CArbon-14 Source Term

CAST

Advisory Group Review of WP 5 Final Synthesis Report (D1.13)

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CAST – Project Overview

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

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

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

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

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Advisory Group Review of WP 5 Final Synthesis Report

Executive Summary

One of the tasks of the CAST Advisory Group is to review the final synthesis reports from the different Work Packages. This report represents the review of the final synthesis report from WP 5, titled "Final report on results from Work Package 5: Carbon-14 in irradiated graphite (D5.19) [TOULHOAT ET AL. 2018].

Ten different CAST partners participated in one or more of the five tasks under WP 5. These activities are reviewed and the significance of the results to the development of the safety case are highlighted.

Overall, it is found that significant progress has been made following on from the earlier CARBOWASTE project. Although there will inevitably be a wide range of properties of irradiated graphite waste forms, a number of areas of consistency came out of the CAST work, particular in terms of the fractional release rate and speciation of released C-14. This consistency will in turn build confidence in the safety assessment.

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1 Introduction

The focus of Work Package 5 was the behaviour of C-14 in irradiated graphite (i-graphite). The tasks carried out in CAST built on the information from the earlier CARBOWASTE project, with the aim of understanding the factors determining the release of C-14 under disposal conditions, specifically by:

- Determining the C-14 inventory and concentration distribution in i-graphites, and factors that may control these;
- Measuring the rate and speciation of C-14 release to solution and gas from i-graphites in contact with aqueous solutions; and
- Determining the impact of selected waste treatment options on C-14 releases and relating this to the nature of C-14 in i-graphite.

Of the various C-14-containing waste forms in the CAST project, the study of i-graphite is possibly unique as the proposed management method varies significantly from country to country. For example, some countries are considering conditioning the waste in order to reduce the volume and/or to permit the disposal of the decontaminated residue as non-radioactive waste. Furthermore, some countries are planning deep geological disposal whereas others are considering near-surface disposal. Another important consideration is the wide variation in the volume of i-graphite that each programme must manage, ranging from small amounts arising from research reactors to the larger volumes from countries with graphite-moderated power reactors.

Five tasks were defined for WP 5, including:

- Task 5.1 – Review of CARBOWASTE and other relevant R&D activities to establish the current understanding of inventory and release of C-14 from i-graphites;
- Task 5.2 – Characterisation of the C-14 inventory in i-graphites;
- Task 5.3 – Measurement of release of C-14 inventory from i-graphites;
- Task 5.4 – New waste forms and C-14 decontamination techniques for i-graphites;

- Task 5.5 – Data interpretation and synthesis – final report.

A total of ten different partners undertook activities in one or more of these tasks. These activities are reviewed in Section 2 of this report, largely based on the summary information in TOULHOAT ET AL. [2018], but also based also on presentations from and interactions with the various project teams throughout the course of the CAST project. The significance of the work, from the current author's point-of-view, is described in Section 3 with special reference to the improved understanding for use in the safety case and safety assessment.

2 Review by Irka Hajdas

2.1 *Determining the C-14 inventory and concentration distribution in i-graphite, and factors that may control this*

2.1.1 Determining the C-14 concentration and inventories.

2.1.1.1 Techniques used to determine C-14 concentration in i-graphite

Two techniques can be applied to measure the C-14 concentration. Counting technique is the one which is commonly used to measure C-14 activity of nuclear waste products whereas a very high sensitivity of the Accelerator Mass Spectrometry (counting C-14 atoms) is considered when sample of low carbon content are analysed. The D1.19 report shows the ability of adaption and utilizing the AMS facilities to measure the highly active products such as i-graphite.

2.1.1.1.1 LSC

This technique is the most used in the WP5 research. It been used to measure the activity of i-graphite and of leachates as reported by RATEN ICN. The method follows procedure of [MAGNUSSON *et al.*, 2007]. Inorganic and organic carbon is released in the sequence of acid stripping (CO2 collected) and wet oxidation of the remaining leachate solution. Both organic and inorganic fractions were measured. Other facilities use this technique as well: ENEA, Andra, FZJ, CIEMAT, IFIN-HH, RWM and potentially IEG NASU. An overview of measurements is given in Appendix 1.

2.1.1.1.2 AMS

Accelerator mass spectrometry is the technique allows measurement of C-14 abundance ($^{14}C/^{12}C$) by counting the C-14 atoms in the sample. The natural levels of C-14 analysed by AMS facilities are on the order of 10^{-12} to 10^{-15} therefore its application in radioactive waste research requires additional efforts and perhaps specialised facilities.

An interesting approach of using the AMS technique was proposed by IFIN-HH. The research unit equipped with two AMS facilities: 1 MV and 9MV tandem accelerator applied technique to direct analysis of i-graphite from the reactor thermal column. The directly pressed graphite targets were analysed dependent on activity: close to natural (0.5 to ca. 30 Bq/g) (Table 2.8.2) at 1 MV AMS and the very active at 9MV facility. It should be noted that the natural levels of C-14 are lower than the standard used OxaII (18.4 dpm/g or 0.31Bq/g). Therefore, the values measured up to 30 Bq/g are already high for a normal operation of a regular AMS facility.

2.1.1.2 Modelling C-14 inventories

Modelling of C-14 inventories in neutron activated graphite of the Ignalina NPP Unit 1 reactor RBMK-1500 graphite stack was performed by LEI (Lithuania). The modelled flux of neutrons in the reactor graphite columns shows the thermal neutrons being the main component in the centre of the core. The results were compared with the C-14 activities obtained by [MAŽEIKA *et al.*, 2015]. The central part of the graphite core having the highest activity in agreement with the modelled flux of the thermal neutrons. But a lack of new published experimental data on C-14 activities from the unit is stated.

2.1.2 Distributions in i-graphite and Factors controlling C-14 inventories.

Effects of Temperature and irradiation were part of investigations of IPNL. Simulations of C-14 behaviour in i-graphite were based on implementations of C-13 and N-14, irradiations and monitoring structural evolution (SIMS, Raman) – effect on distribution of C-14 in irradiated graphite is mainly due to ballistic damage. Dependent on the location and neutron flux C-14 can be dislocated or stabilised. For the disposal purpose the find that the C-14 in the ‘hot’ parts of reactor will be stabilised indicates treatment methods.

2.2 Measuring the rate and speciation of C-14 release to solution and gas from i-graphite in contact with aqueous solutions

2.2.1 Leaching effect

RATEN ICN performed 1 year-long experiment of leaching in alkaline environment both anaerobic and aerobic. The results showed that ca. 1.8% of starting C-14 activity is realized during the leaching. Most of the C-14 was realised during the first phase of leaching.

Andra/EDF experiments of leaching (alkali and ambient atmosphere) of the French i-graphite stacks resulted in C-14 content below the detection limit. The resulting estimates of the leaching rate show quite wide range: 10^{-11} to 10^{-8} m/day. Observed difference in release time of inorganic versus inorganic carbon. Most of inorganic release in the first 100-200 days. (But it is not clear from the report how was this measured).

In the leaching experiment in bentonite water of the Vandellos I NPP graphite CIEMAT finds leaching rate for C-14 lower than 6.15×10^{-9} cm/day, which is comparable to the results of Andra.

Also IFIN-HH have shown that up to 19% of original inventories of C-14 will be released in the early days (first weeks) of storage.

Research of RWM focused on release of C-14 into gaseous phase. The C-14 bound as methane or carbon monoxide and carbon dioxide.

Experimental work performed on irradiated Oldbury Magnox power station graphite was specifically designed for collecting gas phase. The measured C-14 concentration showed that total cumulative release of C-14 occurs in the first 100 days (release over 4 years). It is a small fraction of total inventory (1%) and in a worse-case will not exceed 30%. Most of C-14 remains bound to graphite. Parameters to be used in modelling gaseous release of C-14.

2.2.2 Speciation of carbon

In order to detect the different organic component in deionized water used to leach the graphite, CIEMAT used GC –MS. Acetate (close to detection limit), formate and oxalate were detected. No alcohol or aldehydes were observed.

Speciation of gaseous release was possible in experiments of RWM. Here a collection of methane, CO_2, CO and hydrocarbons is possible.

2.3 Determining the impact of selected waste treatment options on C-14 releases and relating this to the nature of C-14 in i-graphite

2.3.1 Treatment of i-graphite

ENEA investigated methods of removal of C-14. The exfoliation of graphite layers in ultrasonic bath of various solvents showed wide range of removal efficiency (0.2 to 15%). C-14 analysis were performed using wet oxidation &LSC technique.

FZJ tested the leaching procedure at 2 conditions: DIW and 1M NaOH as well as thermal treatment at 1300ºC. The storage in alkaline conditions is estimated to release less than 1% of the total activity therefore fulfils safety requirements for the specific storage in Germany. The thermal treatment appears to be less effective than expected and most probably not an option for the storage of i-graphite in Germany.

CIEMAT investigated how effective the thermal treatment can be in decontaminating graphite. Indication for a compromise between corrosion and removal of C-14 for lower temperature 400-600°C.

IEG NASU plans treatment of graphite from RBM Chernobyl reactor. Removal of layers (cutting) or vacuum pyrolysis are under consideration.

2.4 Summary C-14 in i-graphite

Results of research presented by ten research groups show that the potential release of C-14 in the depository of i-graphite would be on the order of 1% of C-14 inventories. All research results point to a fast release of C-14. Most of inorganic released in the first 100-200 days of storage in the ambient, alkali environment. Speciation of gaseous release (methane, CO_2, CO and hydrocarbons) was completed providing information for modelling of gas release.

3 Review by Fraser King

3.1 *Centre National de la Recherche Scientifique (CNRS/IN2P3) laboratory: Institute of Nuclear Physics of Lyon (IPNL)*

IPNL activities were focussed on Task 5.2 and, in particular, on understanding the effect of in-reactor conditions on the location and stability of C-14. A model system was used for the studies involving C-13 implanted into Highly Oriented Pyrolitic Graphite (HOPG) to simulate C-14. The aim of the studies was to investigate the effects of neutron flux and temperature on the graphite structure, as well as on the stability and location of C-14. This study contributes to a fundamental knowledge of the effect of reactor operations on C-14 distribution and, based on earlier studies, implicitly assumes that the activation of C-13 (rather than of N-14 or O-17) is the predominant route for the formation of C-14 in i-graphite.

It was found that the effects of irradiation and elevated temperature can have synergistic or non-synergistic effects on the degree of disorder of the graphite. For highly disordered graphite, irradiation has little impact on the healing of the structure because the typical reactor temperatures of 200-500°C are insufficient to anneal the original defects. However, smaller degrees of disorder can be thermally annealed. Thus, the structure of the graphite will vary in different locations within the reactor depending upon the local irradiation flux and temperature. Thus, graphite irradiated at a low neutron flux but in a hotter region of the reactor will display little disordering, whereas high fluxes and lower temperatures will result in more disordering. In terms of the leaching behaviour, C-14 may be located within planar sp^2 sites or three-dimensional sp^3 structures. The former are more stable and tend to be associated with the highly ordered graphite structure, and will lead to lower C-14 leaching rates during disposal.

The results of these studies are more useful for supporting the overall safety case arguments rather than being used directly to predict the rate of release of C-14 in the safety assessment itself. The dependence of the distribution and stability of the C-14 on the irradiation history implies that the behaviour of i-graphite under disposal conditions will not only be variable but that it will also be difficult to transfer data between different types or sources of graphite.

3.2 Lithuanian Energy Institute (LEI)

Among other activities, LEI developed a new numerical neutron activation model for predicting the distribution of C-14 in the graphite stacks of an RBMK-1500 reactor. This design contains 2488 graphite columns, which were grouped into 238 groups of similar properties. The new activation code was applied to these different groups and the results were calibrated by reference to measurements on a small subset of samples.

This work, made possible by the CAST and earlier CARBOWASTE projects, demonstrates a significant step forward in the understanding of the C-14 inventory in the Lithuanian RBMK reactor. Such information would be a key input parameter for the safety assessment.

3.3 Regia Autonoma pentru Activitati Nucleare – Institute for Nuclear Research (RATEN ICN)

RATEN ICN participated in two CAST tasks, namely the application of the learnings from the CARBOWASTE project (Task 5.1) and the measurement of C-14 release rates (Task 5.3).

The CARBOWASTE findings were used to determine the inventory of C-14 in an MTR i-graphite thermal column and represents a good example of technology transfer from the earlier EC-funded project.

Leaching experiments were conducted in alkaline solution representative of conditions in a cement-backfill repository. Table 1 and Table 2 summarise the results of the speciation and release rate of C-14, respectively, for both the RATEN ICN measurements and those from other CAST participants. Experiments were conducted on solid samples as opposed to powdered i-graphite and, thus, the results incorporate the effects of not only the dissolution and release of C-14 but also the accessibility of the leachate to the sites at which the C-14 is located in the matrix.

Table 1: Summary of the speciation of C-14 from i-graphite leach tests reported by various CAST participants.

CAST partner	Conditions	Gaseous fraction		Dissolved fraction	
		Organic	Inorganic	Organic	Inorganic
RATEN ICN	Aerobic and anaerobic 0.1 mol/L NaOH, ambient temperature, solid i-graphite	n/d	n/d	32% (aerobic) 65% (anaerobic)	68% (aerobic) 35% (anaerobic)
Andra/EDF	Aerobic and anaerobic 0.1 mol/L NaOH, ambient temperature, solid i-graphite	5% (CO, hydrocarbons)		30%	65%
FZJ	Anaerobic DIW, ambient and 50°C	5% (ambient) 17% (50°C)		95% (ambient) 83% (50°C)	
FZJ	Anaerobic 1 mol/L NaOH, ambient and 50°C	0.4% (ambient) 0.8% (50°C)		99.6% (ambient) 99.2% (50°C)	
RWM	Anoxic, 0.1 mol/L NaOH, ambient temperature, solid i-graphite	1%		99%	

Table 2: Summary of the C-14 release rates from i-graphite reported by various CAST participants.

CAST partner	Conditions	Initial fractional release rate	Steady-state or long-term fractional release rate
RATEN ICN	Aerobic and anaerobic 0.1 mol/L NaOH, ambient temperature, solid i-graphite	9×10^{-4} day^{-1}	4×10^{-5} day^{-1}
Andra/EDF	Various		10^{-11}-10^{-8} m/day
FZJ	Anaerobic DIW, ambient and 50°C		6×10^{-7} day^{-1} (gas, RT) 1×10^{-5} day^{-1} (liquid, RT) 6×10^{-6} day^{-1} (gas, 50°C) 3×10^{-5} day^{-1} (liquid, 50°C)
FZJ	Anaerobic 1 mol/L NaOH, ambient and 50°C		2×10^{-7} day^{-1} (gas, RT) 5×10^{-5} day^{-1} (liquid, RT) 6×10^{-7} day^{-1} (gas, 50°C) 7×10^{-5} day^{-1} (liquid, 50°C)
IFIN-HH	Anaerobic 0.1 mol/L NaOH, solid i-graphite		4-10 x 10^{-5} day^{-1}
RWM	Anoxic, 0.1 mol/L NaOH, ambient temperature, solid i-graphite		2×10^{-6} day^{-1}

In terms of the speciation of released C-14 (Table 1), no gaseous fraction was reported, although it is unclear whether this was confirmed by measurement. In the leachate, the predominance of organic and inorganic fractions depends on the redox conditions, with the former favoured by anaerobic conditions and the latter by aerobic. Two-stage dissolution kinetics were reported (Table 2), with a higher initial rate of the first 7 weeks of exposure and a slower longer-term rate during the remainder of the approximately 1-year test. It remains to be demonstrated whether this bimodal behaviour represents rapid release of C-14 located on free surfaces in accessible pores versus slower release due to matrix degradation or some other time-dependent behaviour.

The data obtained by RATEN ICN as part of Task 5.3 contribute directly to improved treatment of C-14 release in a safety assessment. Release rates were determined under realistic conditions using macroscopic solid samples and take into account factors such as the accessibility of the aqueous environment to the location of C-14 in the matrix. Thus, the measured rates are not unduly conservative, as might have been the case had powdered i-graphite been used.

3.4 *Agence nationale pour la gestion des déchets radioactifs/ EDF (Andra / EDF)*

Andra and EDF reviewed existing C-14 leaching data and conducted a limited number of new studies on the speciation of released C-14. In general, the C-14 leaching rates were very small and mostly below detection limit, although the earlier studies had not been conducted specifically to measure the release of C-14. There was considerable variability in the studies reviewed, with fractional dissolution rates in the range 10^{-11} to 10^{-8} m/day (Table 2). Both solution chemistry and specific surface area of the i-graphite were reported to affect release of C-14. The new speciation studies were conducted on powdered graphite and, therefore, represent the distribution of all C-14 within the matrix (Table 1). In common with other studies, the majority of C-14 released under alkaline conditions remained in the aqueous phase.

The Andra/EDF contribution represents added value for the CAST project as it involved the review of reports from the earlier CARBOWASTE project as well as the results of unpublished, internal leaching studies.

3.5 Agenzia Nazionale per le Nuove Technologie, L'Energia e lo Sviluppo Economico Sostenibile (ENEA)

The focus of the ENEA studies was the development of a decontamination technique with the aim of allowing the conditioned i-graphite to be either recycled or treated as LILW (Task 5.4). A combination of sonication and the use of an organic solvent were used to exfoliate the i-graphite and to release the non-chemically bonded C-14. In general, the removal efficiency was found to be 1-2% of the inventory per hour of sonication using powdered samples. There were some differences depending on the solvent used, and some evidence for a levelling off of the removal efficiency with increasing time. Further development work is presumably required to improve the rate of C-14 removal.

3.6 Forshungzentrum Juelich GmbH (FZJ)

FZJ participated in all tasks within WP 5. There is nearly 1000 tonnes of i-graphite in Germany that needs to be disposed of in the Konrad facility (a small amount having been already disposed of in the ASSE test repository).

Radiographic analysis of i-graphite samples indicates local "hot-spots" of accumulated radionuclides believed to correspond with pores in the material (Task 5.2). Since there were no indications of impurities in these regions, it was inferred that the increased local activity is due to C-14. This in turn suggests that C-14 is primarily produced by activation of N-14 and O-17 as activation of C-13 would be expected to produce a more uniform distribution of activity. This position is contrary to that of IPNL and RWM who suggest that C-13 activation is the primary formation pathway.

Leaching tests were performed in deionised water (DIW) and 1 mol/L NaOH solution at ambient temperature and 50°C (Task 5.3). In all cases, the majority of released C-14 was retained in the aqueous phase, with only 0.4-17% released as volatiles. The highest fraction of volatiles was observed in DIW, possibly because the predominant volatile species is CO_2

which is retained in solution under alkaline conditions. FZJ were particularly focussed on gaseous releases (perhaps for operational safety reasons) and highlighted the benefit of cementitious backfill in limiting releases, even though the total release rate dominated by the dissolved fraction is higher in alkaline solution. Fractional release rates are given in Table 2 and are similar to those reported by others.

A thermal treatment (Ar atmosphere, 1300°C, 19 hours) was investigated for partial decontamination of i-graphite (Task 5.4). Between 5.5 and 8% of the C-14 was removed, thought to comprise the physisorbed fraction and it was concluded that such a minimal decontamination does not warrant the additional effort of a pre-treatment step.

The results of the FZJ work contribute directly to the design and licensing of the Konrad facility.

3.7 Centro de Investigationes Energéticas Médioambientales y Tecnològicas (CIEMAT)

CIEMAT's major contributions to the CAST project were in Task 5.4 (new waste forms and decontamination techniques), although some leaching studies were also conducted (Task 5.3). Unfortunately, in all but one measurement, the C-14 levels were below the detection limit so limited information was obtained from the leaching studies.

An alternative i-graphite waste form (Impermeable Graphite Matrix, IGM) was developed and tested as part of Task 5.4. Because the leaching of C-14 from unconditioned i-graphite is largely associated with release from the pores in the material, powdered graphite is mixed with 20% glass and compacted to a density of 2.2 g/cm^3 to create a low-porosity, "impermeable" waste form. As with the prior measurements, the C-14 release was below the detection limit. A more-sensitive C-14 analytical procedure is required to demonstrate the advantages of the alternative waste form over unconditioned i-graphite. Thermal treatment was also investigated as a decontamination technique, but again it is difficult to draw definitive conclusions because of the challenges of measuring small concentrations of C-14.

3.8 Institutul National de Cercetare-Dezvoltare pentru Fizica si Inginerie Nucleara "Horia Hulubel" (IFIN-HH)

IFIN-HH were involved in Tasks 5.1 to 5.3 of the CAST project. As part of Task 5.2, IFIN-HH determined the distribution and inventory of C-14 on graphite thermal columns from a VVR-S research reactor based on the use of the sensitive accelerator mass spectrometry (AMS) method. A significant gradient in the C-14 content was observed, consistent with the known irradiation characteristics of the reactor during operation.

Leaching tests were conducted in anoxic 0.1 mol/L NaOH on solid i-graphite samples for a period of 270 days (Task 5.3). The fractional leaching rate of dissolved C-14 is of the order of 10^{-5} to 10^{-4} day^{-1} (Table 2) and is consistent with that reported by other participants. A separate gas release experiment was performed, with only small amounts of volatile C-14 released.

The IFIN-HH study demonstrates the importance of the use of AMS as a method for detecting small amounts of C-14.

3.9 Radioactive Waste Management (RWM)

In addition to acting as CAST project manager, RWM contributed existing information on the release of C-14 from i-graphite as part of Task 5.1. Results from a series of seven leaching tests were provided, involving both neutral and alkaline pH, aerobic and anaerobic redox conditions, ambient temperature and 50°C, solid and powdered i-graphite, and different exposure periods. As reported by others, C-14 release exhibits an initial accelerated rate and then decreases to a longer-term slower rate. Also as reported by others, in alkaline conditions, the majority of C-14 is released to the liquid phase (Table 1) at an average long-term fractional rate of 2 x 10^{-6} day^{-1} (Table 2). What little volatile C-14 was released was primarily in the form of either hydrocarbons or CO (detected in a 2:1 ratio) with only 2% released as CO_2.

Additional RWM studies conducted outside of CAST provide further information on the inventory of C-14 (specifically the chemical form and distribution) and the rate and speciation of released C-14. In terms of the C-14 inventory, it is concluded that C-14 exists in i-graphite in elemental form (i.e., as C atoms rather than as C-containing compounds) and is covalently bonded to the matrix. The C-14 is homogeneously distributed throughout the matrix with only a minor fraction concentrated in "hot spots", suggesting that activation of C-13 is the primary formation route. An important implication of these and other studies not widely discussed by the other participants is that a substantial fraction of the C-14 inventory is bound up by the graphite matrix and is not releasable. For gaseous C-14 release, RWM have defined a fraction of releasable C-14 of between 0 and 30%, with a best estimate of 5%.

3.10 *State Institution "Institute of Environmental Geochemistry National Academy of Science of Ukraine" (IEG NASU)*

IEG NASU activities within the CAST project were focussed on managing i-graphite wastes arising from decommissioning of the Chernobyl NPP. There is approximately 6000 tonnes of i-graphite in Units 1-3, with some also stored in cooling ponds and in "technological" shafts. IEG NASU are planning to examine the depth distribution of C-14 within these wastes.

4 Significance of the Outcomes of Work Package 5

In this section, the significance of the WP 5 outcomes for the safety case and safety assessment are considered. In general, quantitative information relating to the inventory or rate of release of C-14 can be used directly for the safety assessment. Mechanistic information and more-qualitative observations are useful for supporting the overall safety case.

Despite the wide range in properties of i-graphite waste forms from different sources, there was a gratifying degree of consistency between the results of many of the WP 5 participants. All partners who studied the release of C-14 under alkaline conditions simulating a cementitious-backfilled repository reported that the vast majority was retained in the aqueous phase with little or no release of volatiles (Table 1). In addition, the long-term (on a laboratory timescale) fractional release rates were mostly in the range of 10^{-6}-10^{-5} day^{-1} (Table 2). This consistency lends credibility to, and builds confidence in, the safety assessment. There are areas of inconsistency, however. For example, there is no unanimous agreement on the predominant activation pathway for the formation of C-14, which has implications for the inventory and distribution of C-14. Some partners propose the activation of C-13 as the primary route, which would result in a generally uniform distribution of C-14 within the matrix. Others suggest the activation of N-14 and/or O-17 is more important, based in part on the observation of a non-uniform distribution of C-14. The C-14 hot spots tended to be associated with pores and cracks in the i-graphite, with obvious implications for rapid release.

Various measurements of the C-14 release rate from i-graphite were reported in the CAST project and are clearly directly implementable in the associated safety assessments for the different partners. As reported by different groups, the release behaviour typically exhibits a fast initial rate (lasting a few days or weeks) followed by a lower steady-state rate during the rest of the test, which generally lasted for a few months up to approximately one year. Different factors were found to impact the release rate, including the composition of the leachate and the specific surface area of the samples (or the surface area to leachate volume ratio). The question is whether such rates, measured over relatively short timescales, are representative of the long-term behaviour in the repository. Some of the rates were measured on solid pieces of i-graphite, whereas others were determined from powdered samples. In the latter case especially, the measured rates represent a conservative upper bound as a fraction of the total inventory in the actual waste is likely to be inaccessible to the repository environment, at least initially. Even laboratory experiments with small pieces of i-graphite machined from larger graphite bricks may over-estimate the C-14 release rate in the repository.

An important consideration for the treatment of the release of C-14 in the safety assessment that did not receive much attention within CAST is whether a significant fraction of the inventory is not releasable. Although the rate of C-14 release was reported to be slow under laboratory conditions which made it difficult to measure, a fractional release rate of 10^{-6} day^{-1} (Table 1) would cause the entire C-14 inventory to be released in less than one-half of one $t_{1/2}$ of C-14. Thus, if sustained over extended periods, the reported C-14 release rates are relatively rapid on both a radiological and a repository timescale. However, work outside of CAST reported by RWM suggests that only a fraction of the total inventory is releasable, in part due to the inaccessibility of the uniformly distributed C-14 and the resistance of the graphite matrix to further degradation under repository conditions. Thus, the assumption that all of the C-14 inventory will be inevitably released is likely to be conservative.

A number of the partners reported on the importance of the sample history on the inventory, distribution, and leachability of C-14. For example, IPNL found that the in-reactor conditions impact the degree of disorder of the graphite and result in spatial variability of the stability of C-14 with a given source. Similarly, IFIN-HH observed a gradient in C-14 content along the length of an i-graphite thermal column. This general variability means that (a) it is difficult to transfer data from one system to another and (b) there will inevitably be wide ranges of inventories and rates in the safety assessment as it will be impossible to fully characterise the properties of all i-graphite to be disposed.

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Appendix 1

Research Team	Reactor	Graphite mass	C-14 spec. activity Bq/g or sample	C-14 inventory Bq	Method used
LEI (Lithuania)	RBMK-1500 reactor	Graphite stack 1700t	1.895×10^5	3.22×10^{14}	Modelling neutron flux and C-14 specific activity
		Other graphite parts of reactor/200t	1.895×10^5	3.790×10^{13}	
RATEN ICN (Romania)	TRIGA 14 MW reactor	Graphite bars B1 B2	450.75±16.36 96.11±21.20		Measured activity of powder graphite LSC
		B1 (340.96g) B2 (500g)	Aerobic: 1330 Anaerobic:450	15.37×10^4 4.8×10^4	Total C-14 [Magnusson *et al.*, 2007] Inorganic (acid stripping)+organic Wet oxidation LSC
ENEA (Italy)	Latina NPP		(8508 to 76744) $\times 10^3$		Wet oxidation&LSC
CIEMAT (Spain)	Vandellos I NPP graphite		(1.1 to 1.35) $\times 10^4$		Drilled graphite powder, combustion at 900°C, LSC (ultra-low activity LSC, Quantulus)
IFIN-HH (Romania)	VVR-S rector thermal core		0.6 to 27 (2.6 to 78) $\times 10^3$	3.1×10^6 to 4.79×10^{10}	AMS Depth profiling C-14 concentration in the graphite rod AMS 1MV AMS 9MV LSC (silica gel+CuO

					combustion)
RWM (UK)	Oldbury Graphite		$(8.4\pm1.1) \times 10^4$		LSC Collecting gaseous products of leaching