99,63 ^{14}N/nitrogen
$^{13}C(n,\gamma)^{14}C$	0.0009	1.07 ^{13}C/carbon
$^{17}O(n,\alpha)^{14}C$	0.235	0.04 ^{17}O/oxygen

In this regard, comparison of carbon 14 leaching behaviour between air cooled reactors (eg. BEPO) and CO_2 cooled reactors (Magnox, UNGG) is of particular interest. In air cooled reactors, it is expected that the large amount of nitrogen in the coolant should lead to a higher surface contamination in nitrogen 14, and thus to a larger carbon 14 labile fraction than in Magnox reactors. Moreover, Magnox graphite has been generally submitted to larger neutron irradiation and temperature, promoting radiolytic oxidation and removal of surface contamination. Such a comparison is provided in Figure 5-9 (McDermott, 2012) where both BEPO and Wylfa Magnox samples results are compared. However, there is no substantial difference between those two samples and interpretation is not straightforward. Indeed, the historical background of air cooled reactors is strongly different from that in Magnox reactors: different graphite type and impregnation process, irradiation and thermal histories. In particular, BEPO reactor has been thermally annealed twice in order to avoid Wigner energy issues. Thermal treatment has been proved to have a recovering effect on graphite structure (Ammar & Rouzaud, 2013) and can thus modify carbon 14 distribution.

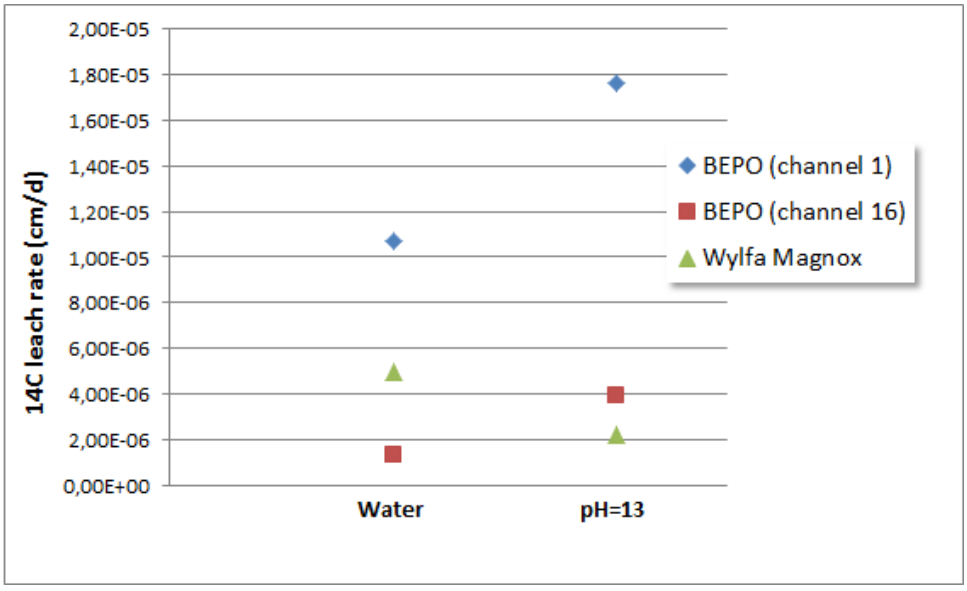


Figure 5-9 – Carbon 14 leach rate in water and alkaline solution (McDermott, 2012)

In contrast, carbon 14 leach rate is significantly higher for BEPO channel 1 than for the other two samples. In BEPO reactor, channel 1 was away from the centre of the core while channel 16 was much closer. As a result, channel 1 samples show a very low radiological inventory and should be structurally close to virgin samples. First molecular modeling calculations on carbon 14 production at the atomic scale have proved that irradiation strongly affects its location within graphite (CARBOWASTE, 2012). Therefore in BEPO channel 16 and Wylfa samples, carbon 14 distribution between graphite surface and bulk may have been disturbed. For BEPO channel 1 samples, such a modification should be negligible, thus explaining higher leach rates.

Hints on carbon 14 location in i-graphite can also be indirectly given by decontamination treatment tests. In reference CARBOWASTE report 4.3.3-b (McDermott, 2012), various oxidizing and acidic environments have been tested in order to promote carbon 14 release. Overall, whatever the acidic species used (HCl, H_2SO_4, H_3PO_4), the carbon 14 release is drastically enhanced compared to water or alkaline solutions. An example is given in Figure 5-10 for Wylfa where pH1 (0.2M HCl) and H_3PO_4 (1M) media show the highest carbon 14 release rates, 18.4% and 26.8% respectively.

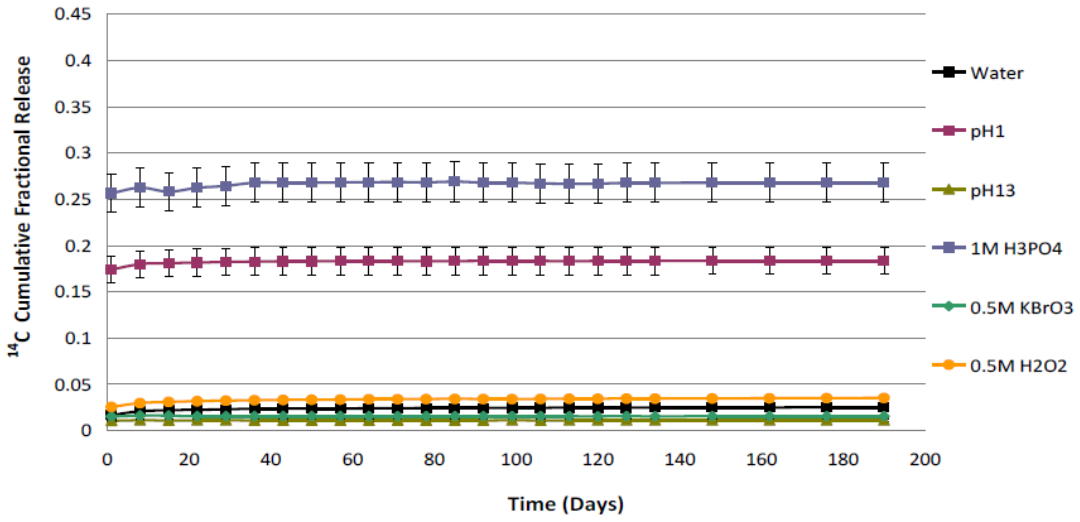


Figure 5-10 – Magnox Wylfa ^{14}C release under different leaching conditions

Chlorine, sulfate and phosphate ions are indeed well known as intercalation elements: they are able to insert between graphene layers, thus promoting the release of species trapped between those layers. Besides such a property is currently much studied within the framework of graphite decontamination processes where it is combined to a thermal treatment to lead to graphite exfoliation and a strong structure breakdown. In the present case, the increase in carbon 14 leaching means that part of carbon 14 might be trapped between graphene layers although no structural characterisation was carried out to check graphite structural evolution in acidic media. It should also be of interest to check the amount of carbon 14 in the gas

phase. Eventually, due to measurement limitations, higher concentrations of acidic species could not be tested to see whether higher amounts of carbon 14 could be leached.

5.3.3 Release mechanism assumptions

As mentioned in the previous section, it is assumed that the carbon 14 fraction that is slowly released arises from carbon 13 activation and is trapped in the graphite bulk. If so this non-leachable carbon 14 fraction should be released as the graphite matrix is corroded, ie. that carbon 14 leaching kinetics should be close to the graphite corrosion rate.

In order to calculate graphite corrosion kinetics, carbon balance assessments must be performed both in solution and in the gas phase. Indeed, graphite mass loss due to corrosion is hidden by water uptake within the graphite porosity which means that a simple mass balance is not appropriated.

Currently, such data is not available. The only data which refers to graphite corrosion studies that were performed in Germany on AVR graphite (Fachinger et al., 2006) and whose experimental conditions are not representative of leaching tests conditions: T=90°C, virgin samples. However, they provide a rough estimate of graphite corrosion kinetics in the order of $2.6E^{-6}$ $g.g^{-1}.d^{-1}$ for tests made in water under air.

Corrosion kinetics were also evaluated on the basis of carbon 14 leaching tests on G2 graphite samples assuming that carbon 14 distribution is homogeneous. From these results carbon 14 release kinetics is calculated to be in the order of $3E^{-7}$ $Bq.Bq^{-1}.d^{-1}$, i.e. one order of magnitude below graphite corrosion values found in Germany on AVR samples ($2.6E^{-6}$ $g.g^{-1}.d^{-1}$). Given the different experimental conditions, it suggests that part of the carbon 14 inventory may be indeed released as graphite is corroded, but a reliable conclusion should require more representative corrosion kinetics.

5.4 Carbon 14 speciation

Irradiated graphite (i-graphite) from gas-cooled reactors contains a range of activation products and carbon 14 is one of the most significant radionuclides on activity level viewpoint. It also presents the drawback to be potentially present in gaseous forms. According to some studies, these gaseous carbon 14 species such as carbon 14 bearing methane ($^{14}CH_4$) could be of a significant impact on the repository sanitary impact (Hoch et al., 2008).This is why it is very important to assess the amount and the rate of carbon 14 released from i-graphite in disposal conditions but also its chemical forms (volatile or non-volatile).

Few studies on i-graphite address carbon 14 leaching, studies addressing the chemical forms of carbon 14 released are even scarcer. To our knowledge, three technical reports addressing chemical forms of released carbon 14 are publicly available. These studies were carried out by British teams from AMEC (Handy, 2006) and Serco (Baston et al., 2006; Marshall et al., 2011; Baston et al., 2012) companies. In both studies carbon 14 leaching experiments are carried out in alkaline conditions near room temperature (25°C) and in aerobic conditions

(under decarbonated air). It should be noted that both studies also focused on tritium released in the gas phase. Information on the release of tritium containing gases is of interest from the viewpoint of the operational safety of a repository but thanks to the short half-life of tritium it is not important in post-closure performance assessments. These results on released tritium are no longer discussed in the following section.

In these studies, the i-graphite samples were submerged in a pH 13 solution (CaOH saturated solution of NaOH for AMEC) intended to represent the water equilibrated with the cementitious materials of a repository. Specific equipment was used to trap carbon 14 volatile species in the off gas of the vessel where the leaching tests were carried out.

5.4.1 Gas phase trapping systems

AMEC (Handy, 2006) used a wet scrubbing device to trap carbon 14 bearing volatile compounds in the off gases. This analysis was performed via a series of four bubblers (see Figure 5-11). The first bubbler filled in with a 0.1 M sodium hydroxide solution was devoted to carbon 14 bearing carbon dioxide trapping. The remaining carbon 14 volatile species in the out coming gas of the first bubbler were then oxidised through a catalyst bed and then flushed through the three last bubblers filled in with the same solution (0.1 M sodium hydroxide). It was not possible to separate carbon 14 bearing carbon monoxide from carbon 14 bearing organic molecules that were both trapped in these three last bubblers.

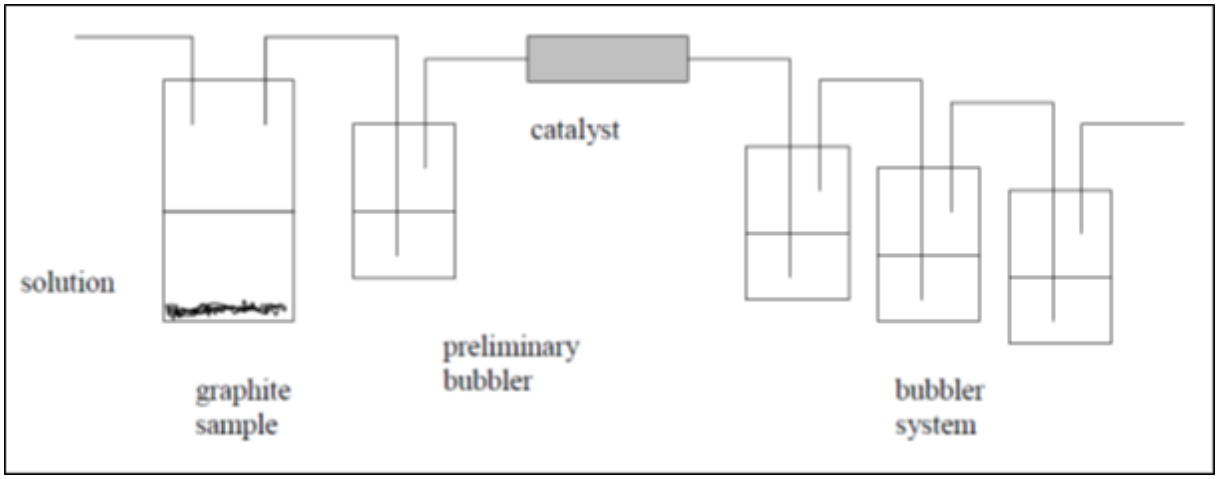


Figure 5-11 - Schematic diagram of the AMEC apparatus used in (Handy, 2006).

The carbon 14 bearing carbon dioxide released was supposed to be trapped in the first bubbler whereas the three last bubblers solutions gave access to the other carbon 14 volatile species. As shown in the experimental results carbon 14 trapped in the first bubbler was always, except for two samplings, under the detection limits. That makes sense because carbon dioxide transforms to carbonate in alkaline media so that any carbon 14 bearing carbon dioxide molecule released from graphite should have been trapped and dissolved to carbonate form into the leaching solution of the reactor vessel. It should also be noted that there is no

available information about the catalyst bed used, the oxidising conditions nor about the catalyst conversion rate (i.e. carbon 14 volatile species transformation rate into carbon 14 bearing carbon dioxide).

AMEC chose a "semi-dynamic" approach to run analysis system. The experiment lasted seven months. The accumulated gas in the leaching reactor vessel was blown out with air and flushed trough the gas phase trapping equipment after prescribed leaching time intervals (once a month except for the first month during which four gas samples were taken). Between gas sampling periods, the vessel where the leaching experiment takes place was isolated (no gas circulation). Nothing is specified concerning purging gas flow rate and duration of the purging period. After each purging process a small volume of the leaching solution (5 cm^3 over the 250 cm^3 in the leaching vessel) was extracted for analysis.

The Serco gas phase trapping system was slightly different from the previous one. It was a dry-bed absorber made of a series of four columns. Three of them were designed to trap tritium compounds whereas the last one was devoted to carbon 14 trapping. In the first Serco published study (Baston et al., 2006) the overall gas stream from the leaching vessel was oxidised through a catalyst bed before flushing through the carbon dioxide trapping column (see Figure 5-12). This column was filled with a granular mixture of sodium hydroxide with calcium oxide (named soda lime). The following study (Marshall et al., 2011) which is considerably more detailed, was completed with a more complex trapping system designed in order to trap and quantify separately ^{14}CO from the other species ($^{14}CH_4$ and other organics). In its principle the trapping system was made of two series of dry-bed absorber above mentioned, but each one with different oxidation catalysts. As shown in Figure 5-13, a first catalyst made of CuO (350°C) oxidised CO into CO_2 while the following one made of Pd (425°C) oxidised the remaining volatile carbon species (organics) into CO_2. Preliminary tests were carried out to confirm that no carbon 14 retention occurred on silica gel. It should also be noted that there is no available information about the catalyst beds selectivity (CO vs. organics).

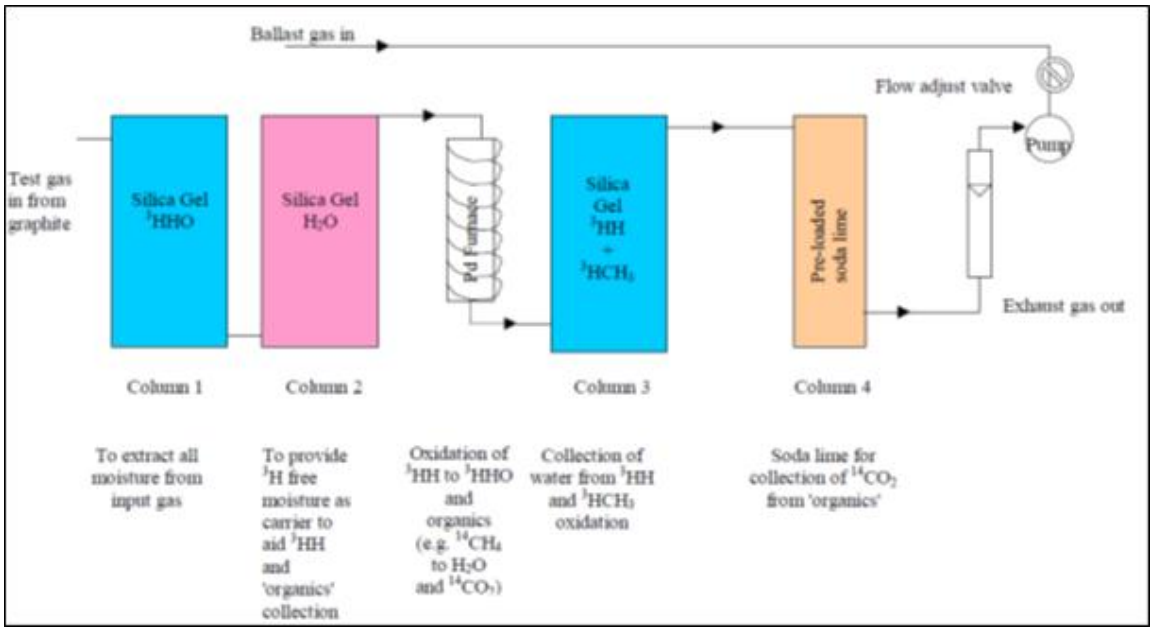


Figure 5-12 - Schematic diagram of the Serco apparatus used in (Baston et al., 2006)

A "semi-dynamic" approach was used by Serco to run analysis system. For the leaching experiment on crushed WAGR sample (Baston et al., 2006), the experiment lasted only 4 weeks whereas for BEPO sample (Marshall et al., 2011) the experiment lasted 14 months. In (Marshall, 2011), the gas trapping system was run weekly (except for the first 7 days) for between 5 to 7 hours to collect the gas phase from the leaching vessel (gas flow rate around 200 ml / mn). The columns were analysed at days 1, 3, 7, 28, 66 and 431. The liquid of the leaching vessel was analysed at the end of the experiment.

5.4.2 Graphite sample

The samples used in the leaching experiments are of different nature. AMEC and Serco used i-graphite from WAGR in studies published in 2006 (Handy, 2006; Baston et al., 2006), whereas a BEPO sample was used in the 2011 Serco study (Marshall et al., 2011; Baston et al., 2012). The main known characteristics of these samples are presented in Table 5-4.

Very little information is published about the samples used in the experiments. It seems that they all come for the WAGR and BEPO cores but there is not available information about operating conditions (operating temperature, neutron flux dose...). No information is also available on the particle size of crushed samples. It should be noted that a key parameter is the

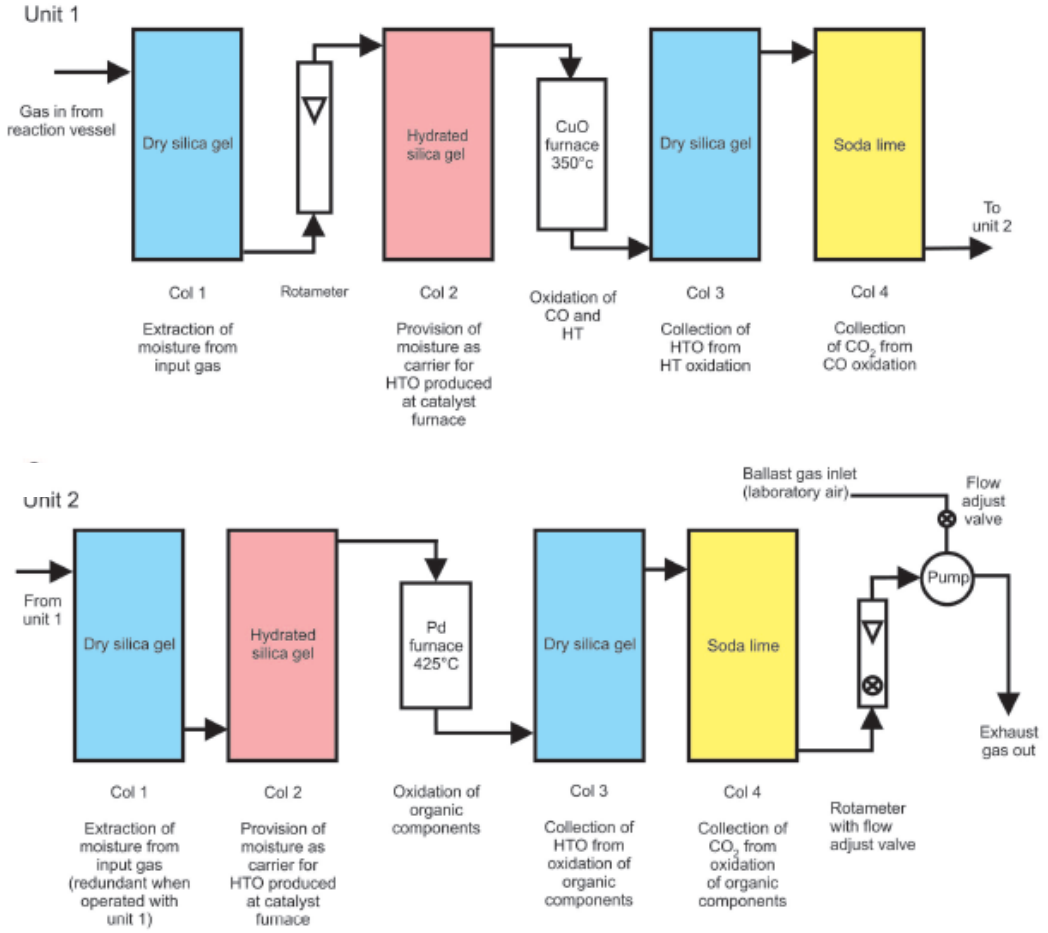


Figure 5-13 - Schematic diagram of the Serco apparatus used in (Marshall et al., 2011) and (Baston et al., 2012)

Table 5-4 - General description of graphite samples used in carbon 14 leaching experiments

Graphite origin	Cooling gas	Report	Sample (mass)	Carbon 14 activity (kBq)
WAGR	CO_2	AMEC [2]	Block (2.2 g)	58.1
WAGR	CO_2	AMEC [2]	Crushed (2.2 g)	59.8
WAGR	CO_2	Serco [3]	Crushed (9 g)	Around 900 (*)
BEPO	Air	Serco [4]	Block (59 g)	2 100

(*) calculated according to published data in [3]

cooling gas that was air for BEPO and CO_2 for WAGR. It can be assumed that for BEPO graphite large amounts of carbon 14 originates from activation of nitrogen from the cooling gas whereas this source of nitrogen did not exists for WAGR. Such an assumption that needs

confirmation would imply that carbon 14 coming from activation of nitrogen adsorbed onto graphite surface (BEPO) should be more easily leachable.

It should be noted that for both studies the initial carbon 14 activity of samples is questioned except for the last Serco study (Marshall et al., 2011) for which mass activity balance was made (final remaining activity in leached graphite sample compared with initial measured activity and the released one).

5.4.3 Results

The amount of carbon 14 released is rather low in both studies. The main results are summarized in Table 5-5.

Table 5-5 – Results on chemical forms of released carbon 14

Graphite origin	Report	Carbon 14 activity (kBq)	Duration	Cumulative Carbon 14 released in Bq (% of the total activity)			
				In liquid		In gas	
				$^{14}CO_2$	Other	^{14}CO	Other
WAGR (block)	Handy, 2006	58.1	7 months	500 Bq (0.86 %)	-	< 6 Bq (< 0.01 %)	
WAGR (crushed)	Handy, 2006	59.8	7 months	475 Bq (0.79 %)	-	< 6 Bq (< 0.01 %)	
WAGR (crushed)	Baston et al., 2006	900	4 weeks	-	-	3.6 Bq (0.0004 %)	
BEPO (block)	Marshall et al., 2011	2 100	14 months	1 430 Bq (0.068 %)	720 Bq (0.034 %)	87.6 Bq (0.004 %)	24.8 Bq (0.001 %)

It is very difficult to compare the cumulative results because of the very different test times: As shown in (Marshall et al., 2011), the carbon 14 release rate generally decreases with time (see Figure 5-14). Generally speaking, it can be observed that:

- As shown in (Handy, 2006) higher carbon 14 activities (>> 100 Bq) and longer duration (Baston et al., 2006) (>> one month) are needed to gain the objective of this kind of study. For example in (Handy, 2006) of 9 gas phase analysis, only 2 results or less were above the detection limit for each sample.

- Surprisingly, no difference was found between crushed and uncrushed sample in (Handy, 2006). This result would mean that carbon 14 released should not depend on the leached surface. This result needs to be confirmed. The authors suspect a possible carbon 14 (and tritium) release during crushing that could explain that result because the short term carbon 14 release observed on intact sample was not observed for the crushed one.

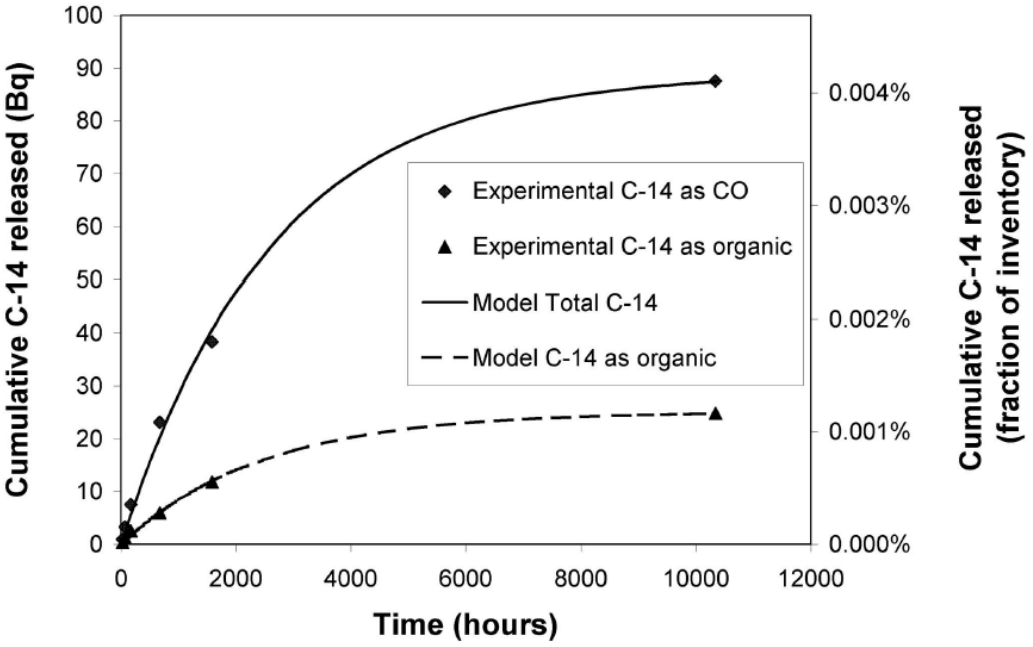


Figure 5-14 - Cumulative carbon 14 released in Bq and in % (Baston et al., 2012)

- It is not possible according to the presented results to draw an overall conclusion on the origin of the remaining carbon 14 in graphite by comparing results on BEPO samples and on WAGR samples. It could be assumed that for BEPO graphite large amounts of carbon 14 originates from activation of nitrogen from the cooling gas (air) whereas this source of nitrogen did not exists for WAGR. Such an assumption that needs confirmation would imply that carbon 14 coming from activation of nitrogen adsorbed onto graphite surface (BEPO) should be more easily leachable.
- It is shown that carbon 14 is mainly released into the leaching solution as carbon dioxide. The carbon 14 gaseous forms represent less than 0.01 % of the total carbon 14 activity of the graphite samples whereas carbon 14 in the leachate accounts for 0.9 % (Handy, 2006). But as shown in (Marshall et al., 2011), it seems that part of the carbon 14 in the leachate corresponds actually to organic species. Indeed, in (Marshall et al., 2011) a comparison was made between carbon 14 measurements in the leachate through pyrolysis and thereafter Liquid Scintillation Counting (LSC), and through LSC after direct acidification of the leachate. In the first case all contained carbon 14 of the leachate was measured whereas in the former, the organic forms only (carbon 14 bearing carbon dioxide molecules were extracted from the leachate by

acidification). It was shown that carbon 14 organic species in the leachate represent about half of the carbon 14 bearing carbon dioxide (720 Bq for soluble organics / 1430 Bq for carbon dioxide).

At last, in (Marshall et al., 2011), an attempt was made to determine a release rate function for both carbon 14 bearing carbon monoxide and carbon 14 bearing organic molecules in the gas phase. A first order function is proposed:

$$a(t) = f.A.\left(1 - e^{-kt}\right)$$ **Equation 5-1**

a is the total activity released up to time t
A is the initial graphite activity
f and k are fitted parameters

That release rate equation fits pretty well with experiments but cannot be associated to any described physical or chemical phenomenon.

It should be noted that according to that release rate equation, the long term cumulative released carbon 14 as carbon monoxide and organic species would never exceed the value $f.A$ where $f = 4.2 \times 10^{-5}$ for carbon monoxide and $f = 1.2 \times 10^{-5}$ for organic species. As indicated by the authors, it could be possible that the trend observed in that study represents the behaviour of the labile fraction of the carbon 14 inventory (associated with absorbed species on the graphite surface). Another release rate, much slower and so not observed during the experiment, could exist at longer timescale for carbon 14 bound more strongly to the graphite.

5.4.4 Comments

It is very important to assess the amount and the rate of carbon 14 released from i-graphite in disposal conditions but also its chemical forms. It is needed to characterise volatile or non-volatile carbon 14 bearing species but not to forget dissolved organic compounds into the liquid. As shown in (Marshall et al., 2011), carbon 14 bearing organics could represent a significant amount of carbon 14 in the leachate. These compounds are also weakly retained in the repository materials and they could transform into volatile compounds due to bacteria effect. They must be taken into account for the repository sanitary impact.

Another very important lesson to be learnt is that such a study needs the use of an important carbon 14 activity and also must be carried out for long time periods (more than a year). Even if results presented in (Handy, 2006) and (Baston et al., 2006) are interesting, useful data come from (Marshall et al., 2011) where the highest carbon 14 activity was used.

The lack of data should at the end, be stressed. Studies addressing the chemical forms of released carbon 14 are very scarce. More experiments are needed, not only for repository sanitary impact assessment but also could be of interest to assess carbon 14 behaviour according to its origin.

6 Conclusion

The release and migration of carbon 14 and chlorine 36, both long half-lived radionuclides, has been identified as a key issue for graphite waste disposal in the CARBOWASTE project. A specific workpackage (WP6) has been dedicated to this topic. Within this framework, the present report provides a short synthesis of the main results and achievements related to carbon 14 and chlorine 36 leaching behaviour under disposal conditions. Detailed results are available across WP6 CARBOWASTE technical reports.

Overall, chlorine 36 experiments were almost exclusively carried out on i-graphite samples from UNGG reactors whereas much more data are available for carbon 14 leaching under disposal conditions, mainly on Magnox and UNGG graphite samples. For both radionuclides, 2 stages have been evidenced for the leaching behaviour in disposal conditions:

- A first stage showing a very rapid release kinetics (labile fraction)
- A second stage showing slow release kinetics (non-labile fraction)

It has been shown for both radionuclides that water uptake kinetics through graphite pores is not a limiting factor that could explain the observed two stages. Unlike non-irradiated graphite, i-graphite is indeed a hydrophilic material with fast water uptake kinetics. The possible relation between carbon 14 and chlorine 36 releases and the graphite coke nature has been suggested several times through the present review. It has been found that the coke directly affects graphite radiological inventory but no clear correlation can be currently established with radionuclide leaching behavior.

More specifically, a huge discrepancy on chlorine 36 leach rates ranging from 10 to 90 % of the chlorine 36 inventory has been evidenced. These results obtained within the framework of the CARBOWASTE project confirmed previous results: chlorine 36 leach rate depends on i-graphite operating temperature. High release rates are observed for samples that were irradiated at low temperatures whereas high irradiation temperatures lead to low release rates. The origin of this phenomenon is still unclear but it is believed that it could be related to 2 different chlorine 36 chemical forms in i-graphite, leading to different release rates. Structural changes in i-graphite due to an annealing effect depending on operating temperature can also be put forward to explain these results. Moreover, it was shown that chlorine 36 labile fraction released in the first stage is a diffusion-driven process through graphite porosity. The study of the non-labile fraction speciation/location is underway.

Carbon 14 leaching rate appears to be very low in disposal conditions when compared to chlorine 36. It is always below 5 % of the inventory. Discrepancies are also observed between different graphite but no sizing parameter can be evidenced. At the beginning of the CARBOWASTE project it was assumed that carbon 14 arising from carbon 13 activation was located into the graphite matrix and was weakly mobile. In contrast carbon 14 arising from nitrogen activation was supposed to be mainly located at the surface of the graphite and so to be much more mobile. That assumption cannot be confirmed based on results on BEPO (air

cooled reactor) samples and Wylfa (Magnox CO_2-cooled reactor) samples but cannot also be ruled out. More experiments are needed to answer.

It should be noted that slight differences are observed between results obtained on British i-graphite (BEPO and Wylfa Magnox) and UNGG graphite. Whereas release rates obtained on BEPO and Magnox graphite can reach more than 1 % (up to 5 %) of the inventory, release rates experienced on UNGG graphite are always lower than 1 %. Radiolytic corrosion that was observed to some extend in UNGG reactors could be at the origin of carbon 14 loss during operation leading to a mobile fraction of carbon 14 lower than in British graphite.

To conclude, thanks to the compilation of all the data collected to date on carbon 14 and chlorine 36 leaching behaviour, a rather clear picture of their expected release rate under disposal conditions has been achieved, at least for the tested reactors. In contrast, there is still work to do regarding the understanding of their release behaviour and of their speciation which is of crucial importance for disposal performance assessments. More especially the key issue of carbon 14 speciation both in solution and in the gaseous phase has not been addressed yet but will be considered within the forthcoming CAST project (CArbon 14 Source Term, IGDTP).

Another key issue concerns the representativeness of leaching data. As shown in WP3 through i-graphite characterisation studies and i-graphite radiological inventory assessment, i-graphite is a heterogeneous material by itself and huge discrepancies have been observed between i-graphite depending on their operation conditions but also on their origin (coke used for graphite manufacturing). Such an issue is not only true from one reactor to another but also within the same reactor (eg. chlorine 36 leach rata variability depending on the irradiation temperature) and between pile samples and other i-graphite operational waste whose leaching behavior has not been addressed within the CARBOWASTE project. These issues should be futher investigated for disposal purposed but for treatment purposes as well.

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