CArbon-14 Source Term

CAST

Definition of a recommended scientific scope of leaching experiments and harmonised leaching parameters (D5.4)

Author(s):

Ekaterina Petrova, Natalia Shcherbina, Steve Williams

Gabriel Piña

Date of issue of this report: 30/10/2015

The project has received funding from the European Union's European Atomic Energy Community's (Euratom) Seventh Framework Programme FP7/2007-2013 under grant agreement no. 604779, the CAST project.

Dissemination Level		
PU	Public	X
RE	Restricted to the partners of the CAST project	
CO	Confidential, only for specific distribution list defined on this document	

CAST – Project Overview

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

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

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

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

CAST		
Work Package: 5	CAST Document no. :	Document type:
Task: 5.3	CAST-2015-D5.4	R = report
Issued by: FZJ		Document status:
Internal no.:		Final

Document title
Definition of the scientific scope of leaching experiments and definition of harmonised leaching parameters

Executive summary

Safety assessment of long-term storage and disposal of irradiated reactor graphite requires an understanding of ^{14}C behavior in the near- and far-fields of a repository site. The release behavior of ^{14}C and its chemical form (i.e. speciation) in the geochemical environment depends on many factors, like graphite type, ^{14}C inventory and speciation in the irradiated graphite, release rate, groundwater composition, pH- and Eh- conditions, etc. Extensive experimental and theoretical investigations have been undertaken in order to describe the effects of these parameters on ^{14}C release from graphite. Additionally, experimental studies from a number of international laboratories have been performed for different graphitic materials, applying different experimental methodologies. This has resulted in an accumulation of large amounts of data on the leaching behavior of ^{14}C that, due to different experimental conditions, are difficult to compare. In the present work, we review and critically assess the data and methods used in earlier projects, in order to highlight the sensitive experimental conditions that influence the release of ^{14}C. A number of recommendations are given to keep these key conditions fixed, in order to achieve a more straightforward comparison of the ^{14}C leaching data obtained in different laboratories. This information is used to develop a recommended unified experimental approach for harmonized leaching studies, which can be used within the CAST project.

List of content

CAST – Project Overview i
Executive summary iii
1 Introduction 1
2 Earlier leaching studies 2
3 Standardized leaching methods 5
3.1 IAEA leaching methodology 5
3.2 ISO methodology 6
3.3 ANS methodology 7
3.4 ASTM methodology 11
4 Discussion 16
4.1 Sample geometry and pre-leaching specimen characterization 16
4.2 Leaching solution 17
4.3 Temperature 19
4.4 Aerobic vs. anaerobic conditions 20
4.5 Release kinetics 22
4.6 Sampling 22
4.7 Leach test vessel 23
4.8 Pre- and post-leaching analytical approach 26
4.9 Evaluation of the result 27
4.10 Proposal for harmonized leaching approach 28
5 Conclusion 32
6 References 33

1 Introduction

Safety case and safety assessment of long-term storage and disposal of irradiated reactor graphite requires an understanding of the behaviour of associated radionuclides, in particular, ^{14}C. This includes the information about radionuclide mobility in the near- and far-field of a repository site. It is well known that mobility of ^{14}C in the repository is controlled by diffusion, release rate of ^{14}C from irradiated graphite and transport of ^{14}C in groundwater. The latter is controlled by ^{14}C speciation in the released fraction and corresponding interactions with the geological environment of the repository, e.g. complexation, adsorption, precipitation etc. In contrast to migration in the aqueous media, diffusion and release of ^{14}C from graphite are considered to be the rate-limiting stages in the process of ^{14}C transport in the repository and are controlled by speciation and local distribution of ^{14}C in irradiated graphite.

Extensive experimental and theoretical investigations have been undertaken in order to describe the localization and speciation of ^{14}C in irradiated graphite [1, 2, 3, 4, 5, 6]. During the life-time of graphite, its properties, like structure or ^{14}C inventory, may vary significantly. These are dependent on the production technology used, on irradiation conditions, i.e. neutron spectrum and fluence, and on temperature, cooling gas, interim storage condition etc. Therefore, idealized cases of ^{14}C distribution in irradiated nuclear graphite have been computed so far, e.g. [1, 2]. Experimental studies on the leaching of ^{14}C from different graphite types (e.g. moderators, reflectors, carbon bricks etc.) by a number of organisations have resulted in a large amount of information. However, the data from different studies are often difficult to compare, as their experimental methodologies utilise application of different leachate composition, or do not clearly specify temperature or redox conditions in leaching test. Thus, an analysis of existing data and leaching methodologies is required to understand the key experimental factors that influence the release of ^{14}C from irradiated graphites and to identify the unified experimental approach for further studies; this will allow a more straightforward comparison of ^{14}C leaching behaviour. By minimising differences between experimental approaches, we intend to build confidence in applying experimental results for the development of models for ^{14}C release from different irradiated nuclear graphite types, as well as for ^{14}C transport in the long-term.

In this review we summarize and critically assess the experimental conditions frequently used for leaching studies on irradiated graphite and their possible influence on reported results. Given that leaching of ^{14}C can be the rate limiting factor for the ^{14}C transport, we describe the parameters that are important to consider in experimental studies for further mechanisms of ^{14}C mass transfer to be built upon.

2 Earlier leaching studies

From 1980’s until now, multiple leaching studies on irradiated nuclear graphite have been carried out internationally [7]. The majority of the studies have investigated release into aqueous solution. As many countries have independently investigated their own graphite, a large variety of different graphite samples have been subjected to leaching experiments (see Table 1). Besides the types of irradiated nuclear graphite, experimental conditions were often varied; usually the experimental conditions in such studies are chosen according to the corresponding national waste management programme. Thus, many different conditions were studied, making comparison of results between studies difficult, e.g.. the temperature of experimentsranged from 20 to 90°C. furthermore, in some experiments, leaching was at ‘ambient laboratory temperature’, which may change over the year and which was not specified. Attempting to simulate different scenarios of long-term storage and disposal, leaching was studied in different media, e.g. distilled water, simulated industrial leachates or groundwater solutions, $H_2SO_4/KMnO_4$, $Ca(OH)_2$ and NaOH solution. Consequently the pH of leachates ranged between 7.2 and 13. The graphite sample was usually of different particle size also, ranging from large graphite pieces to powder and the with amount varying from 0.5 to 700 g. In some studies, the gaseous atmosphere over the leachate was not always controlled or analysed; this atmosphere may be important to ^{14}C leach rates. Last but not least, the kinetics of the release was studied over different time intervals, from 15 to 720 days; given the slow release kinetics of the leaching process at the water-graphite interface, equilibrium in some cases might not be reached.

The various experimental conditions listed in Table 1 indicate no common methodology across the performed experiments, leading to results that are difficult to compare and poor data systematization, especially when compared to standard leach test methodologies [8,9,10,11,12,13,14]. Our review of available standard procedures, i.e. IAEA, ANS 16.1 and ISO [8-10] revealed that some common parameters, like temperature range or leachate composition, are formulated differently as well (see Table 2 in §2.1).

Table 1. Summary of recent leaching studies on irradiated nuclear graphite [7]

Graphite origin	**Technology[1]**	**Duration**	**Leachate, T [°C]**	**Gaseous phase**	**Graphite form**	**Speciation**	**Cumulative ^{14}C release**	**Ref.**
CEGB	Magnox	100 days	Simulated groundwater, 25°C	Unknown	Solid	Not studied	2-steps release, 0.14%	[15]
CEGB	Magnox	100 days	Demineralised water, 20-23°C	Unknown	Solid	Not studied	2 steps release, 0.088%	[15]
Hanford moderator	LWGR[2]	56 days	Water, simulated ground water, 25/50/90 °C	Hermetic vessel, air atm.	Solid (40 g)	Not studied	From 0.004 to 0.050 %	[16]
G2 moderator	UNGG	90 days	Water, 20°C	Hermetic vessel, air atm.	Solid (40 g)	Not studied	From 0.26 to 0.85 %	[17]

---

[1] UNGG : Natural Uranium Graphite Gas reactor, i.e. fueled with natural uranium metal and cooled with CO_2

[2] LWGR : Light-Water-cooled Graphite-moderated Reactor

G2 moderator	UNGG	90 days	UP[3] Water, 20°C	Hermetic vessel, air atm.	Solid (~630 g)	Not studied	≤0.003%	[18]
G2 moderator	UNGG	455 days	UP Water, 20°C	Hermetic vessel, inert gas purge (Ar, N_2)	Solid (~90 g)	Not studied	< 0.05%	[18]
G2 moderator	UNGG	455 days	Lime water, 20°C	Hermetic vessel, inert gas purge (Ar, N_2)	Solid (~90 g)	Not studied	≤0.07%	[18]
Bugey moderator	UNGG	181 days	UP Water, 20°C	Hermetic vessel	Powder (~2 g)	Not studied	<0.1%	[18]
Bugey moderator	UNGG	455 days	UP Water, 20°C	Hermetic vessel, inert gas purge (Ar, N_2)	Solid (~10 g)	Not studied	<0.01%	[18]
Bugey moderator	UNGG	144 days	UP Water, 40 °C	Hermetic vessel, inert gas purge (Ar, N_2)	Solid (~10 g)	Not studied	≤0.034%	[18]
Bugey moderator	UNGG	455 days	Lime water, 20°C	Hermetic vessel, inert gas purge (Ar, N_2)	Solid (~10 g)	Not studied	<0.005%	[18]
SLA2 sleeve	UNGG	455 days	Industrial water pH=7.2	Hermetic vessel, air atm.	Solid (<10 g)	Not studied	≤6.3%	[18]
BEPO moderator	Air cooled pile	190 days	0.01 M NaOH, pH=13, RT[4]	Air atm.	Both solid & powder (0.5 g)	Not studied	≤4.6% of ^{14}C released	[19]

---

[3] Ultra-pure water;

[4] Room temperature

Wylfa moderator	Magnox	190 days	0.01 M NaOH, pH=13, RT	Air atm.	Granulated samples (0.5g)	Not studied	Up to 2.5% of ^{14}C released	[19]
Vandellos I sleeve	UNGG	~380 days	Distilled water, 40°C	Hermetic vessel; partial nitrogen flushing	Solid (~700 g)	Almost no ^{14}C gaseous species detected	Up to 0.11% of ^{14}C released	[20]
Tokai I moderator	Magnox	720 days	Alkaline& H_2SO_4/ $KMnO_4$ solution, T unknown	Unknown	unknown	Not studied	~0.005%	[21]

3 Standardized leaching methods

A number of standard leaching tests have been developed internationally, aiming at a unified leaching approach for solid specimens in order to enable a comparison, exchange and discussion of the results obtained in different laboratories. These methods were developed mainly for immobilized radioactive solid specimens, like glass, without particular consideration of inventory and speciation in the gas phase. Given the specific properties of irradiated nuclear graphite, i.e. a fractional release of ^{14}C into gaseous phase, direct application of this methodology will not be correct. Instead, these techniques were reviewed in the current study, and used as a base for developing a unified leaching method for irradiated nuclear graphite, allowing sampling and comprehensive examination of liquid and gaseous phase. Briefly, these standard methods are summarized in Table 2.

3.1 *IAEA leaching methodology*

The first standard leaching methodology, used by many laboratories worldwide, was proposed by the IAEA [8, 22]. According to IAEA, the test has to be carried out on static conditions in a container, which is chemically inert stable under irradiation and would not sorb ions of interest. A sample of a specific activity greater than 37 GBq/L (1Ci/L) was recommended to have fixed dimensions: diameter = height ≤ 2.5 cm; for samples of lower specific activity, dimensions should be as following: diameter=height=5 cm. A container size should allow the sample upper surface to be covered by at least 5 cm of leaching solution and the ratio of leaching solution to exposed surface area of the sample shall be <10 cm. Demineralized water is identified as a standard leachate media. Strict requirements are also given to the sample preparation. In case of bituminised specimens and other waste forms, only the upper circular surface should be in contact with the liquid phase during the leaching test; the rest is to be covered by a non-permeable film. The leaching test is performed at 25±5 °C with the complete replacement of the leach solution (demineralized water) on the following timescale: daily for the 1st week, weekly the following 8 weeks, monthly the next 6 months, and thereafter twice a year. The method aims at quantification of released radionuclides, whereas speciation of radionuclides was not addressed at all. Examination of the gas phase composition during the leaching test is not considered.

3.2 *ISO methodology*

Further initiatives were undertaken by the International Standards Organization (ISO 6961 [9]) and by the American Nuclear Society (ANSI/ANS 16.1 [10]). The ISO long-term test evaluates the resistance to leaching of different materials, like glass, glass-ceramic, bitumen, concrete, cement, polymers. A representative specimen shall be prepared in the laboratory, simulating an average composition of radioactive waste for certain solidification process. The sampling of real wastes is done by drilling of solidified waste form (core drilled). In contrast to IAEA, these methods do not specify the minimum required activity of the sample. The glass, glass-ceramic or ceramic specimens shall have a cut, non-polished surface, of $5\cdot10^{-3}$ to $1\cdot10^{-4}$ m^2. The methodology requires specific length to diameter ratio of cylindrical sample (preferred shape) ranging from 0.2 to 5 cm. The cement or concrete specimens cured at relative humidity of 65±5% and temperature of 25±5°C, shall have a surface, polished with sandpaper, of $5\cdot10^{-1}$ to $1\cdot10^{-3}$ m^2 (diameter/height $\approx$ 1). The bitumen and plastic samples are prepared by core-drilling or by cutting from larger sample with a surface area of $5\cdot10^{-1}$ to $1\cdot10^{-3}$ m^2 (diameter/height $\approx$ 1). A vessel for leaching is constituted of inert material toward the leachate, the specimen or radionuclides. The leaching solution can be deionised water with maximum conductivity of 150 μS/m, synthesized sea water or disposal site groundwater. Stirring is not considered. The ratio of leachate volume to surface area of specimen is kept in the range 0.1÷0.2 ± 0.02 m. During the test, the vessel remains closed to avoid vaporization. In order to minimize the change in leaching solution composition and to reach a measurable concentration of the radionuclide, the ratio of leaching solution volume to the sample surface is recommended to keep fixed around 10±0.2 cm. The standard temperature is accepted to vary between 17.5 and 27.5°C. Higher temperatures conditions may be optionally tested using an autoclave. Similar to IAEA methodology, no speciation of radionuclides in aqueous or gaseous phase shall be performed by ISO approach.

3.3 *ANS methodology*

According to this methodology, the concentration of all radionuclides shall be monitored both in the initial sample and in the final leachate solution. The pH of leaching solution and of blank leachate is controlled after the sample removal. Chemical composition of the base material (conditioning matrix), waste and additives type and content shall be reported. The geometric parameters of the specimen are not fixed, but shall be determined before and after the leaching, as well as density and weight.

Before the leaching test, a solid specimen shall be rinsed in a volume of demineralised water equal to the leaching volume, for 30 seconds, in order to remove any labile radionuclides, physisorbed or chemisorbed on the surface. The same procedure has to be applied to the leaching container. Both rinses shall be combined and the amount (i.e. activity, a_i^r) of i-species has to be determined by one of the state-of-the-art analytical method. One has to keep in mind that the ANS standard method aims at the quantification of diffusivity of radionuclides in the waste-form. An instantly released fraction of radionuclides, weakly bounded to the surface, may confuse the description of the radionuclide diffusion in the solid bulk. To account for this, the amount of radionuclide in the rinse has to be referred to as the background concentration of i-species in the leachate. The total activity of a radionuclide in the specimen at the beginning of the test, A^i_0, is defined as a difference between the total activity of *i*-species in the as-prepared sample, A^i_p, and the activity in the rinse, a_i^r. If applicable, the values have to be corrected for radioactive decay and reported to a reference time (i.e. the beginning of the leaching test):

$$A^i_0=A^i_p - a_i^r \qquad \text{Eq. (1)}$$

At the end of each leaching step, a representative aliquot of leachate shall be taken to determine the amount of *i*-species in the leaching solution, a^i_n. It is calculated as following:

$$a^i_n = a^i(t_n)-a^i(t_{n-1}) \qquad \text{Eq. (2)}$$

where $a^i(t_n)$ and $a^i(t_{n-1})$ are respective amount of *i*-species in the leaching solution at the end of the *n*- and previous *(n-1)*-step.

The acquired data are evaluated to yield corresponding parameters:

- Incremental fraction leached (a^i_n/A^i_0);
- Incremental leaching rate [$(a^i_n/A^i_0)/\Delta t_n$];
- Cumulative fraction leached $\sum a^i_n/A^i_0$.

Here a^i_n is the activity of an *i*-species released during the leaching period Δt_n, adjusted for the radioactive decay, to the reference time;

$\sum a^i_n$ is the cumulative activity of a *i*-species found in the leachate during the entire leaching test;

$\sum\Delta t_n = t_n - t_0$ is the cumulative leaching time; and

$\Delta t_n = t_n - t_{n-1}$ is the duration of the *n*-th leaching period.

ANS 16.1 standard test foresees partial leaching solution replacement at strictly specified time frames. As well as ISO 6961, ANSI/ANS 16.1 recommends the similar following frequency of the leachate during this leaching test:

- At the early stage: 2, 7, 24, 48, 72, 96, 120 hours;
- twice per week for the second week;
- Once a week for the third, fourth, fifth and sixth week, e.g. 14, 28, 43 and 90 days;
- Thereafter: monthly.

Any change in sampling frequency shall be recorded. The duration of the leaching test shall be at least 6 months at 40°C, and can be terminated when the leaching rate becomes approximately constant.

The leaching rates observed are often controlled by diffusion of radionuclide in the bulk material. In the approximation of a semi-infinite medium (less than 20% of leachable species), the effective diffusivity D_i is calculated as follows:

$$D_i = \pi \left[\frac{a^i{}_n / A^i{}_0}{\Delta t_n}\right]^2 \cdot \left[\frac{V}{S}\right]^2 T \qquad \text{Eq. (3)}$$

Here: V - is the volume of the specimen, cm^3; S - is the surface area of the specimen, cm^2; T - is the mean time of the leaching interval, s.

$$T = \left[\frac{1}{2}\left(t_n{}^{1/2} + t_{n-1}{}^{1/2}\right)\right]^2 \qquad \text{Eq. (4)}$$

If more than 20% has been leached, D_i is calculated from the experimental data as follows:

$$D_i = \frac{G \cdot d^2}{t} \qquad \text{Eq. (5)}$$

Here G - is a dimensionless time factor tabulated as a function of the cumulative fraction leached; d - is a diameter of cylinder, cm; t - is the duration of an entire leaching experiment, s. According to ANS standard leaching method, an appropriate G value is selected from Table A1 of [10] that corresponds to the calculated leaching fraction and length-to-diameter ratio of the specimen.

Alternatively, a graphical method can be applied for comparison of D_{i} calculated for several geometries. The graphs give cumulative fraction leached, $\sum a^{i}_{n}/A^{i}_{0}$, versus a dimensionless time factor Z, showing lines at different l/d, where l and d are dimensions of a length of the cylindrical specimen:

$$\mathbf{Z} = \left[\mathbf{D}_{\mathrm{i}}\left(\frac{\mathbf{S}}{\mathbf{V}}\right)^{\mathbf{2}}\right]^{\mathbf{1/2}} \qquad \text{Eq. (6)}$$

The standard ANS 16.1 [10] provides the information on G for evaluating the effective diffusivity at known geometries and at cumulative fraction leached of more than 20% in form of tables. The results obtained by this standard are expressed by a parameter of leachability of each leached species, called the *Leachability Index*, L. For an i-species parameter L can be defined as follows:

$$L_i = \frac{1}{n}\sum_{1}^{n}\left[\log\left(\frac{\beta}{D_i}\right)\right] \qquad \text{Eq. (7)}$$

where β is constant = 1.0 $\mathrm{cm^2/s}$, D_i is the effective diffusivity of i-species, calculated according to Eq. (3), n – is a number of leaching intervals considered. Typically, the average value of L_i, shall be derived from the ten independent measurements, however using of the first seven leaching intervals can be also appropriate.

The uncertainty of the L_i is defined as follows:

$$C = L_i \pm 1.51 \cdot \sigma_L \qquad \text{Eq. (8)}$$

where C is the 99.9% confidence range of L_i, dimensionless, and σ_L is the standard deviation of the ten L_n values:

$$\sigma_L = \frac{1}{3}\left[\sum_{1}^{10}\left(L_n - L_i\right)^2\right]^{1/2} \qquad \text{Eq. (9)}$$

The accuracy of L_i value has to be reported to one decimal point only.

The United States Nuclear Regulatory Commission recommends that the L_i should be greater than 6 in order to meet the requirement during qualification process for radioactive waste conditioning [23].

Besides that, a detailed description of the analytical method of measurement, along with uncertainty estimation is needed. The results are expressed for every species as incremental leaching rates:

$$R^i{}_n = \frac{a^i{}_n}{A^i{}_o \times S_A \times t_n} \qquad \text{Eq. (10)}$$

where $R^i{}_n$ is the incremental leaching rate for i-species, in kg·m^{-2}·s^{-1}; $a^i{}_n$ is the radioactivity or the amount (in kilograms) of i-leachant found in the solution after each leaching interval n; $A^i{}_0$ is the specific radioactivity or concentration of the i-species in weight fraction, initially present in the specimen; S_A is the exposed surface of the specimen, in m^2; t_n is the duration of n-th leaching period, in s; optionally $A^i{}_0$ and $a^i{}_0$ shall be corrected for the radionuclide decay.

The advantage of this standard procedure is in the detailed description of data evaluation and definition of parameters to be used for further waste classification by waste management organization. However, it does not provide an information on the form of ^{14}C release neither in the aqueous phase nor in the gas phase; this information is important to understand the mechanism of ^{14}C release.

3.4 *ASTM methodology*

Another standard method for determining leaching behaviour of waste-forms has been developed by the ASTM (American Society for Testing Materials), named “Standard Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Waste” (designated as C 1220-92) [11]. This test is applied for leaching of simulated and radioactive monolithic waste forms as glasses, ceramic or cements with surface area to volume ratio within 0.5 to 10 m^{-1}, at temperature of 40, 70 and 90°C. In this test, three leaching solutions relevant to geologic repository conditions are indicated: high purity water, silicate/bicarbonate and brine solutions. Polytetrafluoroethylene (PTFE) vessels are used if the integrated dose from the sample does not exceed 100 Gy [24]. At higher doses, degradation of the PTFE may occur, therefore a stainless steel or fused silica vessel shall be used. The sample support shall be constructed of the same material as the vessel and cleaned to reduce any chemical release. The test is conducted on triplicate specimens and on two blank leachates as a control. Various analytical techniques can be used to quantify the released *i*-species the leaching solutions, such as ICP-MS, atomic absorption, emission spectroscopy and neutron activation analysis. The detection limits for each analysis must be defined. ASTM does not require confined sampling intervals, however recommends to account for the release kinetics on a short- (28 days) and long-term (beyond 364 days).

ASTM methodology recommends the evaluation of the normalized elemental mass loss released from the specimen, in g/m^2, which can be calculated using eq. (11) given in [11]:

$$(NL)_i = \frac{m_i}{f_i \cdot S} \qquad \text{Eq. (11)}$$

where m_i is a mass of the *i*-species in the filtered leachate; f_i is a dimensionless mass fraction of the *i*-species in the specimen before leaching; and S is the specimen surface area, m^2.

In case of radioactive specimens, the evaluation of normalised mass loss $(NL)_i$ from the activity measurements is:

$$(NL)_i = \frac{a^i}{a_0^i} \cdot W_0 \cdot \frac{1}{S} \qquad \text{Eq. (12)}$$

where a^i is a total activity of the *i*-isotope in the filtered leachate, in Bq; a^i_0 is the initial total activity of the *i*-isotope in the specimen, Bq; W_0 is the initial original mass of the specimen, g.

In contrast to other standard methods, ASTM methodology provides a rather simple description of leaching tests, which may be practical for quick industrial tests on wasteform stability. The method foresees derivation of conditional released fraction, which is rather sensitive to the different parameter changes, like *T* or *pH*. It becomes critical for redox-sensitive materials or highly hydrolysed species. Additionally, the method does not imply any speciation studies of radionuclides in released fraction; hence no conclusions about released mechanisms can be drawn. Thus, this method is considered to be inconclusive and inappropriate for leaching studies in frames of CAST project.

Table 2. The standards requirements in Europe and USA

Parameter	ISO 6961-1982	ANSI/ANS-16.1-2003	IAEA (proposal, 1971)
Leaching solution	• Deionized water • Synthetized sea-water • Disposal site groundwater	Demineralized water	Demineralized water
T, °C	40, 70, 90	17.5-27.5	25±5
Vessel	• Polytetrafluoroethylene • Polymethylpentene • Polypropylene	• “Unreactive” material • Excessive evaporation of the leachate is prevented	“Unreactive” material
Specimen geometry	• Cylinder • Cube	• Cylinder – recommended ($h/D=0.2 \div 5$) • Parallelepiped ($\frac{Lenth}{Min. thickness} = 0.2$ to 5) • Sphere • Min. size ≥ 1 cm	Cylinder: • 5 cm x 5 cm (A ≤ 1 Ci/L) • Down to 2.5 cm x 2.5 cm (A ≥ 1 Ci/L)
$V_{leachant}/S_{specimen}$	0.10÷0.20 m	0.10±0.02 m	≤ 0.10 m
Sampling	• 1, 3, 7 days • 2nd week – twice a week • 3rd-6th weeks – once a week • Thereafter - monthly	• 1st day – 2, 7, 24 hours • 2-5 days – every 24 hours • Thereafter – in 14, 28 and 43 days	• 1st week – daily • 2nd– 8th weeks – weekly • Next 6 months – monthly • Twice per year

Parameter	ISO 6961-1982	ANSI/ANS-16.1-2003	IAEA (proposal, 1971)
Test duration	Until the leaching rate becomes virtually constant, but not less than 6 months.	90 days	As long as considered necessary or until leaching rate becomes virtually constant; or if pH of the leachate rises above 8.0.

4 Discussion

Based on these standard methodologies, in the current study we have identified the parameters and conditions that are important to keep constant in leaching experiments, in order to enable a comparative analysis of information on ^{14}C leaching behaviour obtained in different laboratories.

1. Sample geometry and pre-leaching specimen characterisation;
2. Leaching solution type(-s);
3. Temperature;
4. Gas phase composition and analysis;
5. Leaching kinetics (duration);
6. Leaching scheme: dynamic or semi-dynamic; sampling schedule;
7. Leach test vessel;
8. Post-leaching characterization: composition and structural analysis.

Detailed discussions of these parameters is given in following sub-sections.

4.1 *Sample geometry and pre-leaching specimen characterization*

Both intact blocks and powdered samples have been used for leaching tests. Powdered graphite typically has higher specific surface, which facilitates leaching, and in some cases it may be more relevant to the graphite geometry under disposal conditions. In contrast, a block sample is easier to standardize and handle. Besides that, crushing may result in partial release of ^{14}C, entailing underestimation of total released fraction of ^{14}C.

Before starting the leaching experiment, it is recommended to control the following parameters of specimen:

- Initial specimen mass;
- Geometry of specimen, i.e. S/V ratio;
- Specimen density, porosity, microstructure and grain size;
    - For powder samples: particles size distribution, specific surface area; using the fraction with well-known particle size to estimate S/V ratio;

    - For embedded samples: specimen to waste form ratio, composition of the waste form (silicate, polymeric, cement, etc.);
- Total specific activity of ^{14}C;

It is necessary to make sure that specific activity of ^{14}C in the specimen is determined accurately. In case of irradiated graphite, uneven distribution of ^{14}C (so-called hot-spots) can be observed. Therefore, special care has to be taken while determining an initial activity distribution of ^{14}C by analyzing several samples. A total incineration method followed by $^{14}CO_2$ entrapment with 1M NaOH and LSC measurement can be used for determination of ^{14}C inventory.

4.2 *Leaching solution*

Typically, distilled water (MQ), alkali and brine solutions are used as leaching solutions. In the case of simulation of long-term geological disposal of graphite in concrete, alkali solutions are more representative for real disposal conditions. Application of complex solutions, like simulated groundwater [25] might be accompanied by reaction of precipitation. Strictly speaking, the leaching solution composition is specific to every country and disposal site. The more complex the composition of the leachate, the more complicated chemical changes may take place under irradiation, and the more difficult the interpretation of results will become. Therefore, consistent with the standard methodologies [9-12], it seems reasonable to use simplified leachates, like NaOH solution with pH 13, in the model experiments. In case of leaching studies in a simulating groundwater, like granite-bentonitic water [25], the contribution of other components, like Ca^{2+} or Mg^{2+}, to ^{14}C aqueous speciation has to be assessed as well. Typical composition of a simulated groundwater is given as an example in Table 3.

The effect of background electrolyte can be estimated by carrying out a reference leaching experiment in an inert electrolyte, like 0.1 M $NaClO_4$. This electrolyte does not influence any aqueous complexation or redox processes and is used as a standard background electrolyte in most uptake studies [26]. Although this media is not representative to any of real system, it will help to conform conditions from many laboratories to the single comparable system and enable better interpretation of the release mechanism of ^{14}C.

It should be also kept in mind that irradiation-induced processes may occur in aqueous solution due to the radiation field coming from the irradiated graphite. The radiolysis of aqueous solution may cause occurrence of additional molecular and radical species, oxidizing and reducing entities. This, in turn, may change the redox conditions at the later stage of leaching experiment. Therefore, the more simple the leachate composition, the fewer the range of radiolytic products that will occur in the leachate, and hence the less complicated will be the interpretation of experimental results.

Table 3. Composition of the reference Bentonite pore water at 25°C [25].

Component	Total concentration, mol/L
Na^+	$2.738 \cdot 10^{-1}$
K^+	$1.56 \cdot 10^{-3}$
Mg^{2+}	$7.642 \cdot 10^{-3}$
Ca^{2+}	$13.22 \cdot 10^{-3}$
Sr^{2+}	$1.90 \cdot 10^{-5}$
Fe^{2+}	$4.33 \cdot 10^{-5}$
Mn^{2+}	$2.43 \cdot 10^{-5}$
Al^{3+}	$1.91 \cdot 10^{-8}$
Cl^-	$1.6608 \cdot 10^{-1}$
F^-	$1.67 \cdot 10^{-4}$
Br^-	$2.4 \cdot 10^{-4}$
CO_3^{2-}	$2.833 \cdot 10^{-3}$
SO_4^{2-}	$6.163 \cdot 10^{-2}$
$H_2SiO_4^{2-}$	$1.80 \cdot 10^{-4}$
Charge balance	$2.1529 \cdot 10^{-2}$
pH	7.25
Eh	-193.6 mV
Ionic strength, M	0.323

4.3 Temperature

The effect of temperature on fractional release of ^{14}C into the gas phase has been demonstrated with an intact sample of Oldbury Magnox graphite (Fig. 1 and Fig.2a). This behaviour is observed under anaerobic conditions at 50°C and room temperature [27]. The fractional release over the first month is almost doubled compared to the same experiment at room temperature. However, there was a notable decrease in the ^{14}C release rate during the last two months of the experiment. After three months the fractional release of ^{14}C to the gas phase was about $3.6 \cdot 10^{-6}$. The ratio of ^{14}CO to volatile organic compounds was determined to be 0.5 over all sampling periods, similar to the experiment on room temperature. The amount of $^{14}CO_2$ in the gas phase at 50°C was higher than at room temperature, but still contributed only with a small fraction (~4%) to the ^{14}C release, presumably due to its retention in the solution at high pH.

Although some standard techniques require the temperature in leaching test to be kept at 20°C in order to validate theoretical calculation on graphite behaviour, the actual temperature in storage facility may locally reach 50°C. As shown in Fig. 1, the release can be facilitated at higher temperature, which improves the uncertainty of radioanalytical determination of ^{14}C. By comparison, the data on ^{14}C release rate acquired at room temperature are more scattered [16, 17]. This brings us to conclude that temperature control is necessary at room temperature, and it might be reasonable to establish room temperature to be at 25±5°C as a standard temperature [8]. Optionally, other temperature conditions relevant to a specific repository site can be tested.

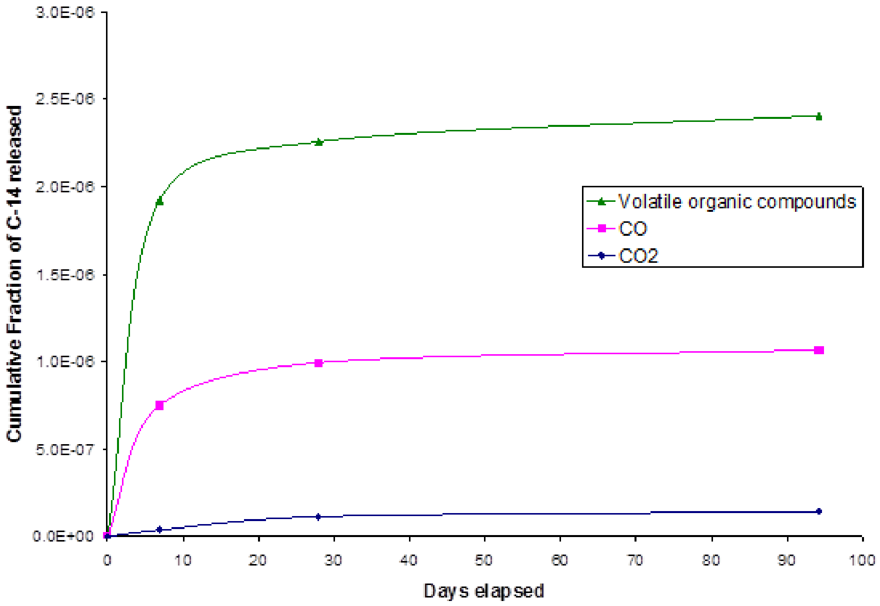

Figure 1. Fractional release of gaseous ^{14}C from leaching of irradiated Oldbury graphite at pH 13 at 50°C under anaerobic conditions [27].

4.4 *Aerobic vs. anaerobic conditions*

Some earlier studies demonstrated that not only solution type and temperature, but also gas atmosphere in contact with leaching solution, affects the ^{14}C leaching rate and speciation in the solution. Baston et al. [27] compared the release of ^{14}C into the gas-phase during the leaching of an intact sample of Oldbury Magnox graphite at ambient temperature under aerobic atmosphere with the equivalent experiment under anaerobic conditions (see Fig. 2a and b). The ratio of ^{14}C-organic compounds to ^{14}CO under anaerobic conditions was about 2, whereas under aerobic conditions it decreased to 1. A remarkably low fraction of gaseous $^{14}CO_2$ was detected in both cases, indicating a probable retention of $^{14}CO_2$ as carbonate in the leaching solution. As carbon is a redox sensitive element, an influence of ambient atmosphere on graphite corrosion and respectively on the behaviour of released species on the water-graphite interface has to be considered. Relevant to the underground repository conditions, anaerobic conditions are recommended for leaching tests as standard. Experimentally this can be achieved by filling the void in the reactor vessel with inert gas (e.g. pure Ar or N_2). Optionally, an effect of the oxygen ingress can be tested on aerobic conditions in parallel, by filling the void in the reactor simply by air.

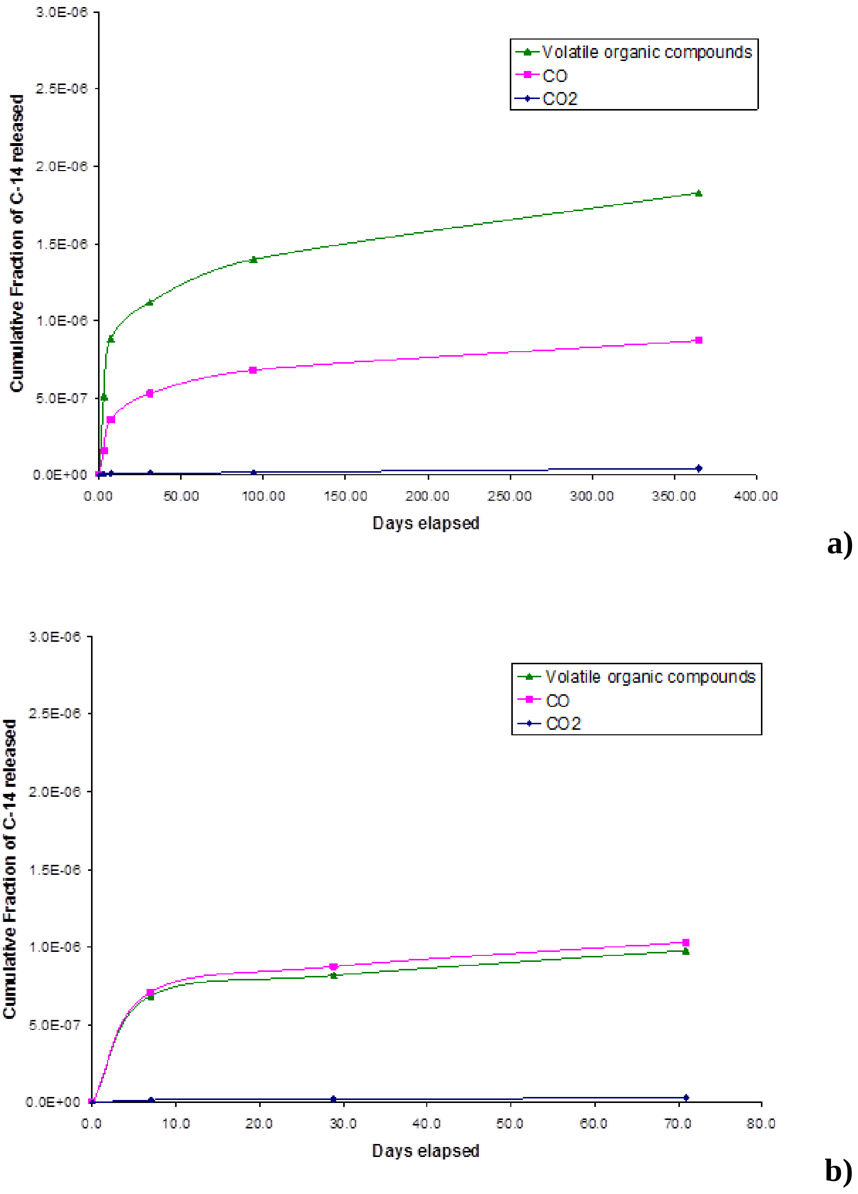

Figure 2. Fractional release of gaseous ^{14}C from leaching of irradiated Oldbury graphite at pH 13 and ambient room temperature under anaerobic (a) and oxic (b) conditions [27].

4.5 Release kinetics

From the kinetic curves given in Fig. 2, the decrease of the release rate with time can be recognized, however the curves never reached a plateau. This indicates at least two kinetically different processes controlling ^{14}C release. First – fast ^{14}C release, which occurs within 10-25 days and corresponds to the release of ^{14}C from the graphite surface. After the surface is depleted in ^{14}C, the slower process of ^{14}C diffusion in graphite subsequently controls the release.

This example demonstrates that the duration of leaching experiments is an important parameter to specify, as the equilibrium in ^{14}C distribution between graphite and leachate might not be reached within an experiment. Thus, the leaching should be long enough to get complete information about radionuclide release. Given that the time required for reaching the equilibrium might take unexpectedly long, experiments shall be carried out, at least, until the establishment of steady-state release rate for ^{14}C. We recommend, therefore, controlling the release in following regime:

- Short-term release up to 25 days: frequent sampling, e.g. daily or weekly;
- Long-term release beyond 25 days: monthly sampling during 1 – 1.5 year [9].

4.6 Sampling

The sampling scheduled for gas and aqueous phases can be adopted from one of above mentioned standard methods. This is particularly important if measured amount of ^{14}C is below detection limit and detection limit is used as a maximum value.

Sampling of a leaching solution can be carried out with complete (1) or partial (2) replacement. The first approach is more frequently used in leaching studies, however low rates of ^{14}C release may result in low concentrations of ^{14}C that are difficult to quantify. Another approach (2) could be more favourable, as concentration of ^{14}C in solution is expected to increase with time, which will correspondingly minimize the measurement uncertainties. Additionally, partial renew of the leachate is considered to be more representative to storage condition with slow water infiltration. The choice of the sampling conditions may significantly depend on the expected leaching rate.

Special attention has to be paid to solution sampling when a powder specimen is tested, to prevent acquisition of solid particles. In this case, the stirring has to be terminated in advance of the sampling, or, alternatively, separation of a sample powder from the solution can be performed by filtration or centrifugation. While using filtration the cross-contamination of filtrate with organic residues from the filter material should be excluded.

Analysis of the gaseous phase is important, as the release of volatile species may occur during the leaching of graphite. In previous studies, it was demonstrated that a significant amount of ^{14}C was released in form of CO_2, CO and volatile organic compounds [27, 28]. Furthermore, distribution of these volatile species between liquid and gaseous phase may differ with redox, *pH* and *T* conditions. In order to get the best understanding of leaching mechanisms, sampling and examination of the gas phase should be performed periodically on the same timescale as with sampling of the solution. Gas sampling has to be done in a dynamic scheme by collecting the entire volume on every leaching step. Analysis of ^{14}C concentration and speciation can be performed using a washing-bottle setup; Hague 7000 is represented in Fig. 4. Alternatively, gas chromatography coupled to mass spectrometry (GC-MS) can be used for more precise measurement. Replicated measurements, i.e. 3 to 4 times, are recommended for the demonstration of data reproducibility.

4.7 *Leach test vessel*

The experimental setup for leaching experiment must enable the control of parameters specified in § 6.Therefore the following recommendations for the setups can be given:

- Gas-tight reactor vessel suitable for the graphite sample (powder or massive specimen) made of an inert and radiation resistant material. For example, Pyrex glass can be recommended for the experiments at room temperature; for elevated temperatures reactors with cross-linked teflon (PTFE) or Polyether ether ketone (PEEK) insert can be used (Fig. 3); using an ordinary teflon is not recommended due to the fast radiation-induced degradation [24,29];

- Metallic tools should be excluded during the sampling of solution in order to avoid adsorption of radionuclides on the surface;
- The sample shall be completely immersed in leachate to provide a contact of all surfaces with the solution; application of net sample holder, made of inert material, e.g. PEEK, inside the leaching vessel shall be considered;
- Stirring the solution in order to facilitate the mass transfer on the graphite-solution interface;
- Long-term experiments (up to 1.5 years) with T and P control;
- The sampling of gas and liquid samples shall be possible in order to analyse the ^{14}C speciation in released fractions;
- At the beginning of the experiment the void in the reactor has to be filled with the corresponding gas, defining redox conditions (Ar or N_2 – for anaerobic conditions, air – for aerobic conditions), and sealed for entire experiment.

As an example, Figs. 3 and 4 represent corresponding typical setups that can be used for leaching studies, i.e. reactor Berghof and bubbler Hague 7000. Such reactors are rather compact, which is suitable for batch studies. Besides enabled temperature and pressure control, such reactor vessel allows sampling of both liquid and gaseous phases for speciation analysis.

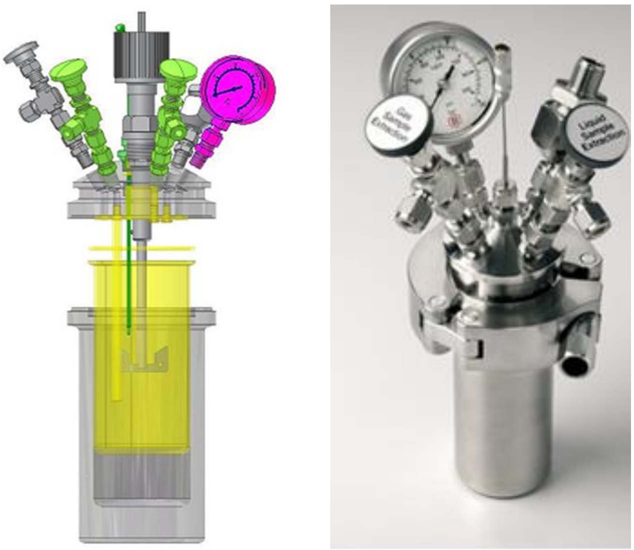

Figure 3. An example of experimental reactor/vessel (reactor Berghof) for leaching test developed for gas and liquid sampling [30].

The system Hague 7000 in Fig. 4 enables evaluation of the ^{14}C-speciation in the gas phase.

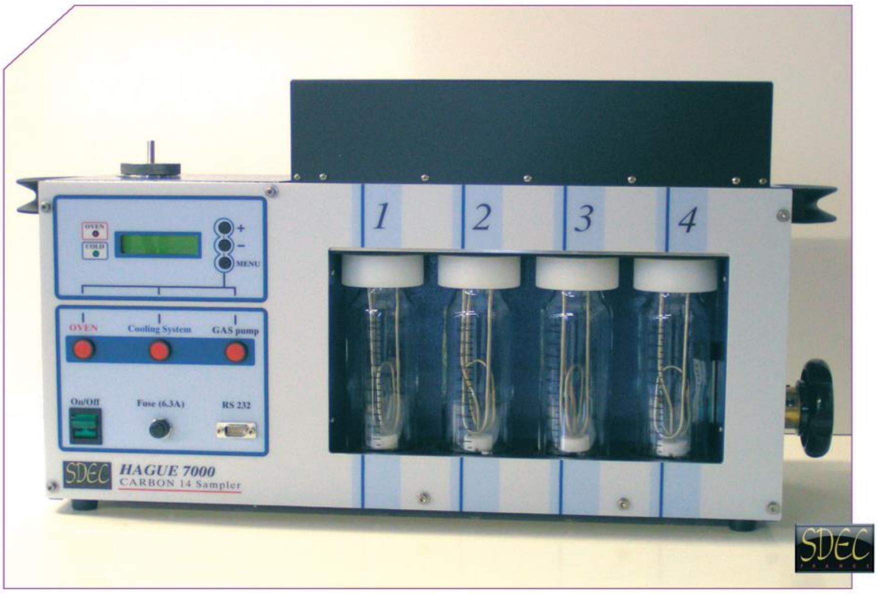

Figure 4. Experimental setup bubbler HAGUE 7000 for speciation studies of ^{14}C in gaseous phase [31].

4.8 *Pre- and post-leaching analytical approach*

Solid sample

Samples should have a geometry that allows a simple determination of the volume and surface area (cylinder, cube). The information about the density will allow calculation of the overall sample porosity, whereas the surface area can be determined using the Brunauer-Emmett-Teller equation (BET). For powder samples it is important to estimate S/V ratio. For that, the fractionation and separation of the fraction with well-known particle size can be performed before bringing the sample in the contact with leachate. Therefore, homogenization process, fraction separation followed by determination of particle size distribution (granulometry) before the leaching test is necessary. Granulometry is also recommended as post-leaching examination in order to estimate the degree of powder agitation during leaching test. Microstructure analysis is recommended before and after the leaching test, in order to assess morphological changes in the specimen.

The initial and final ^{14}C content in the specimen must be determined respectively before and after the leaching test by total combustion method [32]. Liquid scintillation counting (LSC) and sequential absorption with catalytic oxidation can be used respectively for ^{14}C quantification and speciation. Gamma-spectrometric measurements of the graphite samples before and after the leaching test can be performed with use of HPGe detector in order to get additional information on γ-emitting radionuclides.

Leachate

The analysis of a leachate might require samples to be prepared in a manner that eliminates beta-emitters, which might interfere with analytical determination of ^{14}C. The total activity of ^{14}C in leachate can be measured by LSC. The speciation of carbon (i.e. organic and inorganic fractions) can be analysed by TIC/TOC method and in more details by high performance liquid chromatography (HPLC) coupled to mass-spectroscopy (MS).

Gas sample

Any gaseous fraction shall be sampled along with the leachate and analysed by means of sequential washing-bottle setup (Fig. 4) or GC-MS. Due to the low release rates of ^{14}C, a development of more sensitive detection method or concentration procedure for the gas analyses might be necessary.

4.9 *Evaluation of the result*

Leaching can be quantified as follows: (1) the cumulative released fraction (F_n) that correlates with the total leached amount of a certain component over the leaching time (t), and (2) the leaching rate (R_n). These parameters can be derived using Eq. (13) and Eq. (14) respectively:

$$F_n = \frac{\sum a_n}{a_0}, \qquad \text{Eq. (13)}$$

$$R_n = \frac{a_n \cdot V}{a_o \cdot S \cdot t_n} = K \cdot \frac{a_n}{t_n}, \qquad \text{Eq. (14)}$$

where:

F_n - is a dimensionless cumulative leaching fraction in the *n*-step of the assay,

R_n - is a leaching rate in the *n*-step of the assay, in cm/day,

a_o – the initial amount of the component in the assay specimen, in Bq or mg,

a_n - is an amount of a component that has left the assay specimen to the leachate in the *n*-step, in Bq or mg,

t_n – is a duration of the *n*-step of the assay, in days,

V – is a specimen volume, in cm^3,

S - is an apparent or geometrical specimen surface, in cm^2,

K - is a characteristic assay constant, in cm/Bq.

In case of the slow leaching rate or low content of ^{14}C in the specimen, calculation of $a_n = a(t_n)\text{-}a(t_{n-1})$ at each stage can be associated with high uncertainties. It is rather common for subtraction of close values determined by a method with limited accuracy and sensitivity. Therefore it is recommended to determine the value R_n from the cumulative leached concentrations for low-level activity of leachate and/or low leaching rate, substituting a_n with Σa_n and t_n with Σt_n. This expression is used to calculate the effective diffusivity in leaching processes controlled by diffusion phenomena [10, 12, 33].

Calculation of Σa_n from the analytical data is different in the case of static or dynamic leaching conditions. In case of a static process, the amount of ^{14}C defined in an aliquot has to be extrapolated to the whole mass or volume of the leaching solution and added to the amounts defined in the previous stages. In a dynamic experiment, the amount of leachant defined for an aliquot has to be extrapolated to the whole volume or mass of the ^{14}C in the specimen and added to the released fractions detected previously.

Besides the total release, speciation of ^{14}C in the gas phase and liquid phase has to be reported. If detailed speciation in aqueous phase is not possible, quantification of total organic and inorganic fractions is recommended.

4.10 *Proposal for harmonized leaching approach*

Following the above discussion of the standard leaching conditions and parameters, we summarized a recommended unified leaching approach, which will make the leaching tests within CAST project systematic. Keeping these recommended parameters and conditions consistent will enable an inter-comparison of the results from different laboratories and allow benchmarking of the experimental data with those theoretically simulated. Tthe unified leaching scheme is summarized in Table 4.

The specimen of graphite must be of cylinder shape (∅20x20) mm or a powder. The specimen has to be characterized before the leaching in order to determine specific surface area (BET), morphology (Scanning Electron Microscopy, SEM) and particle size (granulometry). The inventory of ^{14}C can be determined by total incineration method. Optionally, a quantification of activation products (AP) is recommended by γ-spectrometry. A control (blank) experiment with inactive nuclear graphite of the same type has to be performed in parallel; geometry must be fixed for both graphite types.

The leaching tests must be performed in any kind of reactors (for example see Fig. 3) made of inert and radiation resistant material, like Pyrex glass, cross-linked PTFE or PEEK, allowing the control of the following conditions:

- The tests are performed at atmospheric pressure and standard temperature of 25±5°C. Optionally, the dependence of ^{14}C release on temperature can be evaluated in order to estimate the activation energy of ^{14}C release.
- As standard leachates 0.1 M NaOH solution (*pH* 13) and 0.1 M $NaClO_4$ solution (*pH* 7) must be used. For proper simulation of ^{14}C release on geological conditions, a synthetic groundwater, recommended by a corresponding national waste management programme, can be used, like bentonite pore water. The control of *pH*, conductivity, γ-spectrometry and ^{14}C content in the leachate before and after the test must be performed.
- The leaching test must be carried out on anaerobic conditions; optionally the effect of ambient atmosphere on leaching behaviour can be evaluated in parallel experiments on aerobic conditions.
- The sampling is recommended to perform in semi-dynamic regime in the following time day-intervals: 1, 3, 7, 10, 14, 21, 28, 35, 42, 72, 98, 126, 156, 182, 210, 238, 266, 294, 322, 350 and 375 days. These periods are optional and can be more flexible. The leaching process shall be monitored during 1 – 1.5 year. A stirring during the entire test is recommended in order to avoid kinetic effects on graphite-solution interface (i.e. uneven distribution of ^{14}C in the solution bulk and near the graphite surface). A sample should be completely immersed in the leachate solution, which can be achieved by placing it in a net sample holder inside the leaching reactor.
- The total concentration of ^{14}C in the leachate must be determined by LSC. The speciation of ^{14}C (i.e. organic and inorganic fractions) in the leachate is to be carried out by HPLC coupled to MS (if applicable). Concentration of gamma-emitting

neutron activation products (AP) like ^{60}Co, $^{152, 154, 155}$Eu, ^{133}Ba, ^{134}Cs, etc. can be determined by γ-spectrometry. In case of a graphite powder as a solid sample, filtration is needed before leachate analysis, in order to avoid an entrapment of small particles.

- The gas phase above the leachate should be sampled along with the leaching solution; ^{14}C inventory and speciation (i.e. organic and inorganic fractions) shall be analysed by sequential absorption in washing bottles with catalytic oven with following LSC measurement. Alternatively, GC-MS having better precision can be used.
- After the leaching test, ^{14}C concentration remaining in the solid specimen has to be determined by total incineration of a specimen with LSC measurement. Additional investigation of specimens' morphology and specific surface area can be performed by SEM and BET respectively. Remaining AP concentration can be determined by γ-spectrometry.
- The results of leaching tests must be evaluated using Eq. (13) and Eq. (14). The leaching behaviour is represented by cumulative leaching fraction (F_n) of ^{14}C as a function of time, and by leaching rate (R_n). These parameters have to be reported for every ^{14}C-species found in gas and aqueous phases.

Table 4. Recommended conditions for leaching procedure

Parameter	Recommendation
Vessel	Pyrex glass; Cross-linked PTFE, PEEK.
Specimen geometry	Cylinder block, ∅20x20 mm; Powder $V_{leachate}/S_{solid}$ 0.1 m
T, °C	25±5 – recommended; other – optional, according to specific national regulations.

Leaching solution composition	0.1 M $NaClO_4$ (pH 7), 0.1 M NaOH (pH 13), synthetic ground/pore water (granite-bentonitic water)
Initial gas phase composition	N_2/Ar (anaerobic); air (aerobic)
Sampling, Δt	1, 3, 7, 10, 14 days 2nd week – twice a week 3rd-6th weeks – once a week Thereafter – monthly
Test duration	1 – 1.5 year
Regime	semi-dynamic; stirring; sample is completely immersed
Analyses	**Pre-leaching**: *Solid phase:* ^{14}C inventory (total incineration), surface area (BET), morphology (SEM), AP inventory (γ-spectrometry), particle size distribution; *Leachate:* Background ^{14}C inventory (LSC), pH, conductivity. **Graphite separation:** filtration or centrifugation. **Post-leaching**: *Solid phase:* remained ^{14}C inventory (total incineration), surface area (BET), morphology (SEM), particle size distribution; AP inventory (γ-spectrometry); *Leachate:* ^{14}C inventory (LSC,), ^{14}C speciation (HPLC-MS), AP inventory (γ-spectrometry), pH, conductivity; *Gas phase:* ^{14}C inventory (LSC), ^{14}C speciation (GC-MS).
Evaluation of results	$F_n = \frac{\sum a_n}{a_0}$ $R_n = \frac{a_n \cdot V}{a_o \cdot S \cdot t_n} = K \cdot \frac{a_n}{t_n}$ F_n and R_n is reported for every ^{14}C-species separately.

5 Conclusion

In this work, we summarize and critically discuss a recommended unified procedure for leaching experiments with graphite for investigation of ^{14}C release. A number of standard procedures and recently reported studies were initially reviewed and a harmonised leaching procedure is proposed. Among recommended parameters are sample geometry, composition of leaching solution (pH, I), temperature, solid to solution ratio and initial gas phase composition (Eh). We also give recommendations for the experimental setup, sampling scheme and experimental regime. For comprehensive description of ^{14}C release mechanism, a number of pre- and post-leaching examinations for ^{14}C inventory and speciation in solid specimen, as well as in liquid and gaseous phase, are recommended.

It was also demonstrated that due to the conflict between simplified and representative approaches, it is not trivial to find a unique option for all studies performed by an international community such as working on the EC CAST project, as in case of a leachate composition. The simplified conditions, used for inter-comparison of leaching tests from different laboratories, cannot always be representative for country-specific geological disposal. A standard unified approach, such as recommended herein, allows, however, an interpretation of every single effect and provides an insight into the release mechanisms of ^{14}C, which can be used in further modelling activities and interpretation of ^{14}C release behaviour in more complex geological systems.

6 References

1 Y. Ma. Simulation of interstitial diffusion in graphite. *Phys. Rev. B,* vol. 76, pp. 075419-(1-5), 2007.

2 K. Nordlund, J. Keinonen, T. Mattila. Formation of ion irradiation induced small-scale defects on graphite surfaces. *Phy. Rev. Let.*, vol. 77, no. 4, pp. 699-702, July 1996.

3 D. Vulpius, K. Baginski, C. Fischer, B. Thomauske. Location and chemical bond of radionuclides in neutron-irradiated nuclear graphite. *J. Nucl. Mat.*, vol. 438, p. 163–177, 213.

4 M. Becton, X. Zeng, X. Wang. Computational study on the effects of annealing on the mechanical properties of polycrystalline graphene. *Carbon,* vol. 86, pp. 338-349, 2015.

5 Y. H. Lee, S. M. Lee, Y. G. Hwang, J. R. Hahn, H. Kang. Defect-induced oxidation of graphite. *Phys. Rev. Let.*, vol. 82, no. 1, pp. 217-220, January 1999.

6 P. Cabrera-Sanfelix, G. R. Darling. Dissociative adsorption of water at vacancy defects in graphite. *J. Phys. Chem.*, vol. 111, pp. 18258-18263, 2007.

7 J. Comte, L. McDermott, L. Petit, L. Petit. Review of leaching data on irradiated graphite. CARBOWASTE-1904-D-6.1.6, CEA-UoM-EDF-Andra, 2013.

8 E. Hespe. Leach Testing of immobilized radioactive waste solids. A proposal for a Standard Method. *At. En. Rev. (IAEA),* vol. 9, no. 1, pp. 195-207, 1971.

9 ISO 6961-1982(E). Long-term leach testing of solidified radioactive waste forms, 1982.

10 ANSI 16.1 Measurement of the leachability of solidified low-level radioactive wastes by a short-term test procedure, American National Standards Institute (ANSI), 2008.

11 ASTM C1220-98. Standard test method for static leaching of monolithic waste forms for disposal of radioactive waste. 2010.

12 ASTM C1308-95. Standard test method for accelerated leach test for diffusive releases from solidified waste and a computer program to model diffusive, fractional leaching from cylindrical waste forms, 2001.

13 DIN 19527:2012-08. Leaching of solid materials. Batch test for the examination of the leaching behavior of organic substances at a liquid to solid ratio of 2 l/kg, 2012.

14 DIN 19528:2009-01. Leaching of solid materials. Percolation method for the joint examination of the leaching behavior of inorganic and organic substances, 2009.

15 I. F. White et al. Assessment of management modes for graphite from reactor decommissioning. Nuclear Science and Technology, Commission of the European Communities, EUR 9232, 1984.

16 W. J. Gray, W. C. Morgan. Leaching of ^{14}C and ^{36}Cl from Hanford reactor graphite. Pacific Northwest Laboratory, report PNL-6769, 1988.

17 W. J. Gray, W. C. Morgan. Leaching of ^{14}C and ^{36}Cl from irradiated French graphite. Pacific Northwest Laboratory, report PNL-6989, 1989.

18 J. Comte, L. Petit. Behavior of radionuclides in UNGG graphite in aqueous media. State-Of-The-Art Review. Carbowaste report 1103-D-WP6.Task.1, 2011.

19 L. McDermott. Characterization and chemical treatment of irradiated UK graphite waste. CARBOWASTE report T-4.3.3-b, 2012.

20 A.G. de la Huebra, R. Muriello Pérez, A. Almodovar Espinosa, Characterization de camisas de graffito irradiadas de la C.N. Vandellos I. CIEMAT Report ITN/TR-62/IF-94, 1994.

21 R. Takahashi, M. Toyahara, S. Maruki, H. Ueda, T. Yamamoto, Investigation of morphology and impurity of Nuclear graphite and leaching mechanism of Carbon-14. IAEA Technical Committee Meeting on Nuclear Graphite Waste Management, Manchester, October 1999, IAEA CD-ROM 01-00120, 1999

22 Characteristics of solidified high-level waste products. IAEA Technical Reports Series No. 187, 1979.

23 NRC 10 CFR 61. Qualified radioactive waste forms. PART 61 – Licensing requirements for land disposal of radioactive waste, May 1984.

24 H. Schoenbacher, M. Tavlet. Compilation of radiation damage test data. Part. 1, 2nd Ed. Technical report CERN 89-12, 1989.

25 U. Berner. Project Opalinus Clay: Radionuclide concentration limits in the cementitious near-field of an ILW repository. PSI-Report 02-26, 2002.

26 A. D. Wiesner, L. E.Katy, Ch. Chen. The impact of ionic strength and background electrolyte on pH measurements in metal ion adsorption experiments. *J. Col. Int. Sci.* vol. 301, pp. 329-332, 2006.

27 G. Baston, S. Preston, R. Otlet, A. Walker, A. Clacher, M. Kircham, B. Swift. Carbon-14 release from Oldbury graphite. AMEC Report AMEC/5352/002 Issue 3, 2014.

28 L. Vendé, C. Landesman, B. Grambow. Report on radionuclide diffusion in water saturated graphite. CARBOWASTE Technical Report T-6.1.5-b, 2013.

29 IAEA-TEDOC-1062. Stability and stabilization of polymers under irradiation, 1999.

30 http://www.berghof.com/en/products/laboratory-equipment/reactors/high-pressure-reactors/overview

31 http://www.bictechnology.co.uk/pdfs/Hague7000.pdf .

---

32 Interlaboratory Radiochemical Analysis Comparison on a Primary Waste Flux. Procedures Report. 5th Euratom FP, Key Action: Nuclear Fission, Contract N° FIKW-CT-2000-00006, 2002.

33 R. Carpentiero et al. Leaching methods for conditioned radioactive waste. Report ENTRAP-WG-B-02, April 2004.