CArbon-14 Source Term

CAST

WP5 Annual Progress Report – Year 1 (D5.2)

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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 as dissolved and gaseous species.

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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WP5 Annual Progress Report – Year 1 (D5.2)

Executive Summary

Work Package 5 of the EC CAST project considers irradiated graphite and related 14C behaviour. The objective of this Work Package is to understand the factors determining release of 14C from irradiated graphite under disposal conditions (to include surface disposal facilities and geological disposal facilities). This is to be achieved by:

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

This is the first annual report of Work Package 5, and details, on an organisation by organisation basis, progress in the Work Package over its first year.

1. IPNL concludes that thermal annealing of graphite in inert atmosphere does not induce any migration of implanted ^{13}C up to 1600°C, even if the structure of the graphite is initially disordered; at 1600°C slight diffusion occurs. Irradiation with Ar^{3+} induces a strong re-ordering of the graphite even at room temperature, compared to He^{2+} irradiation or annealing alone.

2. LEI reviewed the outcomes from the CARBOWASTE Project for the RBMK-1500 reactor. Under task 5.2 new models for the numerical estimation of RBMK-1500 graphite activation are under development. It is expected that some sampling of the Ignalina NPP Unit 1 RBMK-1500 reactor graphite will be done soon. Combining these data and numerical modelling for the induced activity of C-14, it should be possible to estimate the inventory of C-14 in i-graphite of the whole core of Ignalina NPP Unit 1 reactor.

3. IGNS NASU has reviewed information on the graphite characterisation being undertaken as part of the Chernobyl nuclear power plant decommissioning programme. Work on chemical decontamination of graphite has also been reviewed and the overall graphite waste management approach described. A draft report has been prepared for Deliverable D5.3.

4. The main objective of the INR in WP5 is to update the inventory of C-14 in the irradiated graphite arising from TRIGA 14MW reactor thermal column and to define the associated source term, not only as total amount of C-14 but also as inorganic/organic ratio. Data on the leaching rate presented in the literature have been analysed and the most appropriate kinetics used to predict the C-14 releases from TRIGA thermal column irradiated samples in order to establish the design parameters of the leaching experimental set up. Activities performed up to now consisted in the design of the experiments in order to ensure measurable C-14 releases in hyperalkaline environment, both in liquid and gas phases.

5. Andra and EDF have reviewed the data on C-14 release and on the speciation of C-14 in French i-graphites, and presented the outcome in Deliverable D5.1. The main conclusions are that C-14 leaching rate is very slow for the stack graphite, and in most of cases a quasi-steady state leach rate appears to be achieved after the elapse of around 100 to 200 days. Over that period, the calculated mean radiocarbon leach rate lies between 10^{-11} and 10^{-8} m.day^{-1} (meters per day). A faster carbon 14 leach rate seems to be observed for the sleeve graphite (operational waste), which represents a small part of the total inventory in C-14. The nature of the leaching

liquid (deionised or lime or soda water) does not seem to have any clear impact on the C-14 leaching behaviour.

6. Work undertaken by ENEA in the first year considers i-graphite from Latina NPP. This presents a wide range and amount of activation products, with the distribution of activated elements in the bulk of the samples being present mainly in the closed porosity or between the typical graphite layers. Graphite has been exfoliated to extract ^{14}C intercalated between the graphene layers. Three different organic solvents with good solvency properties and water-miscibility have been tested, initially on non-irradiated virgin graphite and then on 15 samples of nuclear i-graphite from Latina NPP moderator. Characterization by means of Scanning Electron Microscopy SEM and Laser Raman Spectrometry has been performed to evaluate the degree of the exfoliation process. A preliminary characterization of the i-graphite samples, in order to estimate the content of radiocarbon ^{14}C, has been carried out.

7. Work of FZJ in CAST Work Package 5 is reviewing characterisation data on the speciation of ^{14}C in MTR and HTR i-graphites and relevant information from CarboDISP, decommissioning projects in Germany and the ASSE test repository. FZJ will leach samples, which have undergone decontamination treatments and untreated samples to confirm a labile ^{14}C fraction, rather than slow diffusion of ^{14}C from within the graphite. Leach tests have been systematically started mainly with RFR graphite. Additional tests have been performed with AVR graphite, as it shows a quite high specific ^{14}C activity. Diffusion tests have been started also for the irradiated RFR graphite. Extensive water-uptake tests have been performed, showing clearly that virgin graphite exhibits little water-ingression and quasi-hydrophobic behaviour. In contrast, irradiated-graphite, as well as heat-treated graphite, behaves in a hydrophilic manner with high and quick water-uptake.

8. CIEMAT’s input to date considers different preliminary studies that have been performed to prepare the leaching experiments on irradiated powder graphite from Vandellós I NPP, and on a graphite glass coating waste form - IGM (Impermeable

Graphite Matrix). CIEMAT's laboratory is being conditioned to work with the equipment needed to prepare samples of i-graphite for use in experiments.

9. Work reported by RWM as input to Task 5.1 considered the release of gaseous C-14 during leaching of irradiated graphite samples from Oldbury Magnox power station under highly alkaline conditions. About 0.07% of the carbon-14 inventory was released, mainly into solution, in one year and about 1% of this released carbon-14 was detected in the gas phase. The rates of release decreased with time. Gaseous carbon-14 was predominantly in the form of hydrocarbons or other volatile organic compounds and CO. Almost all $^{14}CO_2$.was retained in the alkaline leachate.

10. The main objective of the IFIN-HH in the first year of its input to Work Package 5 was to update the inventory of ^{14}C in the irradiated graphite arising from thermal column of VVR-S Reactor and radioactive wastes containing organic and inorganic ^{14}C compounds. IFIN-HH has also characterized the ^{14}C inventory of irradiated graphite from thermal column of VVR-S Reactor, and has started to develop a method, based on the use Accelerator Mass Spectrometry (AMS,) which will be suitable to characterize the distributions of ^{14}C inventory in irradiated graphite. Finally, in order to measure the total release of ^{14}C (and ^{3}H) to solution and gas from crushed and intact i-graphite from the VVR-S Reactor, an apparatus has been designed and manufactured.

This annual report will be updated at the end of each year of the EC CAST project, which will act as a record of achievement for Work Package 5. When the project eventually reaches its conclusion, a final report from the Work Package will be produced, capturing and summarizing learning and achievements over the project's full duration.

Contents

1 Introduction

Work Package 5 of the EC CAST project considers irradiated graphite and related 14C behaviour and is led by Radioactive Waste Management Limited (UK). The objective of this Work Package is to understand the factors determining release of 14C from irradiated graphite under disposal conditions (to include surface disposal facilities and geological disposal facilities). This is to be achieved by:

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

To achieve these objectives, five tasks have been identified:

- Task 5.1 – Review of CARBOWASTE and other relevant R&D activities to establish the current understanding of inventory and release of ^{14}C from i-graphites;
- Task 5.2 – Characterisation of the ^{14}C inventory in i-graphites;
- Task 5.3 – Measurement of release of ^{14}C inventory from i-graphites;
- Task 5.4 – New wasteforms and ^{14}C decontamination techniques for i-graphites; Task 5.5 – Data interpretation and synthesis – final report.

This is the first annual report of Work Package 5, and details, on an organisation by organisation basis, progress in the Work Package over its first year.

2 Organisation Reports

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

Behaviour of 14C (simulated by implanted 13C) and its precursor 14N in graphite: effects of temperature and irradiation

Introduction

Our contribution aims to understand better the inventory of ^{14}C in irradiated French UNGG nuclear graphite. As a matter of fact, according to the French law of June 2006, the graphite waste has to be disposed of after an eventual previous purification. The safety assessment calculations need reliable data related to ^{14}C quantity, location within the graphite and speciation. These data are not easily accessible on irradiated radioactive graphite but some information can be inferred through experiments made on virgin implanted samples.

In order to simulate the presence of ^{14}C, we implanted both virgin nuclear graphite and model HOPG (Highly Oriented Pyrolytic Graphite) graphite with ^{13}C. The virgin nuclear graphite is issued from the moderator graphite of the SLA2 UNGG (Uranium Naturel Graphite Gaz) reactor in France. SLA2 has been manufactured with Lima coke. The fraction of open pores varies from 19 to 25% whereas the fraction of closed pores is in the range 6-7%. The HOPG samples (Grade SPI-1) are issued from SPI 4 Supplies via Neyco Company. The advantage of the model graphite is the absence of pores preventing the release through “shortcuts” due to the interconnected pores (as in nuclear graphite) thereby providing a better understanding of the release mechanisms.

The aim of our work is to understand and therefore simulate the behaviour of ^{14}C during reactor operation. In particular, we try to monitor the independent or synergistic effects of temperature, irradiation and radiolysis on ^{14}C migration. ^{14}C is mainly formed through the activation of ^{13}C. A certain amount may also be generated through the activation of ^{14}N, especially for ^{14}C located close to the open pores (because of the absorption of ^{14}N during maintenance or repair). Some nitrogen may also occur in coke grains. Amounts as high as 160 at.ppm have been detected inside some coke grains.

Consequently, we decided to monitor:

- The migration of implanted ^{13}C used to simulate ^{14}C
- The migration of implanted ^{14}N used to simulate the presence of nitrogen as a precursor of ^{14}C.

The results presented in this document are issued from the PhD work of G. Silbermann (2013) and the PhD of N. Galy that is underway.

Experimental

The nuclear graphite samples have been polished to the micrometer and then annealed at 1000°C for 10h. The HOPG samples have been annealed at 1000°C for 10h. The sample surfaces have then been implanted respectively with:

- ^{14}N at a depth around 400 nm and a fluence of $6x10^{16}at/cm^{-2}$ (concentration at the projected range Rp around 5at.%) for SLA2 samples. No HOPG samples were implanted with ^{14}N.
- ^{13}C at a depth around 300 nm and a fluence of $6x10^{16}at/cm^{-2}$ (concentration at the projected range Rp around 5at.%) for SLA2 and HOPG samples.

The implantations have been performed either at the 400kV IMIO implanter of IPNL in Villeurbanne (by A. Perrat-Mabilon and A. Duranti) or at the 200kV Eaton implanter of the Icube laboratory in Strasbourg (by Y. le Gall).

The implantation results in quasi Gaussian distribution profiles of the implanted isotopes and the profiles have been analysed (before and after treatment) using a Cameca IMS 6f at the Ecole Nationale Supérieure des Mines de Paris at Fontainebleau (by L. Raimbault) or at the Laboratoire Science et Surface at Ecully using an IONTOF ToF-SIMS V (by J. Amalric and J. Brissot).

The sample surfaces have been observed before and after treatment using optical microscopy or secondary electron microscopy (SEM) and the sample structure evolution has been monitored using Raman microspectrometry (in collaboration with J.N. Rouzaud from Ecole Normale de Paris or M.R. Ammar from CEMHTI Orléans, France).

After implantation, the samples have been annealed or irradiated and annealed using several facilities: the annealing platform of IPNL, the 4MV Van de Graaff accelerator at IPNL or the 15MV Tandem Van de Graaff of IPN at Orsay. All the irradiations were performed in dedicated irradiation cells. The common feature of these cells is to enable the heating of the sample during irradiation (up to 600°C or 1000°C, depending on the cell) and to monitor the sample temperature. Depending on the cell, the irradiations can be performed with a gas (to take into account the effects of gas radiolysis at the gas/graphite interface) or under secondary vacuum (to avoid the interaction of oxidants with graphite).

The irradiations have been carried out with ions. The nature and energy of the ions depend on the irradiation facility. Neutrons induce mainly ballistic damage. Indeed, the mean energy of neutrons issued from nuclear fission is around 2 MeV. The elastic collision of the neutrons with the graphite matrix induces the displacement of the carbon atoms that are ejected from their original position with an energy around 284 keV into interstitial position. However, some neutrons, even if the probability is scarce, may have energies as high as 10 MeV. In that case and if the impact is frontal, the energy gained by the ejected atom is of 2.84 MeV. Depending on their energy, the ejected atoms will in turn be able to eject other atoms and create displacement cascades. They will also be able to create electronic excitations and ionisations.

Thus, the consequences on the damage of the graphite structure may differ substantially depending on the irradiation conditions (energy of neutrons and also irradiation due to the induced radioactivity).

In short, irradiation produces two main types of damage in graphite:

1) Ballistic damage resulting in atom displacements as mentioned above that are quantified according to the nuclear stopping power in terms of displaced atoms;

2) Electronic excitation and ionisations induced by β- and photon irradiation (due to the radioactivity) as well as by the recoil atoms. These effects are quantified according to the electronic stopping power (Ziegler et al. 1985).

Thus, all these effects can be simulated using appropriate ion irradiation. Moreover, the effects due to ballistic damage or electronic excitation can be studied coupled or decoupled according to the nature of the ion and its energy and fluence. Using the SRIM code, we have tried to quantify the damages. The calculations were made for different ions and for different energies of these ions. The results are reported in two friezes: one illustrating the effects of electronic excitations (Figure 2.1.1) and the other one devoted to the ballistic damage (Figure 2.1.2).

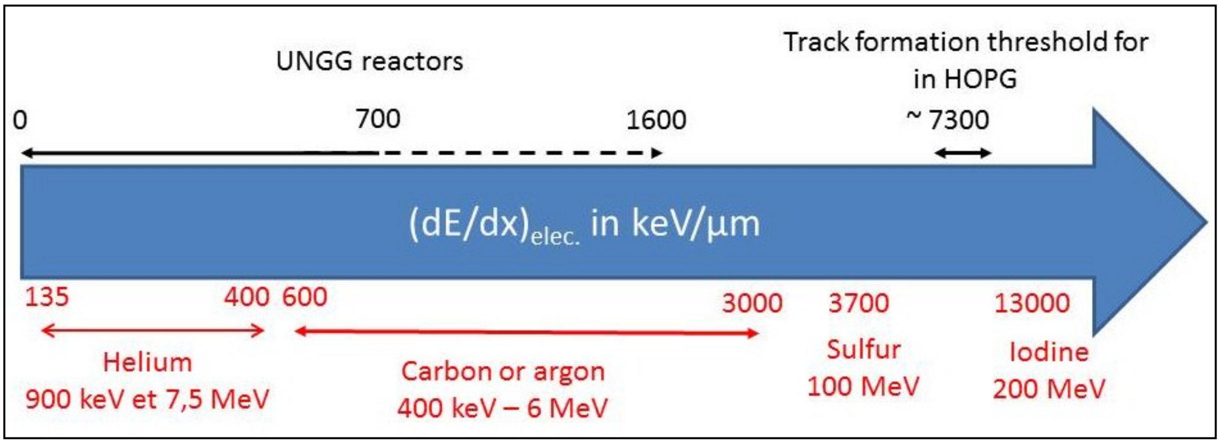


Figure 2.1.1: Electronic stopping power for different ions and ion energies.

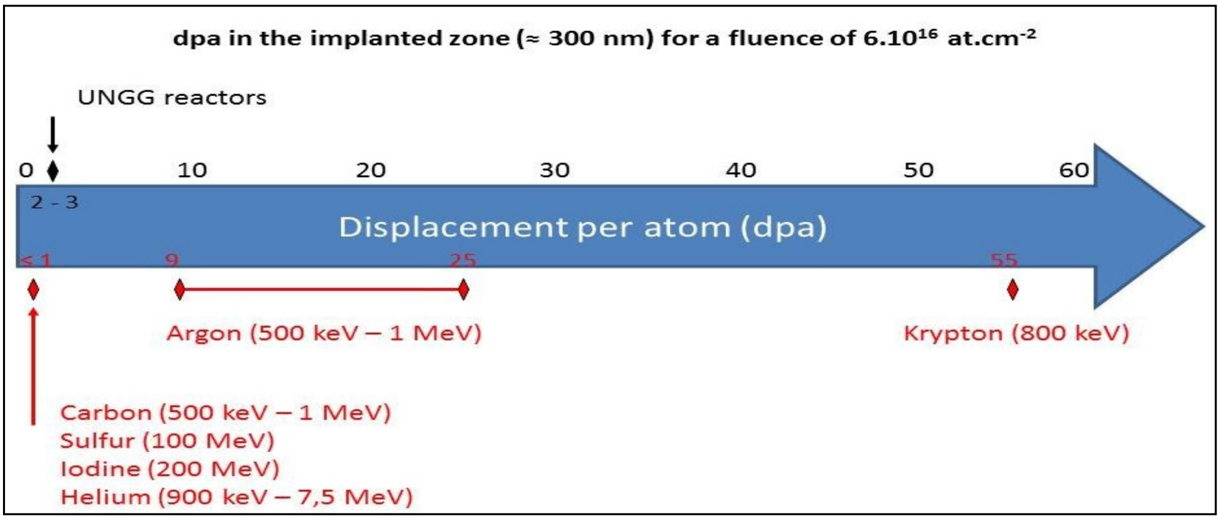


Figure 2.1.2: Displacements per atoms for different ions and ion energies.

Results and discussion

The irradiations reported in this document aim at studying the effects of gas radiolysis as well as the effects of electronic excitations on ^{14}N or ^{13}C release. The study of the ballistic effects is underway and will be presented in the next report.

It is important to note that for all irradiation experiments, the range of the irradiating ion was greater than that of the implanted species. In other words the irradiating ion stopped far beyond the implanted zone. This allowed creating only electronic damage in the implanted zone avoiding ballistic damage in this zone.

Behaviour of ^{14}N

After implantation of the samples with ^{14}N, the samples have been annealed on one hand and irradiated under temperature on the other hand.

The implantation of these samples induced damage in the graphite structure that has been quantified to around 8 dpa at the Rp. This value is of the same order of magnitude as that of radioactive graphite from UNGG at reactor shutdown (around 2-3 dpa).

The samples have been subsequently 1) annealed; 2) irradiated and annealed at the 4 MV VDG facility using He^{2+} or Ar^{3+} ions.

1) The annealing has been carried out in vacuum or inert atmosphere up to 500°C. The results show that annealing leads to a loss of the implanted ^{14}N around 40%.
2) The irradiations have been carried out:

- **With He^{2+} ions** in a gas representative of the cooling gas (mainly CO_2) to evaluate the synergetic effects of gas radiolysis + irradiation of the graphite sample.
  The samples were in all cases heated at 500°C which is the maximum temperature of graphite reached during operating of UNGG.

- **With Ar^{3+} ions** in vacuum to evaluate the effects of irradiation only in the graphite sample.

For the irradiation experiments carried out with He^{2+}, three types of experiments have been carried out. The energy of the beam was tuned in order to stop:

i) in the gas far from the graphite surface,
ii) at the gas/graphite interface,
iii) in the graphite sample; in this case, the He^{2+} ions stopped in the graphite beyond the implanted zone. Therefore, some energy of the He^{2+} ions was also deposited into the graphite. We calculated that the value of this energy in the implanted zone was around 650 keV and thus the value of the electronic stopping power in the implanted zone was around 400 keV/µm (corresponding to an energy deposited into the implanted zone around 110 J), this value being a mean value occurring in UNGG reactors (Figure 2.1.1).

In all cases, the dose deposited in the gas ranged between 13 and 15 MGy.

The results show that:

- The first configuration did not enhance the implanted ^{14}N loss compared to annealing solely.

- The second one resulted in the graphite surface corrosion due to the free radicals produced during the radiolysis of the gas. Some release of ^{14}N was also observed and was attributed to the corrosion of the surface.
- In the third configuration, no corrosion of the graphite surface occurred (because the radicals were formed far from the outer surface) and the loss of ^{14}N profile was of the same order as during annealing only.

For the irradiation experiments carried out with Ar^{3+} (for which the graphite only was irradiated) an important impact of the electronic excitation on the migration of ^{14}N was evidenced. This effect is illustrated in Figure 2.1.3 for an irradiation of implanted graphite samples carried out with Ar^{3+} ions of 6 MeV on SLA2 samples. The irradiation lasted around 7 h and the fluence was around $2x10^{15}$ Ar^{+} ions/cm^2. The electronic stopping power in the implanted region was around 3000 keV/µm (corresponding to an energy deposited into the implanted zone around 560J), this value being a bit higher than the maximum value reached during neutron irradiation in the case of UNGG (around 1600 keV/µm). This figure displays the ^{14}N concentration profiles in function of depth measured by SIMS on the as implanted sample and the irradiated one. The profiles on the irradiated sample have been measured on two different zones (profile 1 and profile 2).

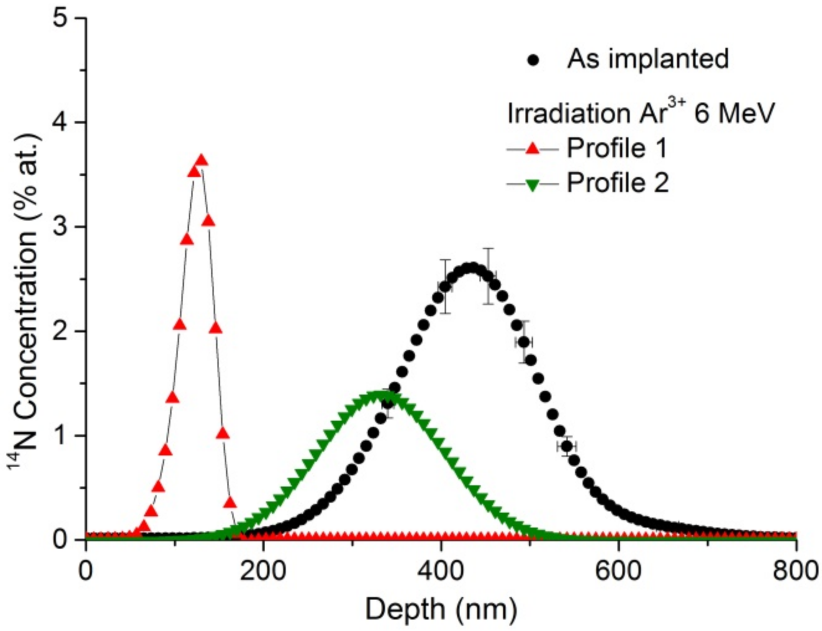


Figure 2.1.3: ^{14}N concentration profiles of as implanted and Ar $^{3+}$ irradiated samples.

It is important to remind that the irradiation has been carried out under secondary vacuum and that the microscopy observations did not reveal any “corrosion” of the surfaces. Thus, according to their position and the respective areas of the profiles compared to the as implanted one, it appears that irradiation induces the release of nitrogen as well as its transport towards the surface. The loss of ^{14}N may reach 65%. Complementary X ray photoelectron spectroscopy (XPS) analyses have been carried out on the irradiated samples at “Science et Surface” by C. Grossiord using a PHI Quantera SXM facility. The results have shown that nitrogen tends to form carbon nitride complexes and several compounds such as C-N, C=N and C≡N.

Finally, extrapolating our results to the behaviour of ^{14}N as precursor of ^{14}C, allows concluding that, prior to its activation, temperature and irradiation effects tend to induce nitrogen migration towards the graphite “surfaces” (as pores for instance) where it is partially released. This occurs all the more as the graphite structure is disordered.

Consequently, temperature + irradiation, as well as the radiolytic corrosion of the graphite surfaces, should lead to the impoverishment of the nitrogen inventory.

Behaviour of ^{13}C

After implantation of the samples with ^{13}C, the samples have been annealed on one hand and irradiated under temperature on the other hand.

The implantation of the samples with ^{13}C resulted in a disordering of the implanted zone around 6 dpa at the projected range Rp. After implantation, the samples have been annealed on one hand or irradiated under temperature on the other hand.

The samples have been subsequently 1) annealed; 2) irradiated and annealed at the 4 MV VDG facility using He^{2+} or Ar^{3+} ions on one hand and at the Tandem facility of Orsay using S^{9+} ions on the other hand.

1) Annealing experiments:

The implanted samples have been annealed from 500°C to 1600°C under vacuum or inert gas. The results (not shown here) put forward that the implanted ^{13}C does not diffuse for temperatures lower than 1600°C. A slight diffusion occurred at 1600°C and the diffusion coefficient could be quantified at around $D \sim 10^{-19} m^2/s$. This diffusion occurs at the same time as the progressive reordering of the graphite structure, as shown in Figure 2.1.4 that compares the Raman spectra of annealed samples to the virgin and the as-implanted SLA2 samples. The spectra were normalized to the G band intensity of the virgin sample. All the spectra display three main bands: the G band centered at a Raman shift around 1580 cm^{-1} corresponding to the ‘‘graphite’’ band (E_{2g} mode) and two ‘‘defect’’ bands, called D1 and D2, centered respectively around 1350 cm^{-1} and 1620 cm^{-1}. We notice that the implantation process results in a strong increase of the ‘‘defect’’ bands. Indeed, the implantation results in sp^2 bond breaking and possible sp^3 carbon hybridization. Subsequent annealing reorders the graphite structure. This corresponds in Figure 2.1.4 to a decrease of the defect band intensity and a decrease of the G band width: the higher the annealing temperature, the higher the reordering of the implanted graphite structure. This reordering proceeds slowly from 500°C to 1300°C. It is far more intense at 1600°C even if the virgin graphite structure is not recovered and would need higher annealing temperatures. Thus the observed diffusion of ^{13}C might be linked to the progressive recovery of sp^2 carbon.

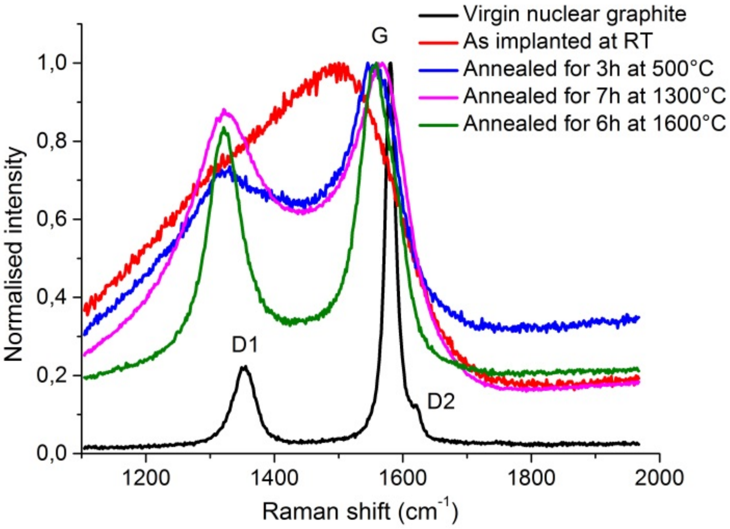


Figure 2.1.4: Raman spectra of virgin, as implanted and annealed samples.

2) Irradiation experiments : the irradiations have been carried out

i) **With He^{2+} ions** in a gas representative of the cooling gas (mainly CO_2) to evaluate the synergetic effects of gas radiolysis + irradiation for the three configurations.
The samples were in all cases heated at 500°C which is the maximum temperature of graphite reached during operating of UNGG.

ii) **With Ar^{3+} ions** in vacuum to evaluate the effects of irradiation only in the graphite

iii) **With S^{9+} ions** in vacuum at the Tandem facility of Orsay of 100 MeV.

i) **For the He^{2+} irradiations** and whatever the irradiation configuration, we did not observe any migration of then implanted ^{13}C. Figure 2.1.5 displays the ^{13}C profiles obtained for the third configuration (where the graphite was also irradiated) for two respective total deposited doses of 7 MGy and 14 MGy irradiation doses.

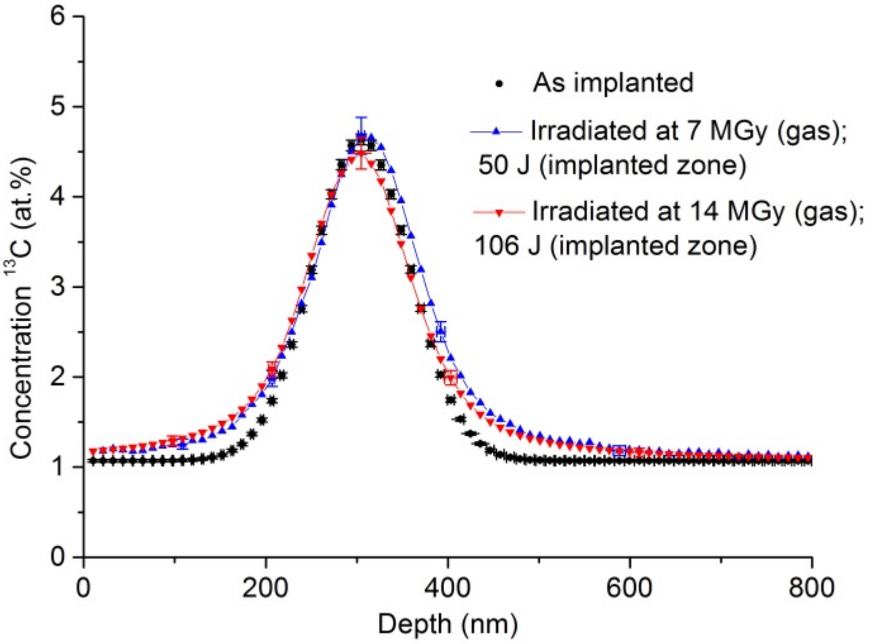


Figure 2.1.5: ^{13}C concentration profiles of as implanted and He^{2+} irradiated samples.

i) **Irradiation with Ar^{3+} ions** have also been carried out but unfortunately, due to a technical problem, we could not obtain any results on ^{13}C release. However, we could obtain the Raman spectra on the irradiated samples. Figure 2.1.6 compares the Raman spectra of annealed samples, He^{2+} irradiated samples (at 500°C) and Ar^{3+} irradiated (at room temperature) samples to the as-implanted one. This figure shows the important role played by the energy deposited into the graphite for the reordering of its structure. In particular Ar^{3+} irradiation induces a strong reordering even at room temperature compared to He^{2+} irradiation or annealing alone.

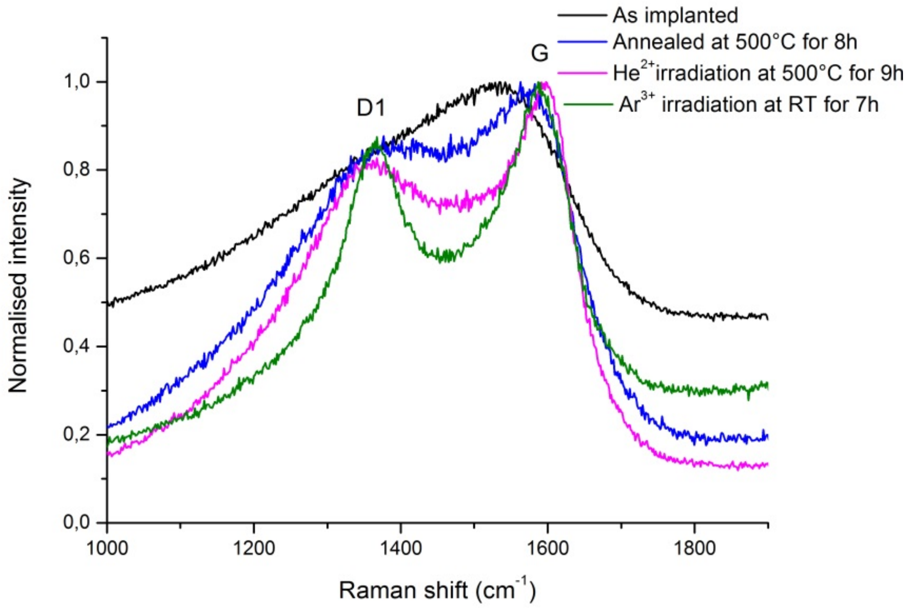


Figure 2.1.6: Raman spectra of virgin, as implanted, annealed samples and He^{2+} / Ar^{3+} irradiated samples.

ii) **The irradiations with S^{9+}** ions were carried out on HOPG samples. The electronic stopping power was around 3700 keV/µm and the temperatures of the samples varied from RT to 1000°C. The results are shown on Figure 2.1.7 and 2.1.8. Figure 2.1.7 displays the ^{13}C concentration profiles measured for the as-implanted sample, the sample irradiated at room temperature and the samples respectively irradiated at 500°C and 1000°C.

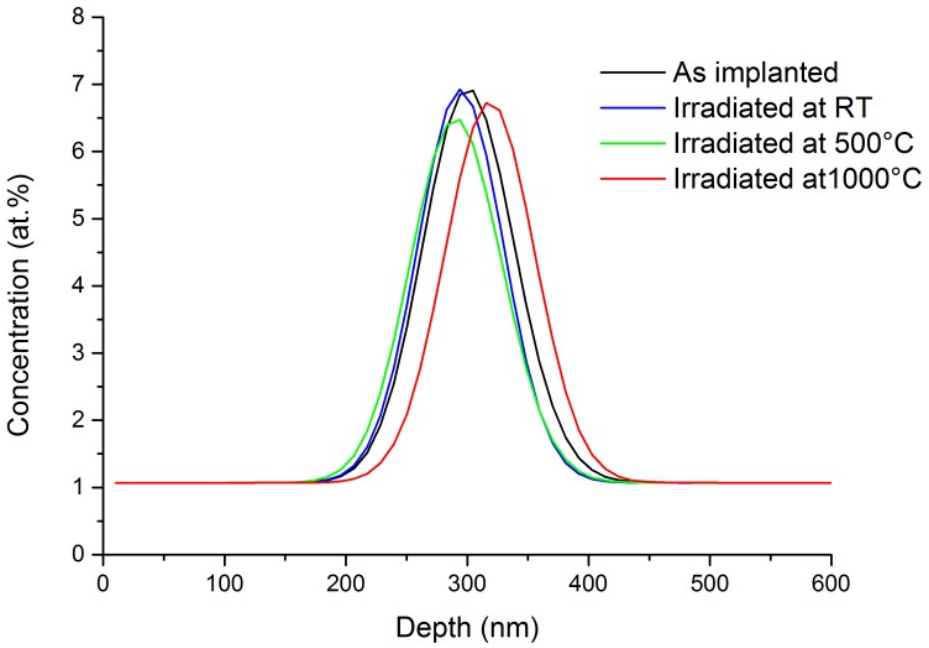


Figure 2.1.7: ^{13}C concentration profiles of as implanted and irradiated samples at RT, 500°C and 1000°C.

Moreover, Figure 2.1.8 displaying the variation of the areas corresponding to each peak shows that the areas of the peaks are similar taking into account the measurements accuracy.

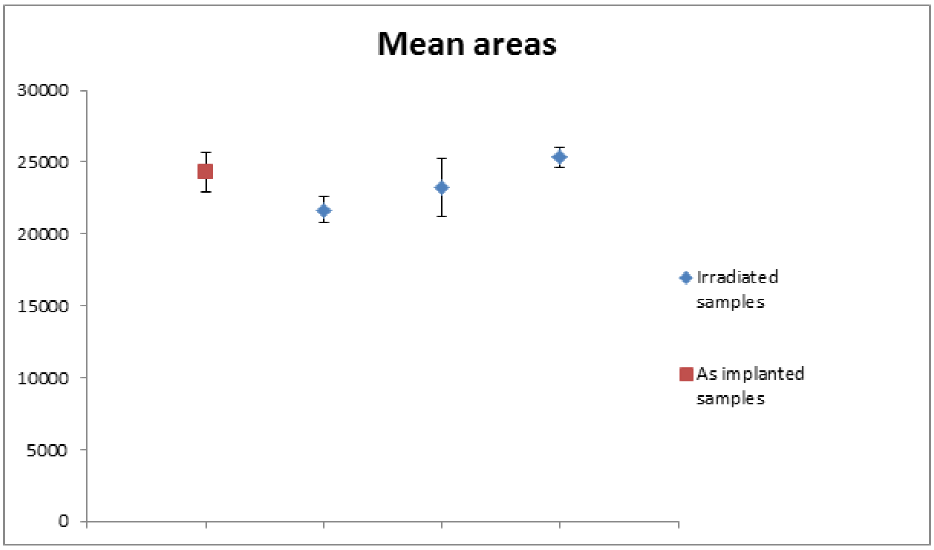


Figure 2.1.8: Comparison of the peak areas of the as implanted an irradiated samples.

Conclusion

Finally, we may conclude that thermal annealing in inert atmosphere does not induce any migration of ^{13}C up to 1600°C, even if the structure of the graphite is initially disordered (around 6 dpa). At 1600°C a slight diffusion occurs. This diffusion might be linked to the reordering of the graphite structure and the “reorganization” of the implanted ^{13}C into carbon clusters.

Concerning irradiation with Ar^{3+} ions, carried out on SLA2 nuclear graphite samples with an electronic stopping power around 3000 keV/µm, they induce a reordering of the graphite structure. We could not obtain any value for ^{13}C release but we can assume that ^{13}C rearranges into new carbon structures as for example clusters.

Moreover, irradiations with S^{9+} ions carried out on HOPG graphite samples with an electronic stopping power around 3700 keV/µm show that the implanted ^{13}C does not migrate even at 1000°C. We still have to check the structure using Raman but it is also highly probable that the implanted ^{13}C rearranges into new carbon structures as for example clusters.

2.2 Lithuanian Energy Institute (LEI) summary

LEI participates in Tasks 5.1, 5.2 and 5.5 within the WP5 of the CAST Project.

During the first year of the CAST Project, LEI concentrated on the performance of the 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" and Task 5.2 – "Characterisation of the C-14 inventory in i-graphites". For the Task 5.1, LEI have to review the outcome of CARBOWASTE in the national context and based on that to provide the input for deliverable D5.5 "Review of current understanding of inventory and release of C-14 from irradiated graphites". For the Task 5.2, LEI have to model the C-14 inventory in a RBMK-1500 reactor core using new data and the final deliverable D5.17 "Report on modelling of C-14 inventory in RBMK reactor core" is scheduled for the month 42 of the Project.

For the Task 5.1, LEI activities are accomplished. The outcomes from the CARBOWASTE Project were reviewed and summarised for the RBMK-1500 reactor. Based on that, the input for deliverable D5.5 "Review of current understanding of inventory and release of C-14 from irradiated graphites" was produced and sent to the NDA for the incorporation into final deliverable.

For the Task 5.2, LEI activities are ongoing. Following the knowledge gained in the CARBOWASTE Project, IAEA CRP, etc., new models for numerical estimation of RBMK-1500 graphite activation are under development. It is expected, that some sampling of the Ignalina NPP Unit 1 RBMK-1500 reactor graphite stack (blocks and rings/sleeves) will be done in the near future and radiological data of the samples will be available, including data on C-14. Combining these experimental data and numerical modelling for induced activity of C-14, the inventory of C-14 in i-graphite of the whole core of Ignalina NPP Unit 1 reactor could be estimated and well supported. For this, new models for numerical estimation of induced activity (direct activation calculation as well as reverse activation calculation) and are under development.

Gathering of new information relevant to the RBMK graphite activation issues is also ongoing. Results, obtained using aforementioned models and data, will better reflect real situation for RBMK-1500 reactors and contribute to the general knowledge of C-14 generation in graphite.

2.3 State Institution "Institute of Environmental Geochemistry National Academy of Science of Ukraine" (IEG NASU) summary

WP5-related R&D at IEG NASU

IEG NASU is involved in the review of the outcome of the IAEA project investigating conversion of i-graphite from decommissioning of Chernobyl NPP into a stable waste form. IGNS will also provide input on the use of graphite in the RBMK reactor, particularly the decommissioning of each category, classification, volume, weight and activity.

It is intended to draw together relevant existing information on the ^{14}C inventory in irradiated graphite, its form and leaching behaviour and treatment and packaging for geological disposal.

IEG NASU will review characterisation data on the speciation of ^{14}C in RBMK reactor, i-graphites and relevant information from decommissioning projects in Ukraine.

Progress in Task 5.1

The inventory of i-graphite in Ukraine is not made completely. In compliance with the requirements of the regulatory documents, the composition and activities of radionuclides accumulated in structural materials and structures during the operation of the NPP power unit must be evaluated before its removal from service.

At present the reactors of Chornobyl NPP, power units 1, 2, and 3 are shut down (1996, 1991, 2000) and are at the stage of final shutdown or preservation stage.

The waste inventory of irradiated graphite of Chornobyl NPP (Units 1-3) is 5687 tonnes (3732m^3) and of emergency graphite is 700 tonnes in the shelter.

After the shutdown of the RBMK reactor the graphite stack and graphite elements of channels may account for as much as 80% of the total amount of radioactive waste. However, the estimates are to a large extent dependent on the impurity content of the graphite.

Table 1. The waste inventory of irradiated graphite waste of Chornobyl NPP

Group	Volume, m^3	Weight, t	$A_{Specific}$, Bq/g	Brand
Graphite stack	3732	5280	~ E+4 – E+5	GR-280
Graphite rings and bushings	328	372	~ E+4 – E+5	GRP-2-125
Graphite displacer control rods	22	35		GR-93

The mass of i-graphite of those reactors still needs to be quantified in more detail.

The duration of the reactor operation the graphite was in the nitrogen–helium medium, incidents due to leakage of water coolant into the stack occurred.

Three major contamination sources for the graphite are:

- Neutron activation of impurities;
- Delivery of radionuclides as a result of technological incidents during the reactor operation;
- External contamination of the graphite by radionuclides of corrosive origin those are present in the cooling pond (CP) water.

Nuclear graphites have been manufactured from a range of raw materials using different manufacturing processes, this includes differing impurity levels. Original impurities in the reactor graphite include a large number (up to 30) of naturally occurring elements with the concentration 10^{-4}–10^{-6}% by mass, many of which form long-lived radionuclides through the neutron reactions.

Graphite waste management

At the Chernobyl NPP a considerable amount of equipment and special items are used during the Power Units operation. Currently, they are stored in cooling pools, technological shafts, and in a reactors core of Units 1-3. A total amount of these special items (long-length waste) is about 26.000 units. According to the design dimensions of these special items, they are from 6 to 22 meters in length and up to 145 mm in diameter.

Technological channels include 19 pieces of the graphite sleeves and 163 graphite rings.

A 'preferred' decommissioning strategy for Chernobyl RBMK Units 1 – 3 envisages safe storage until around 2045 with dismantling complete by 2064.

Removal device graphite rings and bushings

The primary packaging will be the 165 or 200 litre barrels placed in a concrete container GTZ-2.6. The limiting values of total activity in these primary packages should be:

- the 165-litre barrel of long-length special items (cuttings and milling) - 4,32 10^{12}Bq/barrel;
- the 200-litre barrel of graphite of low-and intermediate level (grinding matter) - 4,11 10^{10}Bq/barrel.

- Packages with graphite will be placed in temporary storage (up to 30 years) in an existing store of solid waste;

- Graphite waste emplaced in the storage/disposal container without grouting.

Progress in Task 5.3

IGNS will examine the effect of etching and removing the surface layer of graphite and study the long–term behaviour of 14C in concrete waste packages.

As graphite is bombarded with neutrons, C-14 is produced through neutron capture by carbon-13 (C-13), nitrogen (N-14), and oxygen-17 (O-17) as seen in Equations 1, 2, and 3 [Podruhzina, 2004].

$$\text{N-14} + n \rightarrow \text{C-14} + p \quad \text{(Eqn. 1)}$$

$$\text{C-13} + n \rightarrow \text{C-14} + \gamma \quad \text{(Eqn. 2)}$$

$$\text{O-17} + n \rightarrow \text{C-14} + \alpha \quad \text{(Eqn. 3)}$$

There is far less information of ^{14}C different forms penetration into graphite materials. At the same time the preliminary observation shows that study of radiocarbon penetration process into graphite materials is connected with many difficulties of methodological nature from complex micro relief of surface to wide range in physico-mechanical characteristics.

Removing a graphite material layer by layer can be executed by several ways: cutting, pickling and etc. In the given work the external layers were consecutively deleted by polishing-out and measuring of activity of polished-out material layer after each treatment.

For measuring of activity used technology “vacuum pyrolysis” [Skripkin et al. 1998]:

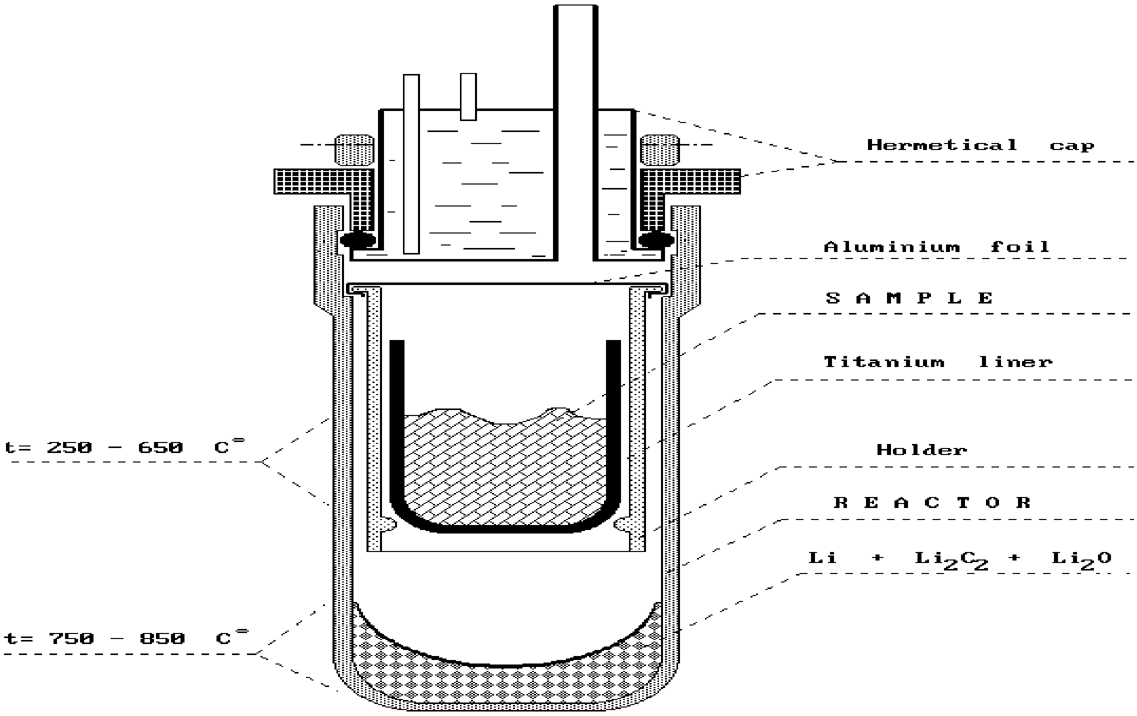
1. Material sample is mixed with manganese dioxide. Addition of manganese dioxide plays an important role. When the temperature is above 550°C the manganese dioxide disintegrates with active oxygen liberation all over the volume of mixture. Oxygen liberation runs quietly, under the broad range of temperatures (550-940°C).

2. Carbon materials therewith are oxidized to carbon oxide and dioxide, and in such kind are absorbed by melted lithium.

3. Resulted lithium carbide is subjected to hydrolysis.

4. Gassing acetylene is converted into benzene on vanadium catalyst.

It allows fractional separation of analysed carbon material during one sample preparation procedure**.** Vacuum pyrolysis is considerable simplification and accelerates LS radiocarbon analyses.



2.4 Regia Autonoma pentru Activitati Nucleare (INR) summary

The main objective of the INR in WP5 is to update the inventory of C-14 in the irradiated graphite arising from TRIGA 14MW reactor thermal column and to define the associated source term, not only as total amount of C-14 but also as inorganic/organic ratio.

In this regard, the INR activities consist in a review of the current knowledge achieved in the understanding the speciation of C-14 from irradiated graphite used in research reactors and in achievement of experimental data on C-14 leaching rate and on its chemical forms in the view of deep geological disposal.

Irradiated graphite from TRIGA 14MW reactor was investigated in CARBOWASTE and showed significant C-14 and Cl-36 activities that impose its deep geological disposal. Preliminary performance assessment initially considered for a near surface disposal was based on C-14 release rates in liquid and gas provided by literature. These values are specific to irradiated graphite irradiated under environmental, thermal, irradiation conditions quite different than in the TRIGA 14MW thermal column. Specific data on C-14 release from TRIGA i-graphite are therefore needed to define the source term both as total release rate and as organic/inorganic ratio.

The INR activities are part of the following tasks:

- *Task 5.1- Review of CARBOWASTE and other relevant R&D activities to establish the current understanding of inventory and release of14C from i-graphites*
- *Task 5.3 Measurement of release of14C inventory from i-graphites*
- *Task 5.5 Data interpretation and synthesis – final report*

Progress in Task 5.1

The INR objective in this task is to review data on MTR i-graphite in order to identify possible correlations of the C-14 content and its speciation with impurity content and irradiation history.

In Romania, first detailed investigation of the irradiated graphite from the TRIGA 14MW research reactor has been performed under CARBOWASTE project. Combining experimental data on C-14 activity with numerical calculations a preliminary inventory of the C14 was estimated to 3.10^{10} Bq.

The C-14 activity decreases along the thermal column due to the thermal neutron flux attenuation (Figure 2.4.1) from 10^{5}Bq/g in the first row next to the reactor core to 2.10^{2}Bq/g in the middle of the column (Table 2.4.1), but it is quite uniform distributed inside a brick, values ranging between 0.9 -1.9 10^{3}Bq/g being measured on different samples from a graphite brick in CARBOWASTE.

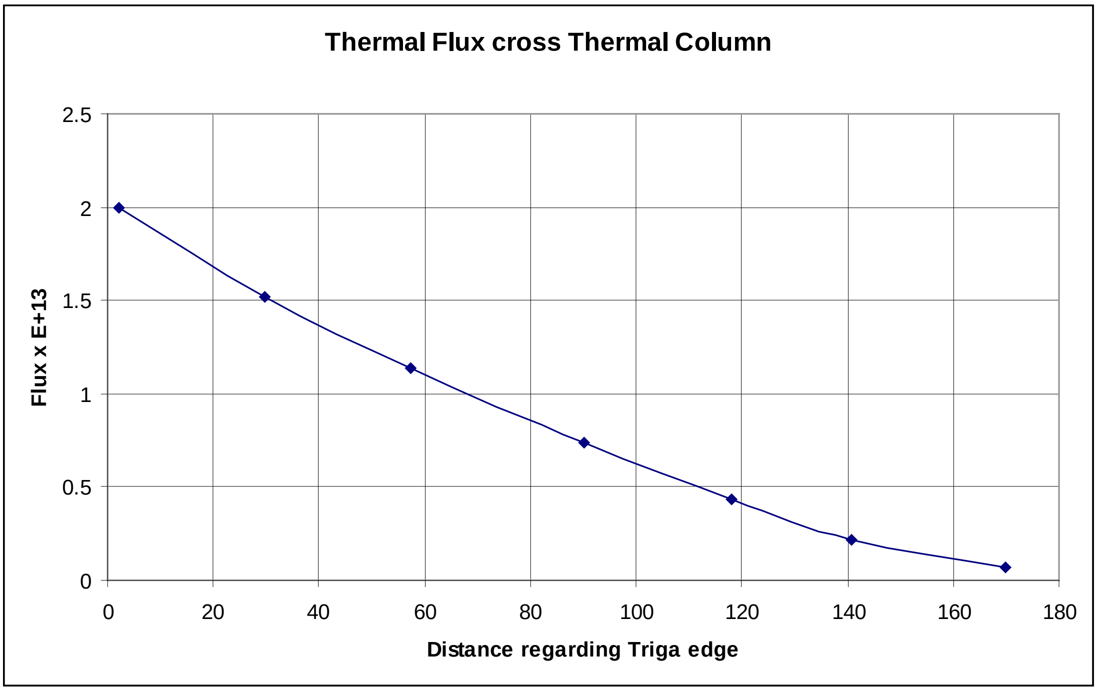


Figure 2.4.1. Thermal flux variation along the thermal column

Table 2.4.1 Predicted C-14 and H-3 activities for different positions along the thermal column

Radionuclide	Predicted Activity (Bq/g)		
	First row	Actual Sample location	Column centre
H 3	3.89E+05	0.973E+04	2.87E+03
C 14	1.12E+05	0.958E+03	2.82E+02

Work done by ICN in CARBOWASTE proposed and assessed a management as a first approach of the i-graphite management the near surface disposal. The C-14 radiological impact assessed using conservative release rates provided by literature does not exceed the dose limit but due to the Cl36 content, deep geological repository has to be considered.

In this content, the INR activities in CAST project aims to define the C-14 source term specific for the TRIGA 14MW thermal column in different disposal environments (since a host rock was not yet selected) with a special focus on the estimation of the C-14 organic/inorganic ratio and on the understanding of their production.

The review of public available results [Jackson and Yates, 2011; Marshall et al., 2011; Carlsson et al., 2014; Takahashi et al.] on C-14 compounds released from irradiated graphite in alkaline environment (specific to a cement-based geological disposal) confirms the CARBOWASTE achievements and showed a large agreement on the following:

- only a very small fraction of the C-14 is released (less than 1%), which can be correlated with the C-14 activated from the nitrogen adsorbed on the surface of the graphite [Jackson and Yates, 2011; Takahashi et al.]

- both organic and inorganic C-14 species are released in alkaline solutions, their amounts depending on the irradiation history and graphite properties [Jackson and Yates, 2011; Marshall et al., 2011; Carlsson et al., 2014]

- C-14 amount released in liquid phase seems to be larger than C-14 amount released in gas phase [Marshall et al., 2011]

- CO_2 dominates the C-14 release in liquid phase, while CO and CH_4 are considered the major compounds released in gas phase [Jackson and Yates, 2011; Marshall et al., 2011; Carlsson et al., 2014]

- either in liquid or gas, C-14 leaching rate decreases in time with 1-2 orders of magnitude, trending to establish a very slow release rate; the process could be quite well described by a first-order kinetics function [Marshall et al., 2011]

- chemical mechanisms leading to $CO_{2,}$ CO^{-}, CH_4 formation are not clearly understood: the graphite could react with the oxygen solved in the water to form CO_2; bulk methane gas is mainly associated with the microbial activity [Jackson and Yates, 2011; Carlsson et al., 2014];

- Canadian studies on the CANDU filling gas (N_2) pointed out that the C-14 atoms created in graphite can be chemically bound with hydrogen, nitrogen or oxygen. They revealed the formation of C-14 atoms which have been quickly converted to simple hydrocarbons or carbon-nitrogen compounds [Carlsson et al., 2014].

Data on the leaching rate presented in the literature were analyzed and the most appropriate kinetics were used to predict the C-14 releases from TRIGA thermal column irradiated samples in order to establish the design parameters of the leaching experimental set up.

ORIGEN simulations have been performed to assess the percentage of C-14 activated from nitrogen based on the N_2 content established in CARBOWASTE [Iorgulis at al., 2013] by inverse method. Only 10% of C-14 is produced from C-13 activation, the rest arising from the nitrogen adsorbed on the pores surface, in the air filling the porosity, and on the graphite sample surface.

Progress in Task 5.3

The INR work in this task is to perform leaching tests on irradiated graphite samples from TRIGA 14MW thermal column in order to determine the leaching rate and to measure the inorganic and organic fractions of C-14 compounds.

These leaching tests will be the first conventional leaching tests performed on thermal column irradiated graphite in environments simulating both cement-based and bentonite-based repository.

Untreated irradiated samples already characterized under CARBOWASTE project will be used for leaching rate and speciation measurements.

The activities performed up to now consisted in the design of the experimental details in order to ensure measurable C-14 releases in hyper alkaline environment, both in liquid and gas phases.

Simulation of the C-14 releases from a sample of 50g with a specific activity of 10^3Bq/g in contact with 300ml of NaOH (Figure 2.4.1) performed using leaching rates reported in literature for BEPO graphite [Marshall et al., 2011] indicated very low amount of C-14 in liquid phase (maximum 2Bq) and even lower amount in gas phase (maximum 0.5Bq). The leaching kinetics considered for these estimations were selected due to the low temperature (40^{o}C) during irradiation, comparable to the temperature environment in TRIGA 14MW reactor (25^{o}C).

Currently, solutions to increase either the measurement sensitivity or the C-14 amount (larger or crushed sample) are investigated.

In connection with WP4 of CAST, efforts are made to realize the experimental set up for the separation of the inorganic and organic compounds.

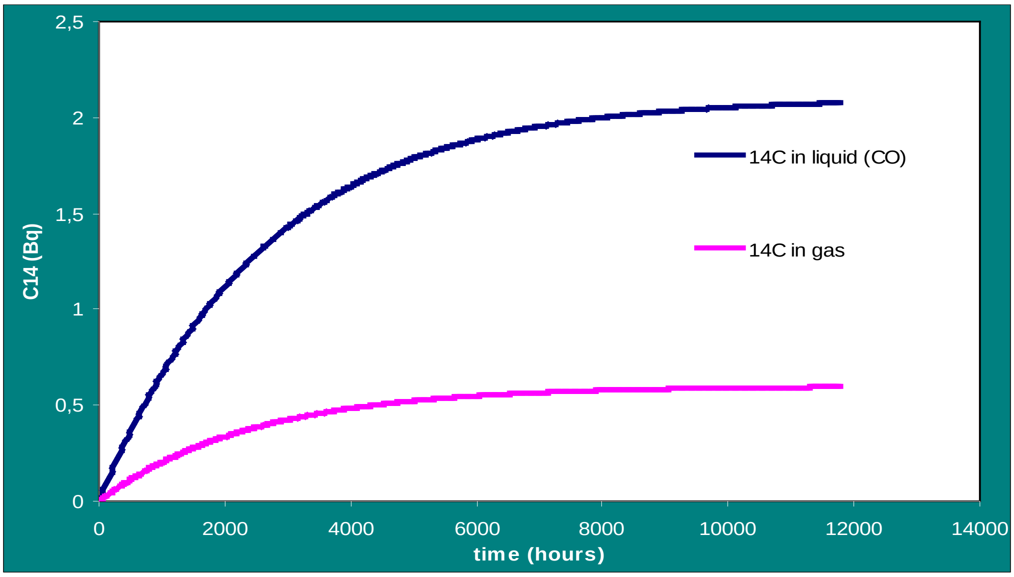


Figure 2.4.1: Simulation of the C-14 releases in liquid and gas phase

Virgin graphite water-uptake tests have been performed on samples with three classes of volumes and weight (1 cm in diameter weighing 5 g, 2.5 cm in diameter weighing 85g and 5 cm in diameter weighing 270g). The uptake function on time showed significant water ingression (compared to the expected hydrophobic behaviour) for all the three groups with a slight dependence on the ratio surface are/volume.

Similar tests will be performed on larger samples (50g) of irradiated graphite.

2.5 Agence Nationale pour la gestion des déchets radioactifs / EDF (Andra / EDF) summary

Andra and EDF are involved in the review of CARBOWASTE and other relevant R&D activities to establish the current understanding of inventory and release of carbon 14 from i-graphites. It is intended to draw together relevant existing information on the carbon 14 inventory in irradiated graphite, its form and leaching behaviour and treatment and packaging for disposal. All partners will review the outcome of CARBOWASTE in their national context.

Andra and EDF are more especially in charge of reviewing the data on carbon 14 release and on the speciation of carbon 14 in French i-graphites. During this first year of the CAST project, the available data on carbon 14 release in French i-graphite were reviewed and presented in deliverable D5.1. The main conclusions can be summarized as follow:

- Carbon 14 leaching rate is very slow for the stack graphite. In most of cases, a quasi-steady state leach rate appears to be achieved after the elapse of around 100 to 200 days. Over that period, the calculated mean radiocarbon leach rate lies between 10^{-11} and 10^{-8} m.day^{-1} (meters per day). The reasons of the variability of this radiocarbon leach rate are still not clear. The studies were carried out on graphite from different origins and with different operational histories.

- A faster carbon 14 leach rate seems to be observed for the sleeve graphite (operational waste) which represents a small part of the total inventory in carbon 14. More investigation is needed to clarify this particular behaviour of carbon 14 of the irradiated sleeve graphite.

- For the experiments reviewed in that report, the nature of the leaching liquid (deionised or lime or soda water) does not evidence any clear impact on the carbon 14 leaching behaviour.

Concerning the implications of these studies for other i-graphite, it seems important to remind that the results obtained on the radionuclide behavior might depend on the history and on the background behind the used i-graphite. The results obtained on the studied French i-graphite cannot be directly and simply extended to other i-graphite.

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

Principle of the Process

The i-graphite from Latina NPP, like as all the graphite coming from moderators exposed to a neutron flux (for Latina NPP is up to 5x1022 n/cm^2), presents a wide range and amount of activation products.

This distribution of activated elements concerns the bulk of the samples, mainly in the closed porosity or between the typical graphite layers. Anyway, there are not usually involved chemical bonds. So that, in order to achieve an exhaustive and valid extraction for activation products, it is important to increase the surface area of the sample. This should allow to the solvent to reach the inner layers/areas (i.e. closed pores, crystallites, etc.) and extract contaminants in solution.

The main idea is to apply an exfoliation-like process on the graphite by organic solvents (liquid-phase exfoliation) to produce un-functionalized and non-oxidized graphene layers in a stable homogeneous dispersion (Khan et al., Choi et al., Hernandez et al. and Bourlinos et al). This process, helped by mild sonication, consists in separating the individual layers in a more or less regular manner. Such a separation, being sufficient to remove all the inter-planar interactions, thanks to the dipole-induced/dipole interactions between graphene layers and organic solvents, results in a dispersion of the graphite in a workable media. This facilitates processing, treatment and easy characterization for the contaminants recoveries (Figure 2.6.1).

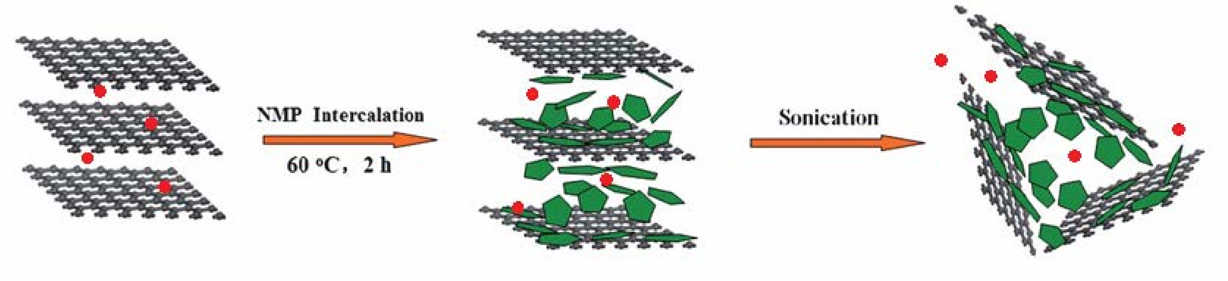


Figure 2.6.1: Representation of the main steps for the graphite exfoliation process promoted by organic solvents and ultrasound assisted

Moreover, no oxidation process is performed nor actions undertaken using super-strong acids. This would lead to non-oxidized products so the graphite would be completely recovered as it is.

The main steps in this process are:

- Organic Solvents choice;
- Low-power Sonication time
- Centrifugation/Extraction
- Removal Efficiency (as % of the recovered activities after treatment with respect to the original values before the treatment)

In order to overcome the van der Waals-like forces between graphite layers to yield a good exfoliation and dispersing the resulted graphene sheets in a stably liquid media, highly polar organic solvents have to be used. As suggested from the scientific literatures, the following ones have been firstly tested:

- N,N-Dimethylacetamide (DMA)
- N,N-Dimethylformamide (DMF)

- N-Methyl-2-pyrrolidone (NMP)

All of them are dipolar solvents, miscible with water, aqueous acid solution and most other solvents; they show good solvency properties, able to dissolve a wide range of chemicals.

As suggested from literature works on graphite exfoliation processes, the optimal ratio powder/solvent has to be equal or superior to 1:100. So we chose 10ml of organic solvent for about 0.1g of each grounded i-graphite sample.

Sonication plays an important role in the experimental process as it facilitates the solubilisation and exfoliation of graphite.

As it mentioned in literature works, the sonication times ranged from 30 min to many hours. The common thing is the bath sonication power should be the lowest possible but there is no reference value. This wide range of sonication time and lack in mention of power is a great problem in reproducibility. The sonication process is sensitive to many factors, as example:

- Sonic energy input to the sample is sensitive to the water level;
- Exact position of the sample in the bath;
- Volume of the dispersion undergoing to sonication;
- Vessel/vials shapes.

Due to this equipment-related variability the results could differ and be critically depending on the sonication time.

In this work, we have chosen from 3 up to10 hours with a variable 100W Sonication Bath (power variable within the range of 30-100%) and 37Hz frequency.

Although the right centrifugation rate should be widely tested in order to remove all large aggregates to be reprocessed by following exfoliation step, in this work we chose a low centrifugation rate (500rpm) followed by a filtration step. The supernatant liquid phases coming from the centrifugation are filtered on PVDF Filter membranes of 0.10 µm of pore size.

Samples description and preparation

ENEA received 15 cylindrical samples from Latina NPP as part of an agreement between ENEA and SoGIN that applied during the previous European Project CARBOWASTE (see e.g. Capone et al. for further information). They are taken from the drilling of the core in two different radial positions (channel 7 and 8): from each sample were removed both the surface layer exposed to the fuel channel and the innermost layer; the approximate mean weight is 5 g.

The removal of the layer exposed to the channel ensures that the activity present in the sample is representative only of the contribution due to neutron activation.

In Table 2.6.1 the masses of the samples, after the outer layer removal, are reported; the mean diameter is 1.7 cm and the mean height is about 1.0 cm (see Figure 2.6.2).

Ch. 08F08							
A1/C3	**A1/C4**	**A1/I2**	**A1/I3**	**A1/S1**	**A1/S2**	**A1/S3**	
3.5476	4.4188	4.1437	4.2189	2.0567	3.9708	3.5290	
Ch. 07S07							
G2/C3	**G2/C4**	**G2/I1**	**G2/I2**	**G2/I3**	**G2/S1**	**G2/S2**	**G2/S3**
3.3065	3.7149	3.3451	3.6853	3.5436	4.1867	4.3726	3.9471

Table 2.6.1: Irradiated-Graphite Samples weights in grams (g)

As mentioned, seven samples come from the Channel 8 (08F08), while the other eight from Channel 7 (07S07); for each of these 2 groups, the samples come from different level named: *S*, Upper, *C*, Central and *I*, Lower.

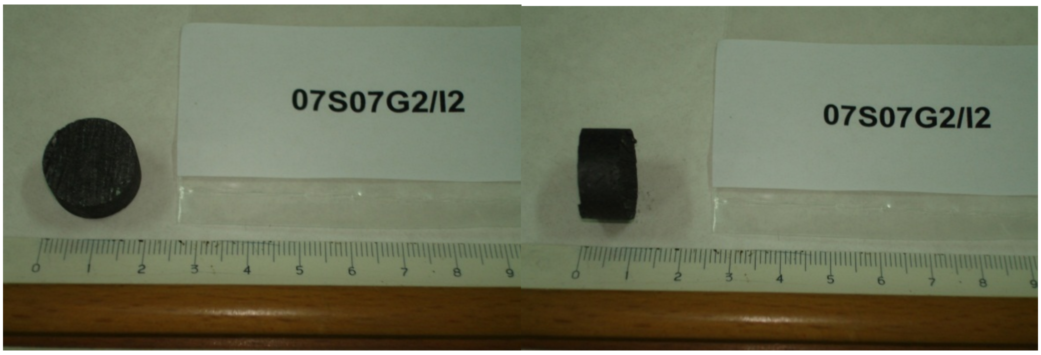


Figure 2.6.2: One of the i-Graphite samples from Latina NPP

All the samples used in this work (non-irradiated and irradiated) are firstly crushed by a miller with titanium knives and then finely grinded by a miller with ceramic knives. The graphite powder obtained is sieved through a 0.5 mm mesh sieve to remove the larger particles. From each of all samples a representative homogenous aliquot were taken and weighted.

Radiocarbon preliminary determination

Radiocarbon has been measured by Liquid Scintillation Counting after pre-treatment of an aliquot of each samples (about 0.12g/sample) by wet acid oxidation with H_2SO_4-HNO_3-$HClO_4$ mixture at 200°C in closed equipment (Figure 2.6.3) under inert gas-flow (N_2) (Lehto et al.). The ^{14}C (as CO_2) were trapped in washing bottles with Carbosorb E (Perkin Elmer). The solutions obtained are completely clear and colourless. An aliquot of each solution is taken has been added with scintillation cocktail and measured by Liquid Scintillation Analyser HIDEX 300SL TDCR in dual-label mode with $^{3}H/^{14}C$ reference standards (L'Annunziata).

The results are shown in Table 2.6.2.

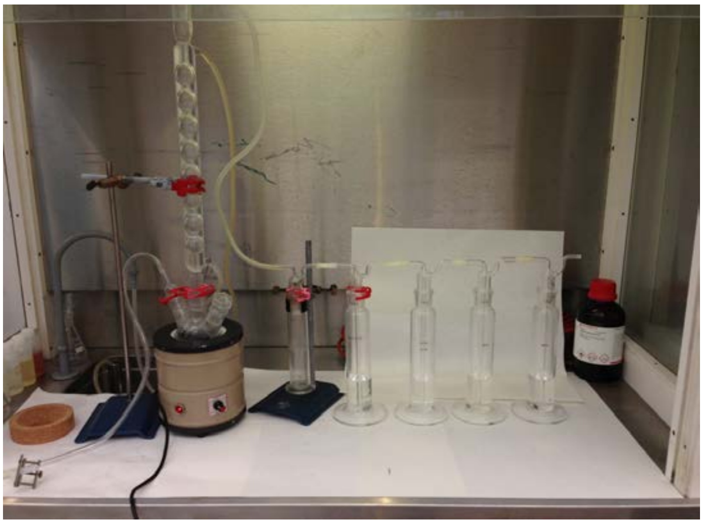


Figure 2.6.3: Wet oxidation apparatus for ^{14}C analysis

Sample	Bq/g	Unc.
08F08A1/C3	**312,9**	±12.1
08F08A1/S3	**306,2**	±7.5
07S07G2/S3	**1467,7**	±7.8
07S07G2/S1	**793,9**	±11.7
08F08A1/I3	**260,9**	±2.2
07S07G2/C3	**1471,6**	±9.1
08F08A1/S1	**160,4**	±12.5
07S07G2/S2	**1497,7**	±7.5
08F08A1/C4	**82,2**	±6.1
07S07G2/I3	**237,1**	±9.6
07S07G2/C4	**238,9**	±9.7
08F08A1/I2	**167,8**	±13.0
08F08A1/S2	**72,1**	±4.7
07S07G2/I1	**292,7**	±7.2
07S07G2/I2	**1241,3**	±11.1

Table 2.6.2: Radiocarbon characterization of the Latina NPP i-Gf samples (by LSC)

First experiments and Results

We started to test the process considering three common and widely used dipolar solvents, as mentioned in the chapter 1 of this report, for their good solvency abilities:

a) N-Methyl-2-pyrrolidone (NMP)

b) N,N-Dimethylacetamide (DMA)

c) N,N-Dimethylformamide (DMF)

As first trial, we performed a sonication bath for 1 hour in a 35W power device on sample of about 0.1 g of non-irradiated graphite in 10 ml of each solvent.

After sonication, the solution appear grey to dark in colour without a distinguishable sedimentation (Figure 2.6.4.a). They are left standing for a day with no change in colour. After that, they are centrifuged for 1 hour at 500 rpm (Figure 2.6.4.b).

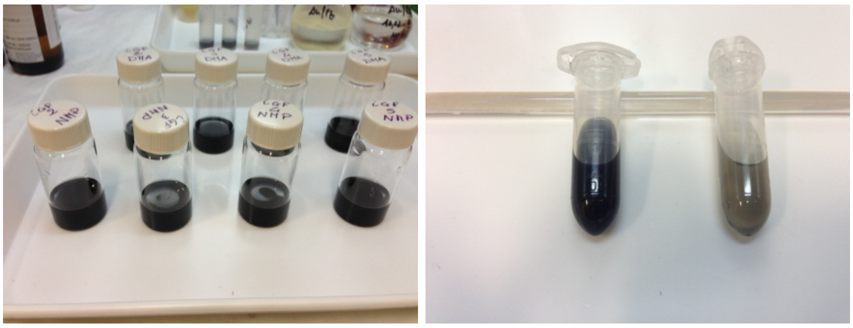


Figure 2.6.4: a. Samples of i-Gf after exfoliation, b. An exfoliated sample of iGf solution before (left) and after (right) centrifugation

All the solution/dispersion are separate from the sedimentations and these last ones are analysed by Electronic Microscopy with a SEM Microscope JSM-5510LV JEOL. The results are shown in Figure 2.6.5.

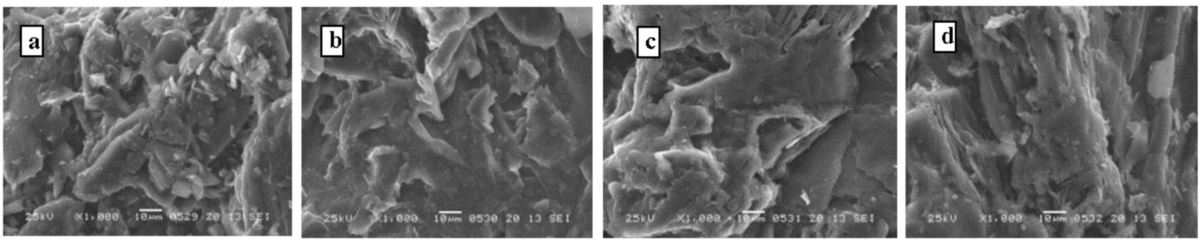


Figure 2.6.5: The SEM images: a) non-irradiated graphite (Virgin Graphite, VG) before organic solvent sonication; b) after 1hour in NMP; c) as in b) but in DMA; d) as the previous but in DMF.

A global smoothing action made by the solvent plus sonication is remarkable on all the samples treated, as we can observe on the rounded edges presents in the all three tests (b, c and d) with respect to the un-treated virgin graphite (a). Only the sample treated with DMF shows exfoliated areas. This is encouraging to go on in this direction and verify the influence of the sonication time.

At this purpose, we started a sequence of tests at different sonication times (3, 7 and 10 h) all in DMF. The solution/dispersion has been analysed by Laser-Raman Spectrometry (Jorio et al.).

The Raman spectrometer is an i-Raman Plus B&WTek Inc. with a CCD detector array. The sampling head is a micro-Raman setup equipped with a notch filter for rejection of elastically scattered light, and coupled to the monochromator-detector assembly by an optical fibre. The objective is a 80x allowing to focus the 532 nm laser 40mW power excitation light to an approximately 3 µm large spot.

A sample of reference graphite is compared to the dispersed in DMF after a combined sonication bath of 7 hours at mild power. The spectrum obtained is in Figure 2.6.6.

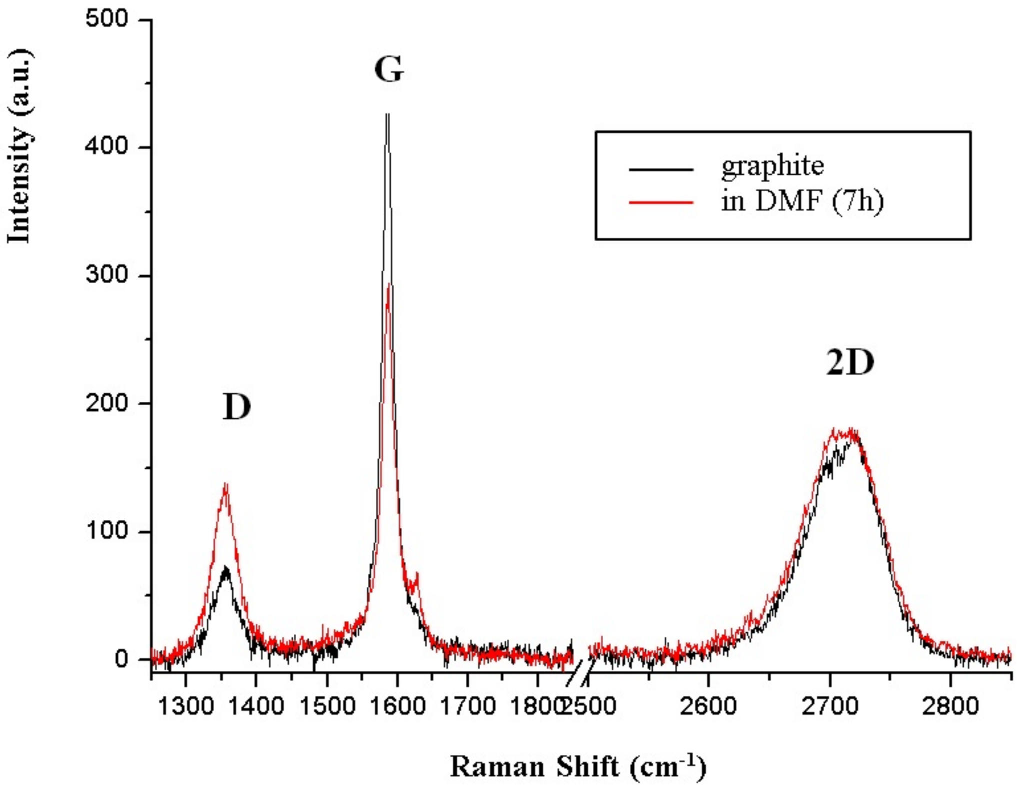


Figure 2.6.6: Raman spectrometry comparison "Reference vs. DMF (7h)"

This shows that the peak at 1350 (D-band) for the 7h/DMF sample is more intense with respect to graphite. This gives evidence of the presence of defects, that is, either edges or topological defects in the sheets. The ratio (I_{2D}/I_G) between 2750 (2D-band) peak and 1600 (G-band) is increased, that is a minor number of layers with respect to original graphite. The 2D band (2750) is indicative of the number of layers, but the broadening reveals an inhomogeneous distribution of the thicknesses.

The same sample at 7h/DMF but diluted in water is compared with respect to graphite. The resulting spectrum is in Figure 2.6.7.

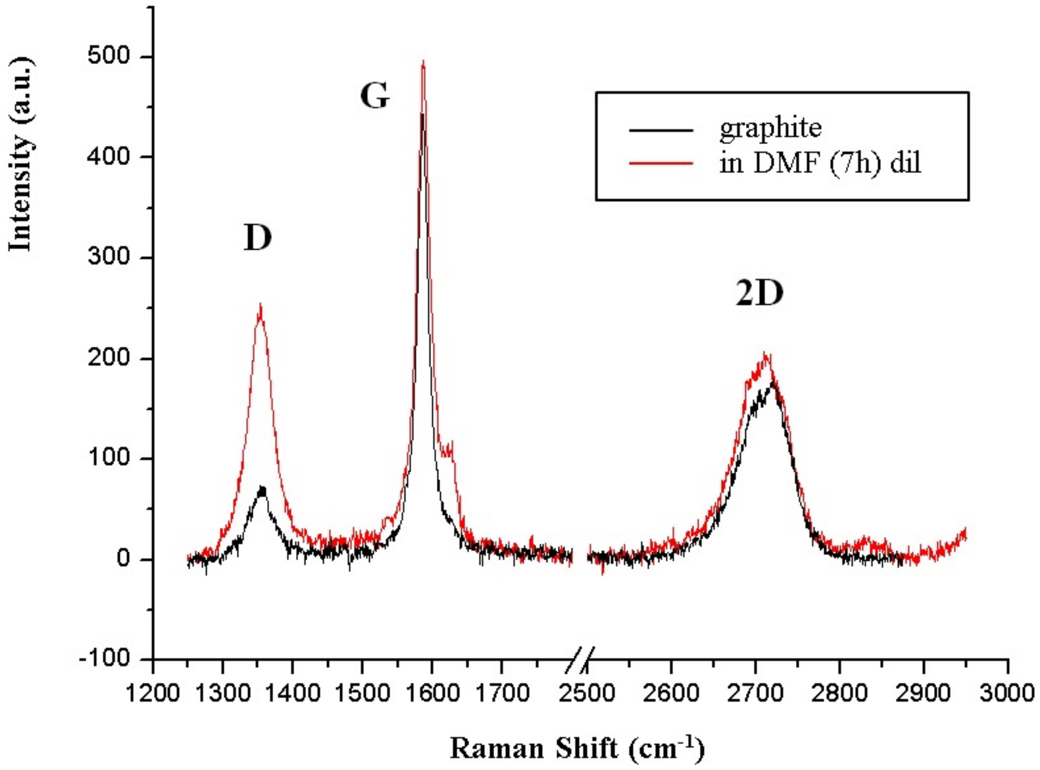


Figure 2.6.7: Raman spectrometry comparison "Reference vs. DMF (7h) diluted"

An increasing disorder and defects are confirmed as it comes from the greater D-band (1350) than graphite one. The ratio I_{2D}/I_G, indicative of the number of layers, reveals an inhomogeneous distribution of the thicknesses (anyway slightly minor than original graphite).

The sample at 7h/DMF is now compared with the 10 hours sonicated in DMF and its spectrum is shown in Figure 2.6.8.

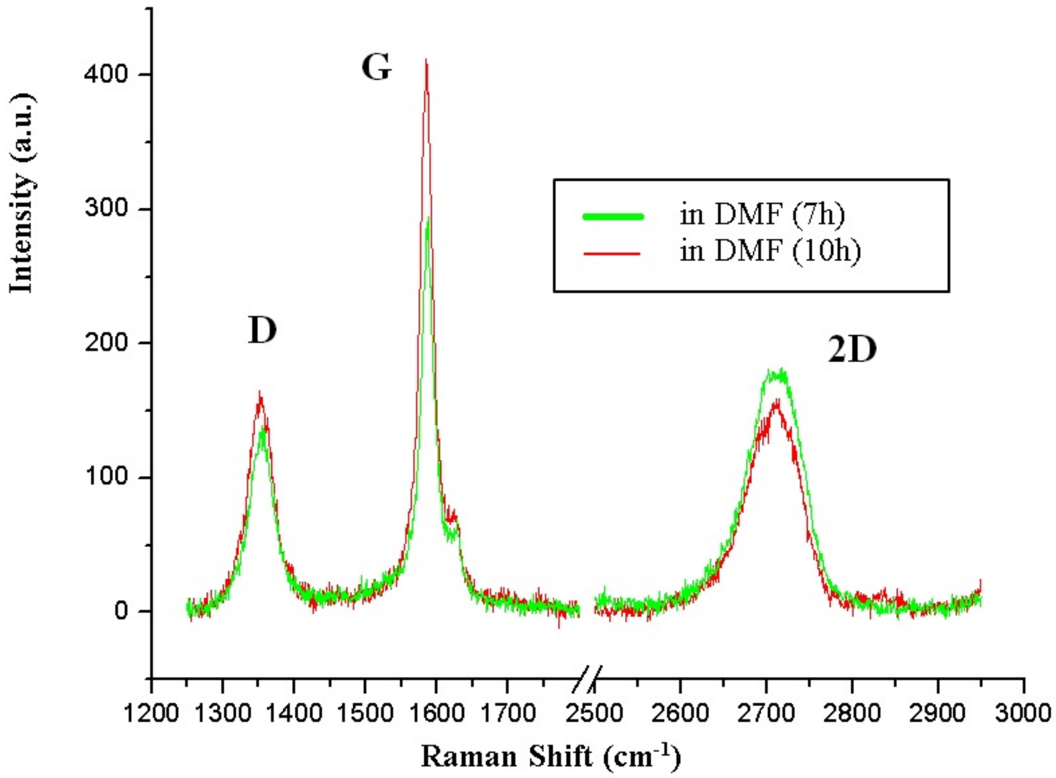


Figure 2.6.8: Raman spectrometry comparison "DMF (7h) vs. DMF (10h)"

It is evident that increasing sonication time leads to a further increase in I_{2D}/I_G and I_D/I_G ratios. This means more disorder and thinner sheets in the solution.

Naturally, all the samples considered are strongly inhomogeneous so all the measurements are dependent on the spot selected, however two effects are worth to be noted:

1) Increased disorder (due to the introduction of new edges as the sheets are cut)

2) Decreased thickness due to the minor layers with respect to the original graphite.

These results seem to be encouraging toward this way to treat the contaminated graphite. The capability of this process to solubilise graphite and remove contaminants seems to be promising and will be better studied in the next years.

Future activities

Thanks to the encouraging preliminary results obtained in this new exfoliation/decontamination in organic solvent route, it will planned a complete set of experiments to better define and set up the right process parameters. At this purpose, it will well defined:

- Time of sonication; it will studied a good compromise between useful time and best exfoliation degree through a set of different batch experiments;
- Good organic solvent/solvents mixture, to gain the easy and economical way to exfoliate the graphite and free the contaminants in solution;
- Apply a liquid-liquid extraction by mean of aqueous/weakly acid solution, to extract contaminants from organic solvent; this would permit a possible continuous extraction process;
- Define the degree of decontamination of the whole process to test the effectiveness and efficiency of this newest way.

The tests will be performed on i-GF samples just to evaluate the degree of removal for contaminants.

It will be also studied classic strong acid mixtures decontamination approaches in order to test the possibility of "combined" organic solvent/acid mixtures processes to obtain satisfying results and complete the overall decontamination steps.

Summary

An exfoliation-like approach is studied for irradiated nuclear graphite by mean of non-oxidizing organic solvents extraction combined with prolonged ultrasound bath as a possible new decontamination method. The graphite has been exfoliated to extract ^{14}C intercalated between the graphene layers. Three different organic solvents with good solvency properties and water-miscible (N-methyl-2-pyrrolidone, N,N-dimethylacetamide, N,N-dimethylformamide) are tested preliminary non-irradiated virgin graphite and then on 15 samples of nuclear i-graphite from Latina NPP moderator. Characterization by means of

Scanning Electron Microscopy SEM and Laser Raman Spectrometry is performed to evaluate the degree of the exfoliation process. A preliminary characterization of the i-graphite samples in order to estimate the content in radiocarbon ^{14}C is carried out.

2.7 Forshungzentrum Juelich GmbH (FZJ) summary

Juelich is involved in the review of CARBOWASTE and other relevant R&D activities to establish the current understanding of inventory and release of ^{14}C from i-graphites. It is intended to draw together relevant existing information on the ^{14}C inventory in irradiated graphite, its form and leaching behaviour and treatment and packaging for geological disposal.

FZJ will review characterisation data on the speciation of ^{14}C in MTR and HTR i-graphites and relevant information from CarboDISP, decommissioning projects in Germany and the ASSE test repository. FZJ will leach samples, which have undergone decontamination treatments and untreated samples to confirm a labile ^{14}C fraction, rather than slow diffusion of ^{14}C from within the graphite. FZJ and Ciemat, supported by Andra, ENRESA and NDA, will identify the parameters that need to be controlled in leach tests to allow a common comparison of results and compare these to existing methodologies.

It has to be noted that the WP5 work at Juelich is part of ongoing PhD theses, which are scheduled to be submitted in 2015. Authorisation by the PhD candidates is necessary prior to publication or citing of Juelich results.

Progress in Task 5.1

The inventory of i-graphite in Germany is going to be actualized. The overwhelming part of 774 metric tons is stemming from two High-Temperature Reactors (HTRs), which are the AVR in Juelich and the THTR in Hamm-Uentrop. In addition there are more than 25 MTR and teaching reactors containing graphite for the moderator, reflectors and/or thermal columns. The mass of the i-graphite of those reactors still needs to be quantified in more detail.

The disposal of i-graphite in the German KONRAD repository is investigated within the German CarboDISP project, which is complementary to the European CARBOWASTE project. KONRAD is a former iron ore mine, which has been operated from 1961 till 1976. The total ^{14}C activity being allowed for KONRAD is only 4 $*10^{14}$ Bq. With an overall storage capacity of 303,000 m^3 this results in 1.32 *10^9 Bq/m^3, as an average. For the disposal of ^{14}C-waste in KONRAD, different limits for the so-called guarantee values result from safety analyses, which have to be considered. Most restrictive ^{14}C limits arise from safety issues for internal operation (T ~ 50 °C), classified by ^{14}C release from the waste container. If a maximum release of <1% of the total ^{14}C inventory can be guaranteed, the limit is 1.8 *10^{10} Bq per container either individual or in average within a batch of containers. This means that about 22,000 waste-containers will be needed to accommodate the allowed total ^{14}C activity of 4 *10^{14} Bq. Taking as a basis a typical Type V KONRAD-Container volume of 10 m^3, this number of containers corresponds to 70% of the total repository volume. If the 1% limit cannot be kept but 14C releases may range up to 10%, then the maximum ^{14}C activity of a waste container must not exceed 1.8 *10^9 Bq resulting in a ten times higher repository volume which exceeds the KONRAD capabilities. And if ^{14}C release cannot be specified the limit is even more restrictive being 1.8 *10^8 Bq per container. Under this background, the CarboDISP project is focussing on the ^{14}C release mechanisms under KONRAD operating and disposal conditions for German i-graphite waste including irradiated carbon brick, which contains a much higher ^{14}C contamination because of rather high nitrogen concentrations already present in the virgin material.

13 metric tons of i-graphite have been disposed in the ASSE test repository. The 42 drums contain moderator and absorber pebbles. It is assumed that the observed enhanced releases of tritium and ^{14}C may be caused by this material. Details on this issue have been discussed in the ‘Entsorgungskommission (ESK’ and can be found on the website of the ‘Bundesamt fuer Strahlenschutz (BfS)’. Up-to-now, it was not possible to get samples or exact release data and/or information on ^{14}C speciation from ASSE. Such measurements could be of interest for CAST.

Progress in Task 5.2

The i-graphite grades, which are investigated in Juelich are mainly taken from the two research reactors FRJ-1 (MERLIN) and AVR, in Juelich. Small samples were provided from FRJ-2 (DIDO), which recently got the decommissioning licence.

Table 2.7.1: ^{14}C and Tritium in German MTR Graphites

Nuclide	MERLIN	RFR (block 3)	RFR (block 4)	DIDO	AVR
^{3}H [Bq/g]	5.1 E+2	3.8 E+1	9.4 E+2	2.7E+06	6.9 E+5
^{14}C [Bq/g]	4.1 E+2	2.8 E+3	9.9 E+3	9,8E+04	8.8 E+4

Additional graphite (~60kg) from the thermal column of the Russian-built Rossendorf research reactor (RFR) was made available to this project. The characterization of this material has been started, for the two blocks, after dividing the blocks into 3cm disks, which can be more easily handled in the radiochemical laboratory. The granulate from the sawing process has been homogenized and measured by LSC techniques, separately for each block (see Table 2.7.1).

For the Juelich work in CAST, the material of block 4 will be used for leaching and treatment experiments, due to the higher ^{14}C activity in the range of 10kBq/g. The tritium content is quite low as compared to other i-graphites, which were investigated so far. The reason might be that the casing of the thermal column was damaged during operation. This resulted in a significant corrosion of this block in the area facing the highest neutron flux, despite the relatively low operational temperature of ~300°C. Thus, it cannot be excluded that most tritium, as well as a part of the ^{14}C, escaped by this radiolytical corrosion process and excess of humidity.

Hot-spots of β and ɣ activation products have been observed also in the RFR graphite. A depth profile is currently established together with SEM and EDX measurements, to find the reasons for the local accumulations as well as the species of activation products and/or agglomerations of impurities.

The other type of i-graphite, which will be further investigated, is taken from AVR. This graphite shows only insignificant radiolytical corrosion attack, due to its operation under helium. The available material is retrieved from cans of broken fuel pebbles and broken pieces of the reflector. For this material, there is practically no chance to restore the full operational history, except by the determination of activation products. From this reason, only material, which has been collected during the sampling of the side reflector of the AVR will be used and characterized, within the CAST project. However, this material is only available as granulate retrieved during the drilling process.

Progress in Task 5.3

A compilation of information on previous leach tests is underway to establish recommendations on harmonized leaching parameters (Deliverable D5.4). Input from other partners (e.g. D5.1) will be incorporated, when available.

Leach tests have been systematically started mainly with RFR graphite, because there is enough material available, in contrast to other i-graphite samples in Juelich. Additional, tests are performed with AVR graphite, as it shows a quite high specific ^{14}C activity.

The parameters for these tests are varied to cover the influence of dry vs. humid storage and temperatures (RT, 50°C, 70°C) as well as different pH values of the leachates.

The releases from i-graphite under dry conditions are rather low and close to the resolution limits of the ^{14}C detection methods (LSC). This finding has been independently confirmed by measurements of the gas-borne activities in THTR, DIDO and storage drums of the RFR graphite in relation to the overall ^{14}C activity in the enclosed graphite structures

For simulating ‘humid conditions’, water has been added into the leach vials in a way that most of the i-graphite granulate is not directly in contact to the liquid phase. Thus, a saturated air/water gas mixture is interacting with the graphite. The set of data measured so far is indicating a much higher release of ^{14}C into the gas phase, by several orders of magnitude as compared to the dry conditions.

This finding might have an important impact, because i-graphite is sometimes not stored under ‘clinical’ or dry conditions and subject to atmospheric humidity. For this reason, the exposure tests under dry conditions have been stopped and continued after injection of water into the vials with dry i-graphite.

Test with different pH and temperatures are continued. Results will be reported later.

As conventional leach tests are long-term experiments by nature, ‘accelerated leach tests’ have been undertaken to achieve indicative results in a shorter time period.

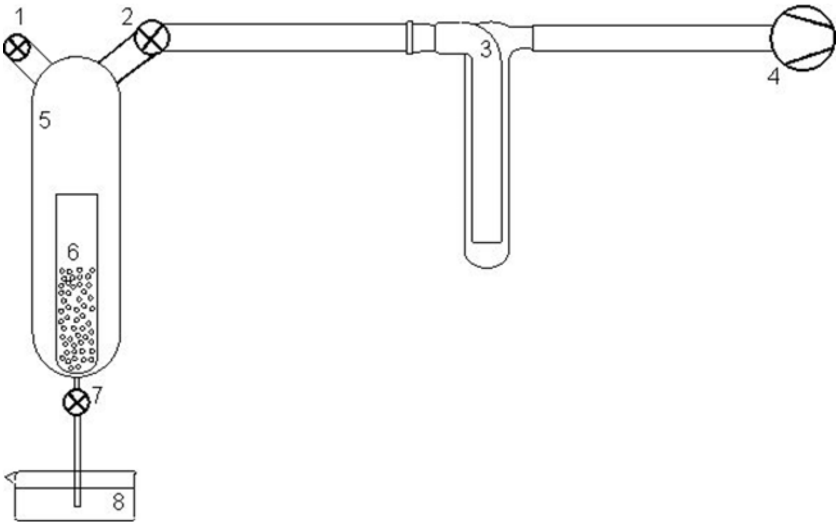
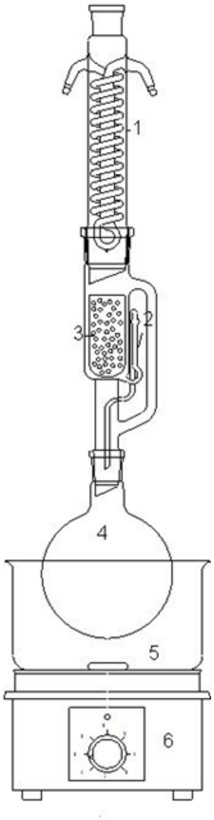


Figure 2.7.1: Apparatus for ‚Accelerated Leaching‘ /developed by L. Kuhne/

1 Valve, 2 Valve and connection to Cold Trap, 3 Cold Trap, 4 Vacuum pump, 5 Reaction vessel, 6 Glass fibre container with graphite sample, 7 Bottom valve for sucking leachates, 8 Leachate reservoir

The idea behind these tests is that the pore water is directly extracted by vacuum, not waiting for slow diffusion processes. The evaporating pore water is then captured in the cold trap and not mixed or diluted in the leachate around the sample. After the evacuation, the sample is shortly contacted with the leachate closing valve 2 by opening valve 7. After a given contact time the vessel is flushed by inert gas via valve 1 and the leachate flows back to the reservoir. Then, the evacuation is started again and the evaporating pore water is again collected in the cold trap. It is expected that the captured pore water has a higher ^{14}C concentration as compared to conventional leach tests and that the detection limit for ^{14}C can be lowered, as only insignificant dilution takes place.

Another type of ‘harsh’ leach tests has been undertaken by applying the Soxhlet extraction process to the RFR graphite and to compare the results to former tests with MERLIN and AVR samples.



1 Cooler

2 Reflux tube

3 Extraction sample

4 Vessel with extraction fluid

5 Heated bath

6 Magnet stirrer

Figure 2.7.2: Sketch of a Soxhlet Extraction Apparatus

Diffusion tests have been started also for the irradiated RFR graphite to determine the diffusion coefficients on a separate way. Other diffusion test are performed with graphite embedded in geopolymer to compare this material against normal concrete.

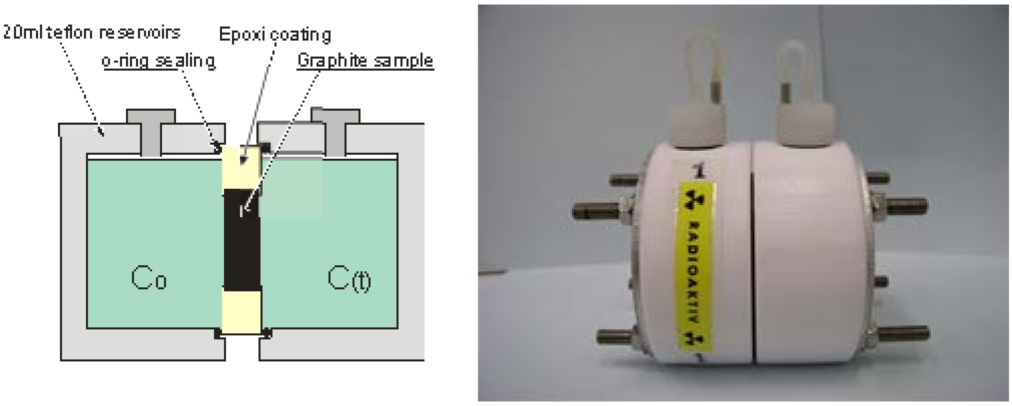


Figure 2.7.3: The apparatus for the diffusion experiments

Extensive water-uptake tests have been performed, showing clearly that virgin graphite exhibits little water-ingression and quasi-hydrophobic behaviour. In contrast, irradiated-graphite as well as heat-treated graphite behaves hydrophilic with high and quick water-uptake. It is intended to investigate this effect for different treatment methods.

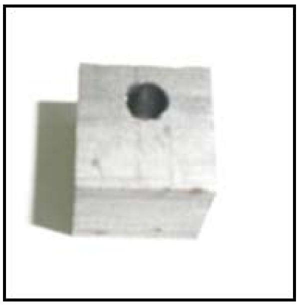
Concerning leach tests on pre-treated i-graphite samples, it has been decided to produce new leach samples from RFR graphite, because the available material from former purification tests is not enough to start systematic leach tests. In addition, leach data of those samples have not yet been measured before treatment, as it is now underway for the untreated RFR graphite. The treatment will be done by successive heating up to 1300°C under inert gas with purging of air after cool-down. This procedure allows following the release rates of ^{14}C, during each heating step. This will be done for granulate and massive RFR samples. The treated i-graphite will then be used for leach tests.

2.8 Centro de Investigationes Energéticas Médioambientales y Tecnològicas (CIEMAT) summary

From October 2013 until July 2014 different preliminary studies have been performed to prepare the leaching experiments on:

- Irradiated Powder Graphite from Vandellós I NPP. These samples of graphite are available in our laboratories, and in
- Graphite Glass Coating Waste Form, IGM (Impermeable Graphite Matrix), material developed by FNAG and which will be prepared in the CIEMAT facilities.

At present, the laboratory is being conditioned to work with the equipment needed to prepare samples of i-graphite such as the sample that is shown in Figure 2.8.1.



20% glass matrix (inorganic binder)
80% graphite
Cubic geometry (1 cm^3)
Weigh: 2 g

Figure 2.8.1. Sample of graphite with IGM

Leaching process and speciation

These preliminary studies have been related with leaching process and speciation. The experiments of leaching which permit to analyse gaseous and liquid phase, originated during the process, are being designed:

- The measurements will be performed, in a polyethylene container (Figure 2.8.2), at:
  - 6 and 24 hours,
  - 7 and 14 days,
  - 1, 2, 4 and 6 months,
  - 1and 2 years

Figure 2.8.2. Container where will be performed the leaching process

At present, the necessary modifications in order to make the taking of samples for the analysis of volatile species are being considered.

➢ Regarding to these experiments, it was decided to carry out the leaching tests in the following media:

- Pure water
- Granite-Bentonitic water (synthetic) at pH = 7 (Table 2.8.1)

Table 2.8.1. Composition of granite-bentonitic water

Compound	**Approximate Concentration mg/L**
Cl^-	6300
NO_3^-	110
SO_4^{2-}	1900
HCO_3^-	30
SiO_2	10
Br^-	10
Ca^{2+}	120
K^+	20
Mg^{2+}	630
Na^+	3500

It is expected starting the experiments with the samples of i-graphite in the last quarter of the year 2014.

- From leaching process two phases (liquid and gaseous) will be obtained. In these phases will be analysed ^{14}C and the organic and inorganic carbon compounds which are formed. The volatile species will be measured with Gas Chromatography coupled with Mass Spectrometry and the dissolved species is under study.

For the analysis of volatile species, at present, all the steps to make the purchase of the necessary equipment are underway, in particular the documentation to buy the equipment GCMS 7890B (Figure 2.8.3) from Agilent has already been prepared. It is foreseen that at the end of this year or in the first quarter of next year it may be possible to work with the equipment.

Figure 2.8.3. GCMS 7890B equipment

This is the same equipment which will be used for the analysis of volatile species formed in the leaching process with stainless steel from José Cabrera NPP (Work Package 2).

If the instrument is not in our laboratories or it has been not possible to make the set-up of the equipment, Ciemat is contacting with the Mass Spectrometry Center of Complutense University to make us the analysis.

2.9 Radioactive Waste Management Limited (RWM) summary

Radioactive Waste Management Limited (RWM), a wholly-owned subsidiary of the Nuclear Decommissioning Authority in the UK, is contributing a summary of the results and understanding from their existing studies on carbon-14 release from irradiated graphite to WP5 of CAST under Task 5.1.

The release and migration of gaseous carbon-14-containing species has been identified as a key issue for geological disposal of intermediate-level radioactive wastes in the UK. There are 9,987 TBq of carbon-14 in the 2010 UK baseline inventory [2010 UK RWI, 2011]. It has been calculated that if carbon-14 is released to the biosphere in the form of methane, then risk guidance levels may be exceeded if the release rate is greater than ~6 x 10^4 TBq/year. The majority of the carbon-14 in the UK radioactive waste inventory is present in irradiated graphite and this graphite has the potential to be a source of gases containing carbon-14 if it undergoes degradation or reaction in a repository environment. Recent scoping calculations have shown that, if it is assumed that the carbon-14 in graphite reacts to form carbon-14-bearing methane ($^{14}CH_4$) and that this migrates as a free gas to the biosphere, there could be a significant impact on the calculated risk from the gas pathway [NDA, 2012]. Therefore an understanding of the release of carbon-14 from irradiated graphite under disposal conditions is of importance to the post-closure safety case for a geological disposal facility (GDF) in the UK.

The current UK baseline for the disposal of irradiated graphite wastes envisages packaging in waste containers that will be emplaced in disposal vaults, which will be backfilled with a cement-based material designed to maintain a high pH environment in the vaults following their resaturation with groundwater. Conditions in a GDF are expected to become anoxic in the post-closure period as a result of the consumption of available oxygen by metal corrosion processes.

In initial experimental studies in the UK, small releases of gaseous carbon-14 were measured from samples of irradiated graphites (from the Windscale Advanced Gas-cooled

Reactor (WAGR)[BASTON et al. 2004, HANDY, 2006] and the British Experimental Pile 0 reactor (BEP0) [MARSHALL et al, 2011, BASTON et al 2012]) on immersion in alkaline solutions. The majority of the carbon-14 remained in the graphite although there was also some release of carbon-14 in a form that was retained in the liquid phase (possibly as the aqueous species $^{14}CO_3^{2-}$ resulting from the release of $^{14}CO_2$). In the measurements on BEP0 graphite, gaseous ^{14}CO and $^{14}CO_2$ were not distinguished, but the fraction of CO_2 in the gas phases was assumed to be negligible, due to its high solubility in alkaline solution. All of these studies were performed under oxic conditions and the impact of anoxic conditions on the speciation of released carbon-14 was not known.

Subsequent work has examined the release of gaseous carbon-14 from irradiated graphite from Oldbury Magnox power station [BASTON et al 2012, BASTON et al 2014]. The main objectives were to:

- determine the speciation and rate of gaseous release of carbon-14 from irradiated Oldbury graphite when in contact with alkaline solution under anoxic conditions and compare this to the release under oxic conditions;
- scope the effects of changes in pH, particle size and temperature on carbon-14 speciation and rate of release under anoxic conditions; and
- provide data and understanding for a possible update to the treatment of the releases of carbon-14 from irradiated graphite in assessment models.

Oldbury Graphite Studies

Experimental Summary

Eight segments (each about 30g in weight) of irradiated Magnox graphite were obtained. The segments had been cut from a cylindrical spacer piece obtained from an installed set that was removed from Oldbury Reactor 2 in 2005, some 38 years after installation.

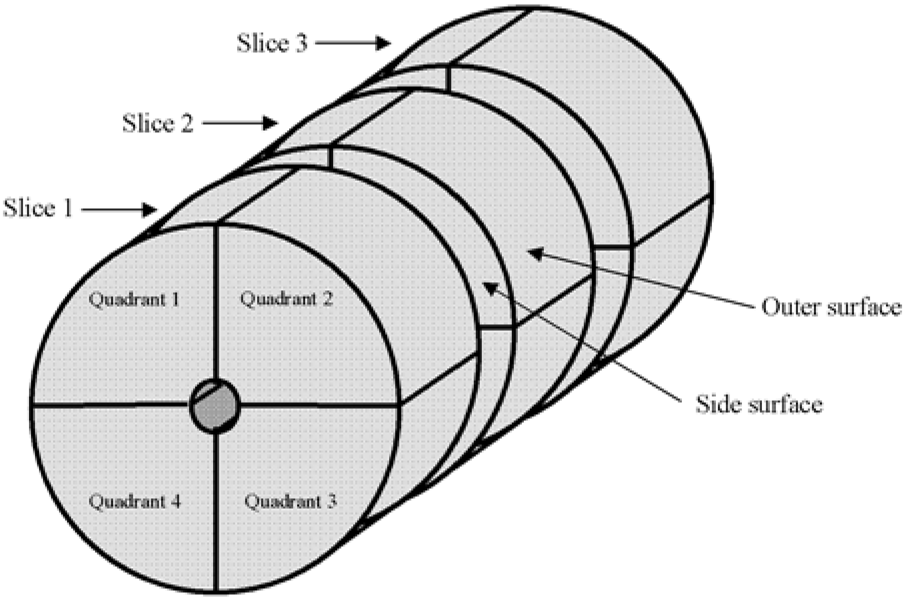


Figure 2.9.1: Schematic diagram of graphite sample locations [BASTON et al 2014].

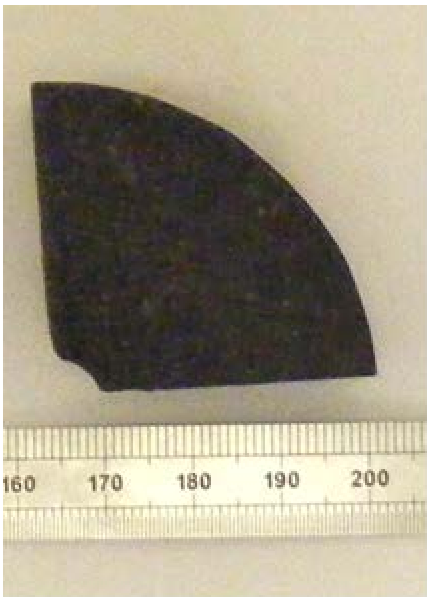


Figure 2.9.2: Graphite quadrant 635-BLOCK-1-2-2 [BASTON et al 2014].

Powdered sub-samples of the outer and inner (i.e. cut) surfaces of two of the segments were analysed for their radionuclide content to provide an estimate of the radionuclide inventory in each experiment.

Table 2.9.1. Specific activities of Carbon-14 measured in four samples taken from irradiated graphite block [BASTON et al 2014].

C-14 Specific activity (Bq g^{-1})			
1-2-3 Side	**1-2-3 Outer**	**1-3-1 Side**	**1-3-1 Outer**
$7.3 \times 10^4 \pm 0.9 \times 10^4$	$9.4 \times 10^4 \pm 1.0 \times 10^4$	$7.6 \times 10^4 \pm 0.5 \times 10^4$	$9.4 \times 10^4 \pm 0.7 \times 10^4$

The mean specific activity is $8.4 \times 10^4 \pm 1.1 \times 10^4$ Bq g^{-1}.

Seven leaching experiments were performed, each using a single segment of the irradiated graphite. Six experiments were designed to measure gaseous releases (with solution analysis on termination in some cases) and one to measure solution phase releases (only) with time for up to about one year after immersing the graphite in solution. The solution release experiment was performed independently from the gas release experiments, to avoid the possibility of disturbing the conditions in the reaction vessels in the gas-sampling experiments. Duplicate gas-release experiments and the solution release experiment were performed under anoxic, pH 13 conditions (in 0.1 mol dm^{-3} NaOH solution) at ambient temperature (‘baseline’ conditions) to simulate the post-closure conditions for disposal of graphite wastes in a cement-based GDF. The effects of oxic conditions, near-neutral pH, higher temperature (50°C) and reduced particle size (powdered sample) on the rates and speciation of gas-phase releases were investigated in variant experiments. Details of the seven experiments are summarised in Table 2.9.2.

Table 2.9.2: Summary of experimental conditions for leaching of irradiated Oldbury graphite [BASTON et al 2014].

Code.	Name	Solution pH	Atmosphere	Temperature	Graphite form	Duration
Run 1	Oxic	13	Air	Ambient	Intact	3 months
Run 2	Baseline 1	13	Nitrogen	Ambient	Intact	12 months
Run 3	Baseline 2	13	Nitrogen	Ambient	Intact	12 months
Run 3b	Solution sampling	13	Nitrogen	Ambient	Intact	12 months
Run 4	Neutral pH	7	Nitrogen	Ambient	Intact	3 months
Run 5	Powdered graphite	13	Nitrogen	Ambient	Powder	3 months
Run 6	Higher temperature	13	Nitrogen	50°C	Intact	3 months

The speciation of gaseous carbon-releases was investigated using a sampling apparatus capable of separating carbon dioxide, carbon monoxide and volatile hydrocarbons / organic compounds. A schematic diagram of the experimental set-up is shown in Figure 2.9.3.

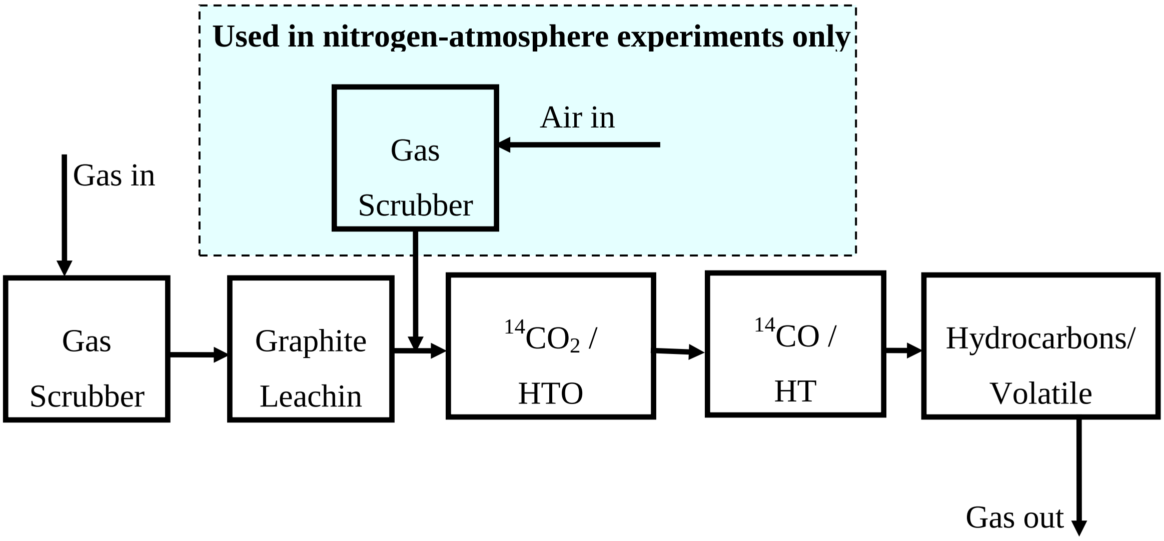


Figure 2.9.3: Schematic diagram of experimental apparatus [BASTON et al 2014]

Summary of Results

The cumulative activities of $^{14}CO_2$, ^{14}CO and $^{14}CH_4$ released to the gas phase on leaching are presented in Table 2.9.3. Figure 2.9.4 shows the total cumulative fractional release of carbon-14 to the gas phase from each experiment and compares this to the more limited data obtained for irradiated WAGR and BEP0 graphites.

Figure 2.9.5 shows the cumulative fractional release of carbon-14 to solution in the solution monitoring experiment (Run 3b). The solution concentrations in the gas monitoring experiments were measured only at the end, to avoid breaking the integrity of the system during the experiments. Figure 2.9.5 shows the uncertainty on the solution measurements as error bars, with the errors introduced by the uncertainty on the graphite inventory shown as the pink and blue lines (these are the upper and lower bound on fractional release based uncertainty in the graphite inventory and do not include uncertainties in solution concentration. In the solution monitoring experiment (Run 3b), 0.06% of the carbon-14 (1.6 kBq) was leached into solution in one year and appeared to still be rising. Solution phase measurements at the end of the baseline gas monitoring experiments showed similar fractional releases of carbon 14 in the range 0.06 to 0.08% at 12 months. Powdered graphite released 0.04% of the carbon-14 into solution in 3 months.

Table 2.9.3: Cumulative gaseous release of carbon-14 from irradiated Oldbury graphite [BASTON et al 2014].

			Cumulative Gaseous C-14 Release			
Run	**Conditions**	**Time (days)**	**CO_2 (Bq)**	**CO (Bq)**	**Organic (Bq)**	**Total**
1	Oxic, single piece of graphite pH 13, 20°C	7.0	0.04 ± 0.001	1.73 ± 0.02	1.67 ± 0.01	3.44 ± 0.02
		28.8	0.05 ± 0.001	2.13 ± 0.02	1.99 ± 0.01	4.17 ± 0.03
		70.9	0.07 ± 0.002	2.51 ± 0.03	2.38 ± 0.02	4.96 ± 0.04
2	Anoxic, single piece of graphite pH 13, 20°C	2.9	0.01 ± 0.001	0.44 ± 0.02	1.42 ± 0.07	1.87 ± 0.07
		7.0	0.03 ± 0.001	1.00 ± 0.04	2.45 ± 0.09	3.48 ± 0.09
		31.0	0.04 ± 0.002	1.47 ± 0.04	3.11 ± 0.09	4.62 ± 0.1
		94.0	0.05 ± 0.002	1.89 ± 0.05	3.88 ± 0.10	5.82 ± 0.11
		365.0	0.12 ± 0.004	2.42 ± 0.05	5.08 ± 0.12	7.62 ± 0.13
3	Anoxic, single piece of graphite, pH 13, 20°C	2.3	< 0.01	0.54 ± 0.03	0.94 ± 0.05	1.48 ± 0.06
		7.3	< 0.02	0.86 ± 0.04	1.96 ± 0.07	2.82 ± 0.08
		31.2	< 0.03	1.07 ± 0.04	2.34 ± 0.07	3.41 ± 0.08
		99.2	0.08 ± 0.04	1.37 ± 0.04	3.02 ± 0.09	4.47 ± 0.11
		366.0	0.29 ± 0.04	2.03 ± 0.05	4.46 ± 0.12	6.78 ± 0.13
4	Anoxic, single piece of graphite, pH 7, 20°C	7.1	30.7 ± 1.6	1.43 ± 0.07	3.45 ± 0.18	35.6 ± 1.6
		30.1	49.8 ± 1.7	1.7 ± 0.1	4.46 ± 0.19	55.9 ± 1.7
		93.1	121.9 ± 4.0	2.41 ± 0.11	5.44 ± 0.19	129.7 ± 4.0
5	Anoxic, graphite powder, pH 13, 20°C	7.0	0.09 ± 0.01	0.39 ± 0.02	0.91 ± 0.05	1.39 ± 0.05
		28.0	0.10 ± 0.01	0.68 ± 0.03	1.31 ± 0.05	2.09 ± 0.06
		91.0	0.52 ± 0.02	0.88 ± 0.03	1.52 ± 0.05	2.92 ± 0.07
6	Anoxic, single piece of graphite, pH 13, 50°C	6.9	0.10 ± 0.01	2.05 ± 0.11	5.26 ± 0.23	7.41 ± 0.26
		28.0	0.31 ± 0.02	2.72 ± 0.12	6.18 ± 0.23	9.21 ± 0.26
		94.2	0.39 ± 0.02	2.92 ± 0.12	6.59 ± 0.24	9.9 ± 0.27

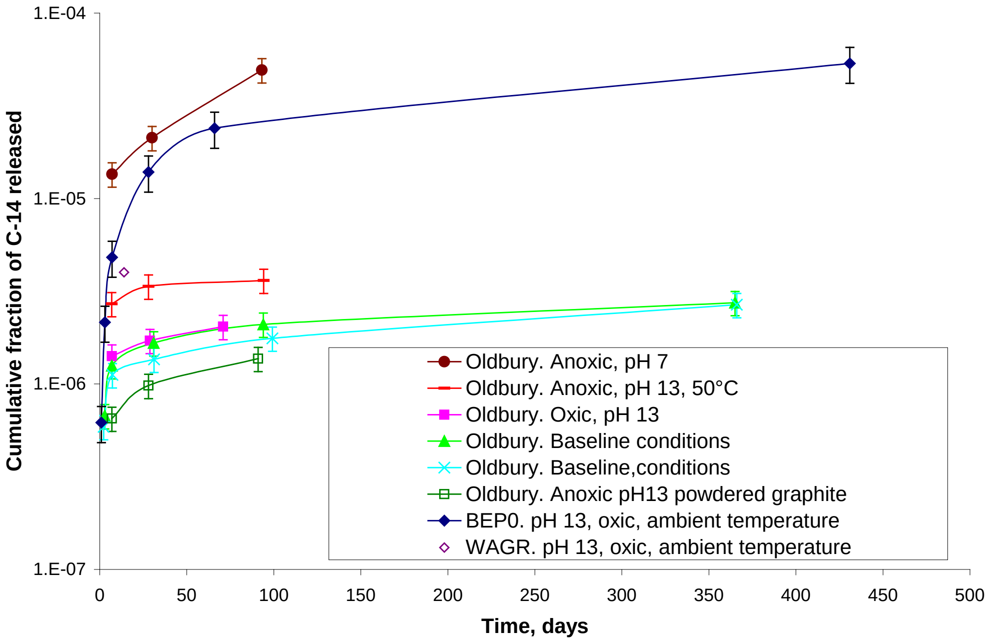


Figure 2.9.4: Total cumulative releases of carbon-14 from Oldbury graphite to the gas phase compared with data for BEP0 and WAGR graphites; error bars show combined uncertainty of carbon-14 content of the graphite and the measurement in the gas phase [BASTON et al 2014].

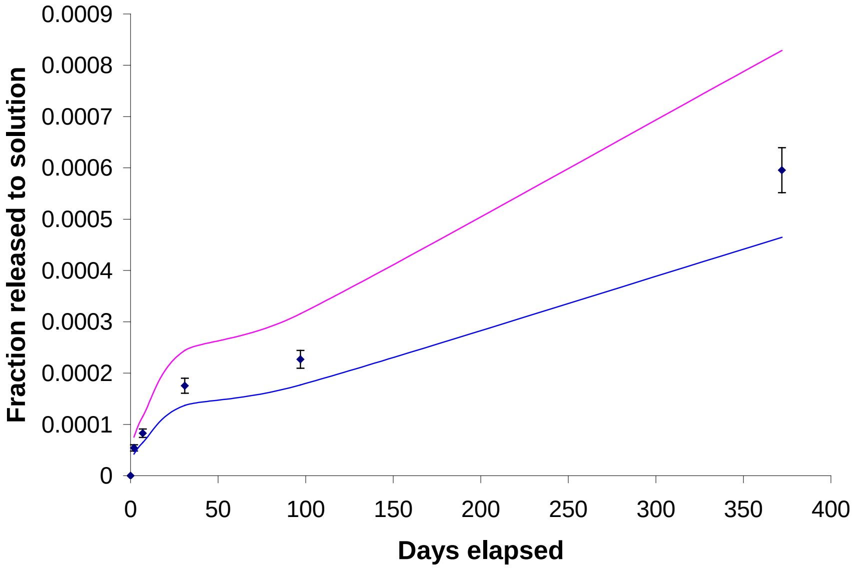


Figure 2.9.5: Fractional carbon-14 releases to solution in Oldbury graphite leaching experiment under anoxic conditions at pH 13 and ambient temperature. Error bars show the uncertainties on solution concentration measurements; pink and blue lines show systematic errors based on the uncertainty in the graphite inventory [BASTON et al 2014]

Conclusions from the Study

The main conclusions from the study are given below.

- Under baseline conditions (anoxic, under pH 13 solution, ambient temperature), the predominant carbon-14 release was to the solution phase, with about 0.07% of the carbon-14 inventory being released into solution in one year. About 1% of the released carbon-14 was released to the gas phase.

- In all five of the gas-phase release experiments under high-pH conditions, broadly similar levels of total carbon-14 release were observed to the gas phase from each of the five graphite segments on comparable timescales.

- In all seven experiments, for both gaseous and solution-phase release, an initial phase of rapid carbon-14 release was observed, which was followed (beyond about 28 days) by a longer term phase of slower release.

- Under baseline conditions (anoxic, under pH 13 solution, ambient temperature, single piece graphite sample):

  - an initial rapid release of ~3 Bq of carbon-14 to the gas phase was observed in the first week, which represents ~ 10^{-6} of the carbon-14 in the graphite;

  - the rates of release decreased with time but detectable quantities of carbon-14 were found in all gas samples. For the final cumulative sampling period, which ran from three to twelve months, a release of ~2 Bq was measured;

  - the gaseous carbon-14 was predominantly in the form of hydrocarbons and other volatile organic compounds and CO. The ratio of carbon-14 in hydrocarbons / organic compounds to CO was approximately 2:1. Less than 2% of the gas-phase release was in the form of $^{14}CO_2$.

- When the graphite was powdered, the rapidly releasable fraction of carbon-14 to the gas phase was found to be lower (by a factor of ~2) than from leaching intact segments, whereas the total solution phase release after 91 days was higher (by about 65%). This contrasting behaviour is most likely due to a loss of loosely-bound volatile carbon-14 species during the powdering process and an overall increase in release rate, primarily to solution, due to the increased surface area of the sample.

- At pH 7, levels of ^{14}CO and carbon-14 bearing volatile organic compounds were similar to the baseline values. However, the overall gaseous carbon-14 release was at least an order of magnitude higher than the baseline, due to significantly more $^{14}CO_2$ being released as gas from solution rather than being retained as dissolved carbonate.
- There is some evidence that increased temperature increases the release rate of carbon-14, but this observation is from a limited set of data.
- Under oxic conditions the total carbon-14 gaseous release rate was similar to the baseline condition values but the ratio of organic compounds to CO was closer to 1:1. The rates of carbon-14 release from Oldbury graphite were significantly lower than those measured previously from irradiated BEP0 graphite under oxic conditions, but the ratio of hydrocarbon / organic species to CO was higher.
- The differences between the fractional releases of carbon-14 from Oldbury and BEP0 graphites are likely to be due to differences between the original graphites, their irradiation histories, operating temperatures and coolant gases. The results of this study do not allow us to determine whether any one of these differences is a dominant effect although a wider comparison of irradiated graphites might.

Application in modelling gas generation

A tool commonly used in gas generation calculations for UK waste is SMOGG (Simplified model of gas generation) [SWIFT & RODWELL, 2006]. SMOGG models the generation of bulk and radioactive gases from waste packages or groups of waste packages. SMOGG includes a model for the generation of carbon 14 from irradiated graphite, which was developed on the basis of only limited data on gaseous carbon-14 releases from the sources available at the time. As a result of this study and other recent work [McDermott, 2011], an updated conceptual model for carbon-14 releases from irradiated graphite has been proposed, a revised mathematical model has been formulated and the data obtained for Oldbury Magnox graphite have been fitted to illustrate how the proposed model may be parameterised [BASTON et al, 2014].

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

The IFIN-HH activities in WP5 are part of the following tasks:

- Task 5.1 Review of CARBOWASTE and other relevant R&D activities to establish the current understanding of inventory and release of14C from i-graphite
- Task 5.3 Measurement of release of14C inventory from i-graphite
- Task 5.5 Data interpretation and synthesis – final report

The main objective of the IFIN-HH in the year 1 of WP5 was to update the inventory of ^{14}C in the irradiated graphite arising from thermal column of VVR-S Reactor and radioactive wastes containing organic and inorganic ^{14}C compounds.

IFIN-HH has characterized the ^{14}C inventory of irradiated graphite from thermal column of VVR-S Reactor, and has started to develop a method, based on the use of Accelerator Mass Spectrometry (AMS) which will be suitable to characterize the distributions of ^{14}C inventory in irradiated graphite.

In order to measure the total release of ^{14}C (and ^{3}H) to solution and gas from crushed and intact i-graphite from the VVR-S Reactor, an apparatus has been designed and manufactured.

Irradiated graphite inventory at IFIN-HH

The inventory of i-graphite at IFIN-HH is going to be actualized and is stems from thermal column VVR-S Reactor. The overwhelming amount of ^{14}C is located in the thermal column of VVR-S Reactor. The mass of i-graphite of the thermal column is estimated to be 5.3 metric tons. In addition there is more than $6x10^{10}$ Bq of ^{14}C contained in organic and inorganic compounds as radioactive wastes stored at the Radioisotopes Production Centre from IFIN-HH.

The total ^{14}C activity being allowed to be stored at the National Radioactive Waste Repository, which is the only national radioactive waste repository, is only $5x10^{11}$ Bq. It has to be mentioned that the National Radioactive Waste Repository is designed to store irradiated graphite and radioactive waste containing ^{14}C from all Romanian nuclear facilities. This restrictive ^{14}C limits arise from safety issues for internal operation because the release of ^{14}C cannot be specified. Under this background, the CAST project objective to understand the ^{14}C release mechanisms from irradiated graphite under geological disposal will provide possible solutions to waste management.

The VVR-S nuclear reactor from IFIN-HH is a research reactor with a maximum thermal power of 2 MW moderately cooled and reflected with distilled water, fuelled with enriched uranium 10% in the beginning and 36% subsequently.

Commissioned in 1957 and dedicated to nuclear physics research and radioisotopes production. Until 1984 the reactor was operated by nuclear fuel type EK-10 (10% enrichment) and from 1984, this fuel was replaced by S-36 (36% enrichment). The reactor was operational until 1997 when the reactor was definitively shut-down. On average, the reactor was operated 5 days per week at full or variable power levels. During 40 years of operation, the VVR-S reactor produced 9.59 GWd. The maximum flow of the thermal neutrons was 2×10^{13} n/cm^{2}s.

A horizontal cross section of the reactor core is presented in the Figure 2.10.1.

Currently, the VVR-S Reactor is undergoing the decommissioning. [DECOMMISSIONING PLAN, 2008]

The i-graphite grades, which are investigated in IFIN-HH have been taken from thermal column of the VVR-S Research Reactors. The mobile thermal column (Figure 2.10.2) is made of 5 graphite discs placed on a mobile truck. Graphite bar-made discs are installed into a 20 mm wall thickness aluminium cylinder. Initially, the thermal column is provided with a cooling system that axially penetrated the graphite plate connected to the water-cooling system. As from the exploitation experience, it was concluded that this system is not necessary; it was given up. The horizontal tubes of the cooling system were filled with nuclear grade graphite rods of the same type as the discs of the thermal column (Figure 2.10.3).

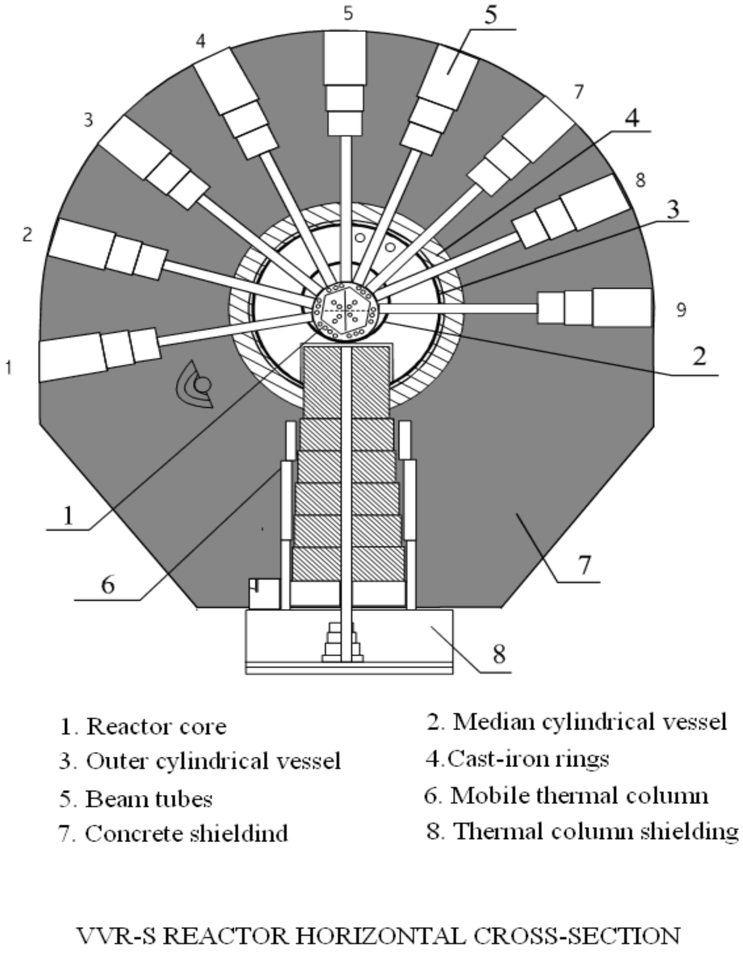


Figure 2.10.1 Horizontal cross section of the reactor core

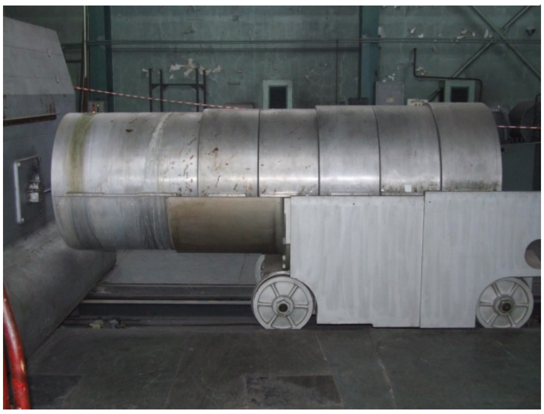


Figure 2.10.2 Thermal column

Figure 2.10.3 Thermal column first disc

Irradiated graphite samples preliminary characterisation

Small samples have been provided from the graphite rods of the first graphite disc located near reactor vessel. Two pieces of i-graphite have been cut from one of the graphite rods to be more easily handled in the radiochemical laboratory. One piece was cut from rod's edge near the reactor vessel (**Sample no 1**) and the other piece from the opposite part of the rod (**Sample no 2**). (Figure 2.10.4)

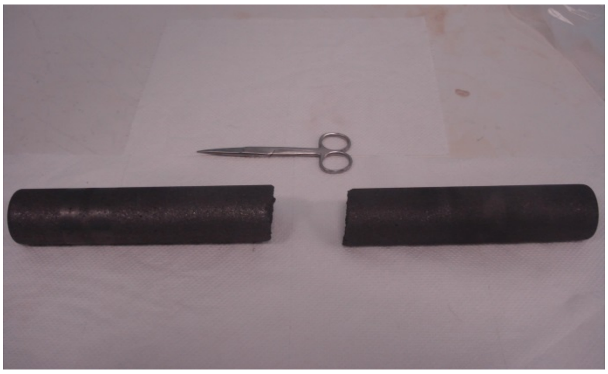


Figure 2.10.4 Irradiated graphite samples

The characteristics of the i-graphite samples no 1 and no 2 (mass, dimensions and dose rate) are presented in Table 2.10.1.

Table 2.10.1 Graphite samples

Sample	Mass (g)	Diameter (cm)	Length (cm)	Rate dose (μSv/h)
No 1	460	4.4	21.0	140
No 2	480	4.4	21.2	18

The estimation of the radionuclide inventory of the i-graphite has been determined by gamma spectrometry using an Ortec Gamma HPGe detector type GMX. For the radionuclides hard to detect, the specific and the total activity of ^{3}H and ^{14}C in the i-graphite of thermal column components have been calculated by means of the scaling factors method using ^{60}Co as the reference radionuclide and the thermal neutron flux distribution in space, according to the data from the literature [ANCIUS et al., 2005; DRAGUSIN, 2006].

The final radionuclide specific activity inventory of the i-graphite from the thermal column of the VVR-S Reactor is presented in Table 2.10.2 (main radionuclides).

Table 2.10.2: Radionuclide specific activity in VVR-S Reactor thermal column

Graphite sample	**^{3}H [Bq/g]**	**^{14}C [Bq/g]**	**^{60}Co [Bq/g]**	**^{154}Eu [Bq/g]**
No 1	**13.6 E+4**	**3.4 E+4**	**3.4 E+3**	**1.3 E+3**
No 2	**10.4 E+2**	**2.6 E+3**	**2.6 E+2**	**3.3 E+1**

The result of the specific activity estimation for the key radionuclide ^{60}Co in the thermal column has been validated by dose rate measurements. The contributions to the dose rate of other radionuclides, like ^{154} Eu and ^{152} Eu have been neglected because are smaller than 5%.

Our results have demonstrated that the ^{14}C activity decreases along the thermal column due to the thermal neutron flux attenuation) and for the first disc decreases from 3.4x10^{4}Bq/g next to the reactor core to 2.6x10^{3}Bq/g at the opposite face..

The total ^{14}C activity of the first graphite disc was calculated, because this disc contains between 90% and 95% from the total activity of the thermal column. The total ^{14}C activity of the first graphite disc is estimated to be: 10^{10} Bq.

Additional graphite sample from are needed to be collected and analysed from the second and the third disc of the thermal column of VVR-S Reactor, in order to have a more complete characterization of the i-graphite. The characterization of this material will be carried out next year.

2.10.3 ^{14}C inventory of irradiated graphite characterisation by AMS machinery

IFIN-HH has started to develop a method, based on the use Accelerator Mass Spectrometry (AMS) to characterize the distribution ^{14}C inventory in i-graphite. The method will be suitable for a continuous measurement of the ^{14}C concentration in the depth of the material, providing a depth profile throughout the thickness of the graphite samples.

The AMS (1.0 MV Tandetron AMS System Model 4110Bo-HVE) selects and counts the number of impurity atoms of an element in a sample (e.g. ^{14}C /C). It consists of an ion source, a tandem particle accelerator, several electromagnetic filters and a sensitive charged particle detector. The graphite samples (irradiated and non-irradiated samples) to be analyzed are loaded into the ion source were they are collided by a $^{+133}$Cs accelerated ion beam to produce sputtered ions from the target. Due to the tandem accelerator employed by the AMS method, only negative ions are extracted and will be used in the analysis. The depth profiling of the concentration of ^{14}C in the bulk of the sample is performed by taking advantage of the digging process performed by the focused Cs beam into the carbon material of the sample. The analysis is done step by step, as the sputter beam is advancing into the bulk of the sample creating a crater. The released atoms were selected and detected with a time resolution corresponding to 20 nm of depth.

For the time being, **virgin graphite** samples of the same type as the graphite from the thermal column of VVR-S Reactor are under investigation, in order to determine ^{14}C and ^{3}H initial concentrations. The results will be reported in the next annual report.

2.10.4 Evaluation of total ^{14}C and ^{3}H in the irradiated graphite

The IFIN-HH has developed a separation technique, based on silica gel columns coupled with oxidation at high temperature over a CuO catalyst bed coupled with LSC device and the measurements of ^{14}C release rate to gas and solution of from irradiated graphite (intact and crushed samples from thermal column of VVR-S Research Reactor for a better understanding of the release mechanism of ^{14}C.

Experimental methodology:

- Oxidation of the irradiated graphite samples in oxygen atmosphere;
- Oxidation of the resulted gases at high temperature over a CuO / Pt/Al_2O_3 catalyst bed;
- HTO and ^{14}CO trapping at liquid nitrogen temperature;
- Conversion of CO_2 at NaCO3 using NaOH water solution;
- determination of ^{3}H and ^{14}C activities using a LSC device**.** **(** TRICARB 2800 TR)

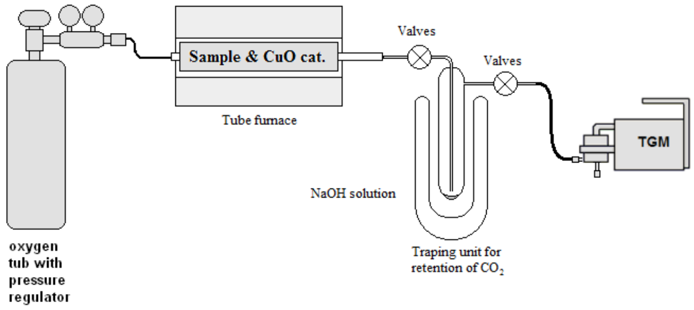


Figure 2.10.5 Apparatus designed for the total ^{14}C and ^{3}H activity measurements

The activities performed up to now consisted in the design of the experimental details and manufactured of the apparatus needed to measure the total ^{14}C activity of the i-graphite samples. (Figure 2.10.5)

2.10.5 Conclusions

- the first estimation of the inventory of the i-graphite arising from the VVR-S thermal column has been determined
- experimental methodologies and apparatus for the total ^{14}C activity measurements have been developed.

3 Summary

Work Package 5 of the EC CAST project considers irradiated graphite and related 14C behaviour. The objective of this Work Package is to understand the factors determining release of 14C from irradiated graphite under disposal conditions (to include surface disposal facilities and geological disposal facilities). This is the first annual report of Work Package 5, and details, on an organisation by organisation basis, progress in the Work Package over its first year. The achievements of each organisation are noted below:

1. On the basis of its work to date, IPNL concludes that thermal annealing of graphite in inert atmosphere does not induce any migration of ^{13}C up to 1600°C, even if the structure of the graphite is initially disordered. At 1600°C a slight diffusion occurs, which might be linked to the reordering of the graphite structure and the "reorganization" of the implanted ^{13}C into carbon clusters. Concerning irradiation, carried out on SLA2 nuclear graphite samples with an electronic stopping power around 3000 keV/µm, reordering of the graphite structure is induced. Although no value for ^{13}C release could be obtained, a related working assumption is that ^{13}C rearranges into new carbon structures, e.g. clusters. Irradiations carried out on HOPG graphite samples with an electronic stopping power around 3700 keV/µm show that the implanted ^{13}C does not migrate even at 1000°C. Future work will check the structure using Laser Raman Spectrometry but it is also highly probable that the implanted ^{13}C rearranges into new carbon structures as for example clusters.

2. LEI concentrated on the performance of the 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" and Task 5.2 – "Characterisation of the C-14 inventory in i-graphites". For the Task 5.1, the outcomes from the CARBOWASTE Project were reviewed, summarised and reported for the RBMK-1500 reactor, and for Task 5.2 new models for the numerical estimation of RBMK-1500 graphite activation are under development. It is expected that some sampling of the Ignalina NPP Unit 1 RBMK-1500 reactor graphite stack (blocks and rings/sleeves) will be

done in the near future and radiological data of the samples will be available, including data on C-14. Combining these experimental data and numerical modelling for induced activity of C-14, it should be possible to estimate the inventory of C-14 in i-graphite of the whole core of Ignalina NPP Unit 1 reactor.

3. Work of IGNS NASU in the EC CAST project is targeted to provide input on the use of graphite in the RBMK reactor, particularly the decommissioning of each category, classification, volume, weight and activity (the inventory of i-graphite in Ukraine is not finished: in compliance with the requirements of the regulatory documents, the composition and activities of radionuclides accumulated in structural materials and structures during the operation of the NPP power unit must be evaluated before its removal from service.). IEG NASU will review characterisation data on the speciation of ^{14}C in RBMK reactor, i-graphites and relevant information from decommissioning projects in Ukraine. IEG NASU is also involved in the review of the outcome of the IAEA project investigating conversion of i-graphite from decommissioning of Chernobyl NPP into a stable waste form.

4. The main objective of the INR in WP5 is to update the inventory of C-14 in the irradiated graphite arising from TRIGA 14MW reactor thermal column and to define the associated source term, not only as total amount of C-14 but also as inorganic/organic ratio. Data on the leaching rate presented in the literature have been analyzed and the most appropriate kinetics were used to predict the C-14 releases from TRIGA thermal column irradiated samples in order to establish the design parameters of the leaching experimental set up. INR will perform leaching tests on irradiated graphite samples from this thermal column in order to determine the leaching rate and to measure the inorganic and organic fractions of C-14 compounds (these leaching tests will be the first conventional leaching tests performed on thermal column irradiated graphite in environments simulating both cement-based and bentonite-based repository). Activities performed up to now consisted in the design of the experimental details in order to ensure measurable C-14 releases in hyperalkaline environment, both in liquid and gas phases.

5. Andra and EDF have reviewed the data on C-14 release and on the speciation of C-14 in French i-graphites, and presented the outcome in Deliverable D5.1. The main conclusions are that C-14 leaching rate is very slow for the stack graphite, and in most of cases a quasi-steady state leach rate appears to be achieved after the elapse of around 100 to 200 days. Over that period, the calculated mean radiocarbon leach rate lies between 10^{-11} and 10^{-8} $m.day^{-1}$ (meters per day). The reasons of the variability of this radiocarbon leach rate are not clear (note that studies were carried out on graphite from different origins and with different operational histories). A faster carbon 14 leach rate seems to be observed for the sleeve graphite (operational waste), which represents a small part of the total inventory in C-14. The nature of the leaching liquid (deionised or lime or soda water) does not seem to have any clear impact on the C-14 leaching behaviour.

6. Work undertaken by ENEA in the first year of the EC CAST project considers i-graphite from Latina NPP. This presents a wide range and amount of activation products, with the distribution of activated elements in the bulk of the samples being present mainly in the closed porosity or between the typical graphite layers. In order to facilitate extraction of these activation products, it is important to increase the surface area of the sample, and it is planned to apply an exfoliation-like process on the graphite by use of organic solvents (liquid-phase exfoliation) to produce un-functionalized and non-oxidized graphene layers in a stable homogeneous dispersion. Graphite has been exfoliated to extract ^{14}C intercalated between the graphene layers. Three different organic solvents with good solvency properties and water-miscibility have been tested, initially on non-irradiated virgin graphite and then on 15 samples of nuclear i-graphite from Latina NPP moderator. Characterization by means of Scanning Electron Microscopy SEM and Laser Raman Spectrometry has been performed to evaluate the degree of the exfoliation process. A preliminary characterization of the i-graphite samples, in order to estimate the content of radiocarbon ^{14}C, has been carried out.

7. Work of FZJ in CAST Work Package 5 is reviewing characterisation data on the speciation of ^{14}C in MTR and HTR i-graphites and relevant information from

CarboDISP, decommissioning projects in Germany and the ASSE test repository. FZJ will leach samples, which have undergone decontamination treatments and untreated samples to confirm a labile ^{14}C fraction, rather than slow diffusion of ^{14}C from within the graphite. FZJ and Ciemat, supported by Andra, ENRESA and RWM, will identify the parameters that need to be controlled in leach tests to allow a common comparison of results and compare these to existing methodologies. Leach tests have been systematically started mainly with RFR graphite, because there is enough material available, in contrast to other i-graphite samples in Juelich. Additional tests have been performed with AVR graphite, as it shows a quite high specific ^{14}C activity. Diffusion tests have been started also for the irradiated RFR graphite to determine the diffusion coefficients in a different way. Extensive water-uptake tests have been performed, showing clearly that virgin graphite exhibits little water-ingression and quasi-hydrophobic behaviour. In contrast, irradiated-graphite, as well as heat-treated graphite, behaves in a hydrophilic manner with high and quick water-uptake.

8. CIEMAT's Work Package 5 input to date considers different preliminary studies that have been performed to prepare the leaching experiments on irradiated powder graphite from Vandellós I NPP, samples of which are available in CIEMAT's laboratories, and on a graphite glass coating waste form - IGM (Impermeable Graphite Matrix) – material that has been developed by FNAG and that will be prepared in the CIEMAT facilities. CIEMAT's laboratory is being conditioned to work with the equipment needed to prepare samples of i-graphite for use in experiments to be reported as part of CAST WP5.

9. Work reported by RWM considers the release of gaseous C-14 from irradiated graphite samples from Oldbury Magnox power station. Key conclusions from the study are that under baseline conditions, the predominant carbon-14 release was to the solution phase, with about 0.07% of the carbon-14 inventory being released into solution in one year and with about 1% of the released carbon-14 being released to the gas phase. An initial rapid release of ~3 Bq of carbon-14 to the gas phase was observed in the first week, and subsequently the rates of release decreased with time

but detectable quantities of carbon-14 were found in all gas samples. For the final cumulative sampling period, a release of ~2 Bq was measured. Gaseous carbon-14 was predominantly in the form of hydrocarbons and other volatile organic compounds and CO, and less than 2% of the gas-phase release was in the form of $^{14}CO_2$. The differences between the fractional releases of carbon-14 from Oldbury graphite and that released from BEP0 graphite – a subject of previous study - are likely to be due to differences between the original graphites, their irradiation histories, operating temperatures and coolant gases; the results of this study do not allow determination of whether any one of these differences is a dominant effect although a wider comparison of irradiated graphites might.

10. The main objective of the IFIN-HH in the first year of its input to Work Package 5 was to update the inventory of ^{14}C in the irradiated graphite arising from thermal column of VVR-S Reactor and radioactive wastes containing organic and inorganic ^{14}C compounds. IFIN-HH has also characterized the ^{14}C inventory of irradiated graphite from thermal column of VVR-S Reactor, and has started to develop a method, based on the use Accelerator Mass Spectrometry (AMS,) which will be suitable to characterize the distributions of ^{14}C inventory in irradiated graphite. Finally, in order to measure the total release of ^{14}C (and ^{3}H) to solution and gas from crushed and intact i-graphite from the VVR-S Reactor, an apparatus has been designed and manufactured.

This annual report will be updated at the end of each year of the EC CAST project, which will act as a record of achievement for Work Package 5. When the project eventually reaches its conclusion, a final report from the Work Package will be produced, capturing and summarizing learning and achievements over the project’s full duration.

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