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CArbon-14 Source Term

CAST

WP5 Annual Progress Report – Year 3 (D5.9)

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CAST – Project Overview

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

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

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

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

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WP5 Annual Progress Report – Year 3 (D5.9)

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WP5 Annual Progress Report – Year 3 (D5.9)

Executive Summary

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

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

This is the annual report of Work Package 5 that covers activities undertaken in Year 2 of the EC CAST project, and details, on an organisation by organisation basis, progress in the Work Package.

1. The aim of work undertaken by IPNL is to simulate the behaviour of ^{14}C during reactor operation and evaluate the independent or synergistic effects of temperature and irradiation on ^{14}C migration. ^{14}C is mainly formed through the activation of ^{13}C but a certain amount may also be generated through the activation of ^{14}N. In this study, ^{13}C is mainly used to simulate ^{14}C release from the matrix carbon.

Ion irradiation in both ballistic and electronic regimes disorders the graphite structure, promoting the formation of sp3 bonds. On the contrary, temperature has reordering effects in both regimes, resulting into the formation of new sp2 structures. Moreover, in the ballistic regime, graphite reordering is even more pronounced as temperature increases, because it enhances the mobility of vacancies and interstitials created during irradiation. Therefore, the synergistic effects of ballistic irradiation and temperature favour graphite reordering.

Whatever the irradiation regime and even for temperatures as high as 1000°C, the implanted ^{13}C is not released from the graphite matrix. It stabilizes into sp3 or sp2 structures, whose relative proportions depend on the irradiation regime and temperature.

2. LEI reviewed the outcomes from the CARBOWASTE Project for the RBMK-1500 reactor for Task 5.1. Under task 5.2 new models for the numerical estimation of RBMK-1500 graphite activation are further developed. Sampling of the Ignalina NPP Unit 1 RBMK-1500 reactor graphite has been already done by the NPP staff and it is expected that some of the measurement results will be publically available. Combining these data, the data from the other sources and numerical modelling for the induced activity of ^{14}C, it should be possible to estimate the inventory of ^{14}C more precisely in i-graphite of the whole core of Ignalina NPP Unit 1 reactor. Task 5.5 is a forthcoming activity for the next reporting period.

3. The main objective of the RATEN ICN in Work Package 5 is to update the inventory of ^{14}C in the irradiated graphite arising from TRIGA 14MW reactor thermal column and to define the associated source term, not only as total amount of ^{14}C 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 ^{14}C 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 ^{14}C releases in hyperalkaline environment, both in liquid and gas phases.

4. Andra and EDF are in charge of reviewing the data on ^{14}C release and on the speciation of ^{14}C in French i-graphites. During the first year of the CAST project, the available data on 14C release in French i-graphite were reviewed and presented in Deliverable D5.1. During the second year, the data on the speciation of released ^{14}C in French i-graphites were reviewed. The report has been issued at the beginning of this third year as Deliverable D5.8.

5. Work undertaken by ENEA considers i-graphite from Latina NPP. An exfoliation-like approach is studied for irradiated nuclear graphite by means of non-oxidizing organic solvents extraction combined with a prolonged ultrasound bath as a possible new decontamination method. The graphite is intended to be 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) have been used in preliminary test with non-irradiated virgin graphite. A complete set of experiments to better define and set up the right process parameters is reported. The effects of process parameters such as sample weight and time of sonication have been assessed.

6. Within the last reporting period the activity of FZJ was focused on the leaching behaviour of nuclear graphite. This activity involves: (1) the pre-leaching characterization of irradiated graphite from Rossendorf research reactor (RFR), (2) setting up the leaching equipment and (3) test phase of leaching experiment using inactive nuclear graphite. Pre-leaching characterization included porosity measurements, g-spectrometry and autoradiography analysis followed by SEM for detailed identification of the hot-spot composition. The leaching conditions were selected according to the harmonized leaching procedure summarized in D 5.4.

7. The main efforts of the CIEMAT in the third year of its input to Work Package 5 were focused in the design, development and implementation of the leaching experiments on irradiated powder graphite from Vandellós I NPP, and on a graphite glass coating waste form denominated IGM (Impermeable Graphite Matrix). After

some preliminary test, the use of powder graphite was finally discarded for leaching and a method intended to obtain monolithic specimens with regular shape from small graphite pieces had to be developed. To date, four leaching periods on graphite cylinders and IGM has been performed. The set-up of the equipment intended for speciation studies (GC-MS and IC) has been completed and the analysis methods both for gas and liquid samples have been stablished.

8. The main objective of the IFIN-HH in the third year of its input to Work Package 5 was to complete the characterization of the ^{14}C inventory in graphite samples collected from graphite column of the VVR-S reactor based on the use Accelerator Mass Spectrometry (AMS) 1 MV facility and 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 using an experimental apparatus designed and manufactured by IFIN-HH.

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

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1 Introduction

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

- Determining the ^{14}C inventory and concentration distribution in i-graphites, and factors that may control these;

- Measuring the rate and speciation of ^{14}C release to solution and gas from i-graphites in contact with aqueous solutions; and

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

To achieve these objectives, five tasks are being undertaken

- 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 third annual report of Work Package 5 and details, on an organisation by organisation basis, progress in the Work Package over its third 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 implanted ^{13}C (simulating ^{14}C) in graphite: effects of irradiation and temperature

The contribution of IPNL aims at understanding better the inventory of ^{14}C in irradiated nuclear graphite at reactor shutdown. We simulate the behaviour of ^{14}C during reactor operation and evaluate the independent or coupled effects of temperature and irradiation on ^{14}C migration and graphite structure modification. In this study, ^{13}C implantation into graphite is used to simulate ^{14}C issued from the matrix carbon. Moreover, to evaluate the effects of irradiation on structure modification, it is necessary to work on model graphite such as HOPG (Highly Oriented Pyrolytic Graphite).

During the third year, we continued the study on the irradiation effects on ^{13}C behaviour and graphite structure modification according to:

- The irradiation regime (ballistic or electronic);
- The initial structural state of graphite (more or less damaged through preliminary implantation).

Moreover, to study the microstructure evolution the Raman studies were completed by High Resolution Electron Microscopy (HRTEM) analyses.

The following new conclusions may be drawn based on previous and new results:

1) When the HOPG graphite structure is already strongly damaged through preliminary implantation (more than 1 dpa[1]):

Firstly, to complete the study in the electronic regime, new irradiation experiments were carried out in a domain where electronic excitations are predominant. It was achieved using

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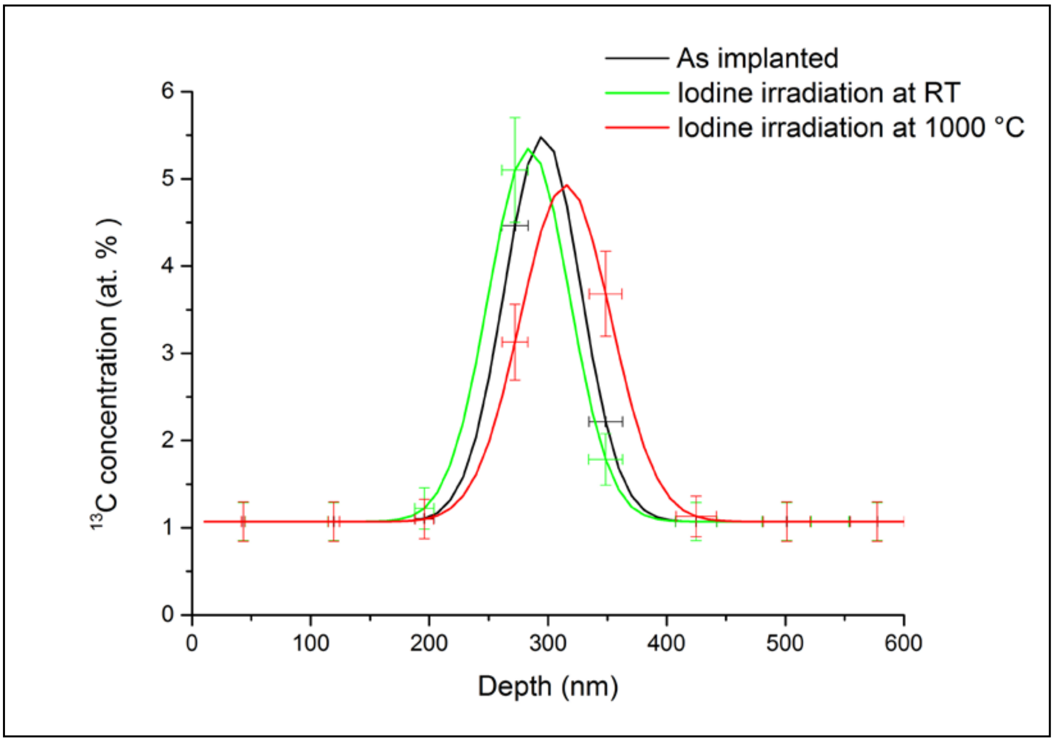
[1] dpa - displaced atoms.

iodine 200 MeV for which the electronic stopping power Se ~ 16700 keV/µm is far above the track formation threshold in HOPG (Se ~ 7500 keV/µm). As for the previous experiments, the samples have been first implanted with ^{13}C at a fluence of 6x10^{16}at.cm^{-2} (concentration at the projected range Rp around 5 at.%)

When the swift heavy iodine ions penetrate HOPG the ion excites solid electrons. The energy of the excited electrons is then transferred to the lattice via electron-phonon coupling and provides ultrafast local heating along the ion path. A cylindrical damage region of several nm diameter called an ion track may be created when the electronic energy loss is larger than the threshold value (thermal spike model). It is generally assumed that the ion track is formed when the atomic temperature rises beyond the melting point of the material. Such heating occurs in a localized region of nanometer size on a time scale of ~10 ps. These extreme conditions are generally not reached in UNGG (Uranium Naturel Graphite Gaz) type reactors but according to previous results obtained for experiments carried out with sulfur ion irradiation below the track formation threshold, we wanted to check the graphite structure modification and implanted ^{13}C behaviour beyond the track formation threshold.

Two irradiations were carried out at room temperature (RT) and 1000°C with iodine ions of 200 MeV (flux ~1x10^{11} ions.cm^{-2}.s^{-1} and a fluence ~2x10^{15} ions.cm^{-2}). The results presented in Figure 2.1.1 show that, whatever the irradiation temperature and compared to the as-implanted sample, the ^{13}C profile remains a stable event at 1000°C and almost no ^{13}C release is observed within the uncertainties of the data. The Raman spectra show that irradiation favors the formation of sp3 bonds and that implanted ^{13}C probably stabilizes into these structures.



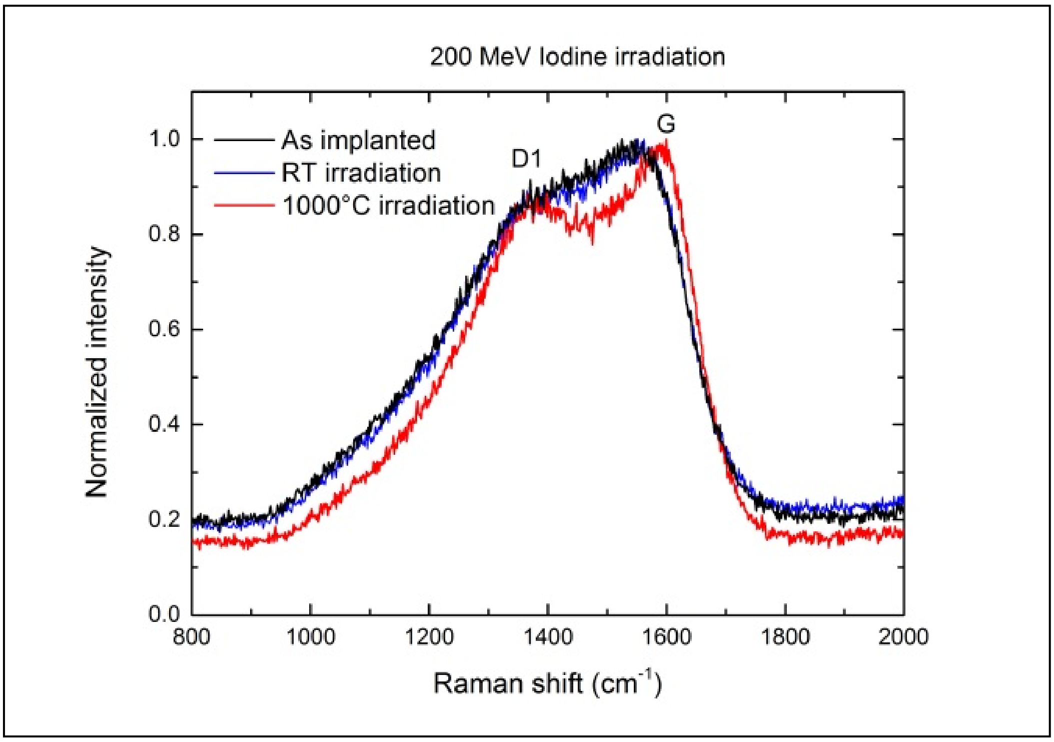


Figure 2.1.1: Evolution of the implanted ^{13}C concentration profile for Iodine irradiations carried out at RT(room temperature) and 1000°C measured by SIMS (top) and corresponding Raman spectra (wavelength 514 nm) (bottom)

Thus, even if locally very high temperatures are reached through partial melting of the material, the irradiation in the predominant electronic regime allows only a small recovery of the sp2 structure to be achieved. It seems that the implanted ^{13}C stabilizes mainly into sp3 structures. This result is similar to that obtained with irradiations carried out at lower electronic stopping power Se with sulfur ions (below the track formation yield).

Figure 2.1.2 records the Raman results for ID_1/IG variation for different samples: virgin HOPG, HOPG implanted with ^{13}C at a fluence of $6x10^{16}$at.cm^{-2} and the implanted and irradiated samples at different temperatures where D_1 and G are respectively the defect and graphite bands. This figure shows that ID_1/IG decreases for argon and carbon irradiations thereby indicating a reordering of the graphite structure. On the contrary, ID_1/IG remains almost unchanged for sulfur and iodine irradiations.

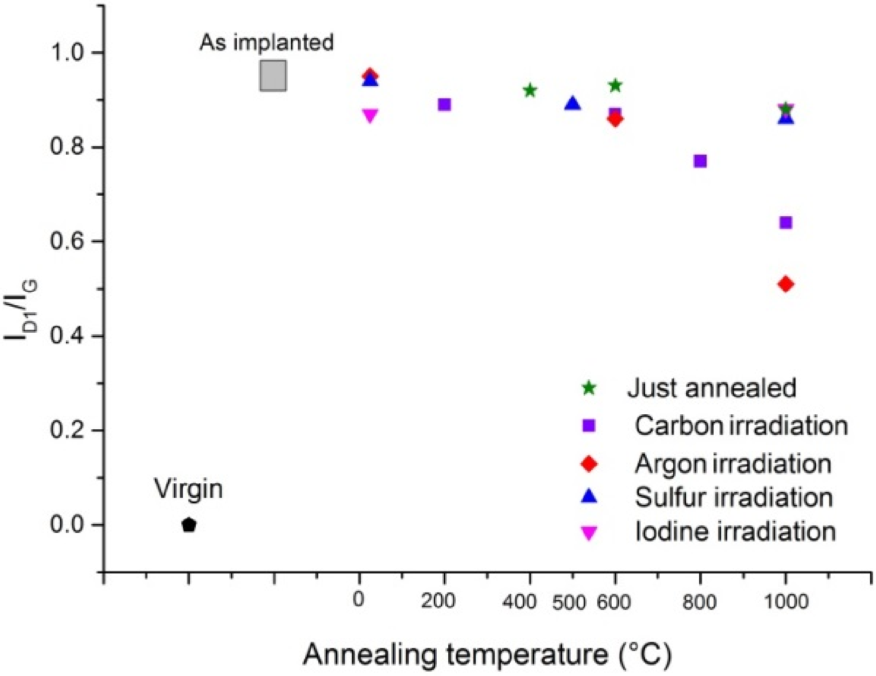


Figure 2.1.2: I_{D1}/I_G variation for virgin HOPG, as implanted HOPG and implanted HOPG irradiated at various temperatures with different ions

Thus, for already strongly damaged graphite, the coupled effects of temperature and irradiation in a ballistic regime allow graphite restructuring contrary to irradiation in a prevalent electronic regime. This could be connected to the fact that in a ballistic regime, the mobility of the preexisting and created vacancies and interstitials during irradiation is enhanced by the temperature increase, thereby allowing the graphite restructuration. Therefore, it seems that ballistic irradiation and temperature have synergistic effects favoring graphite reordering.

New results have been obtained by HRTEM. The HRTEM images are recorded in the plane of the irradiating ion path and the implanted ^{13}C path (note that the irradiating ion stops far beyond the implanted ^{13}C path). The HRTEM results have been obtained after processing images according to Rouzaud et al. (2002) and Galvez et al. (2002). The processing allows gaining information on the disorder level of the samples through values such as the angular dispersion α of the graphene layers around a mean value m or the interlayer spacing d. These values are inferred from skeletonized images as shown in Figure 2.1.3. Figures 2.1.4 and 2.1.5 present the new results obtained from HRTEM experiments. These figures represent respectively the values of the angular dispersion FWHM_α around a mean value FWHM_m and the interlayer spacing d measured at different depths along the ion path used for irradiation. We have also represented the domain of the values representing the virgin HOPG (black dashed lines). The respective domains for the as-implanted samples, sulfur and carbon irradiated samples are encircled with blue, pink and red dashed lines close to the maximum implantation depth of ^{13}C (Rd around 300 nm); the higher the values, the higher the disorder of the structure. These values are therefore fully in agreement with the Raman results and clearly show that both temperature and ballistic irradiation regime (in this case carbon irradiation) tend to reorder the already disordered HOPG structure whereas in an electronic irradiation regime (in this case sulfur irradiation) the already disordered HOPG structure cannot recover.

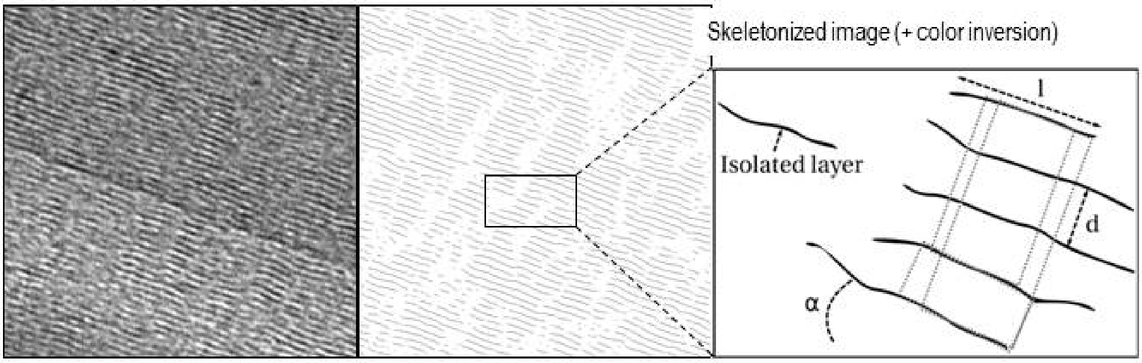


Figure 2.1.3: Scheme of the quantitative processing performed on the skeletonized images

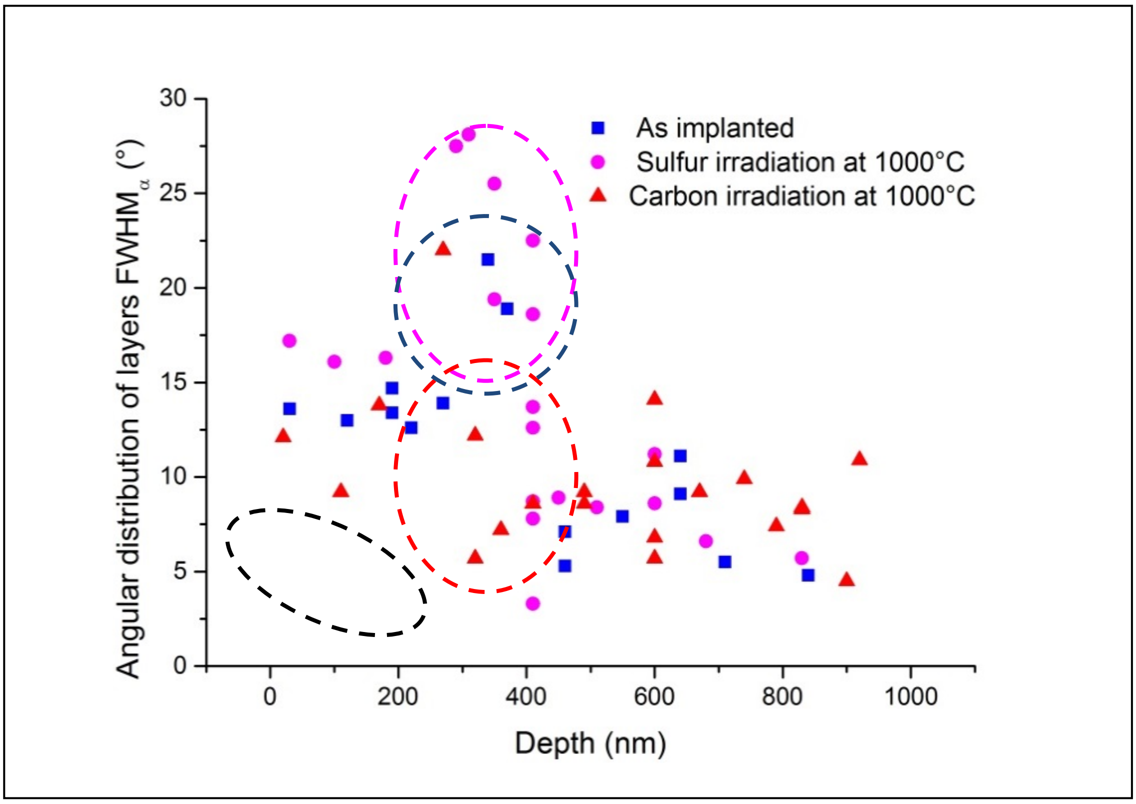


Figure 2.1.4: Angular dispersions of the graphene layers of the irradiated samples compared to the as implanted one measured by HRTEM. The zone of the virgin one is represented by the black dashes.

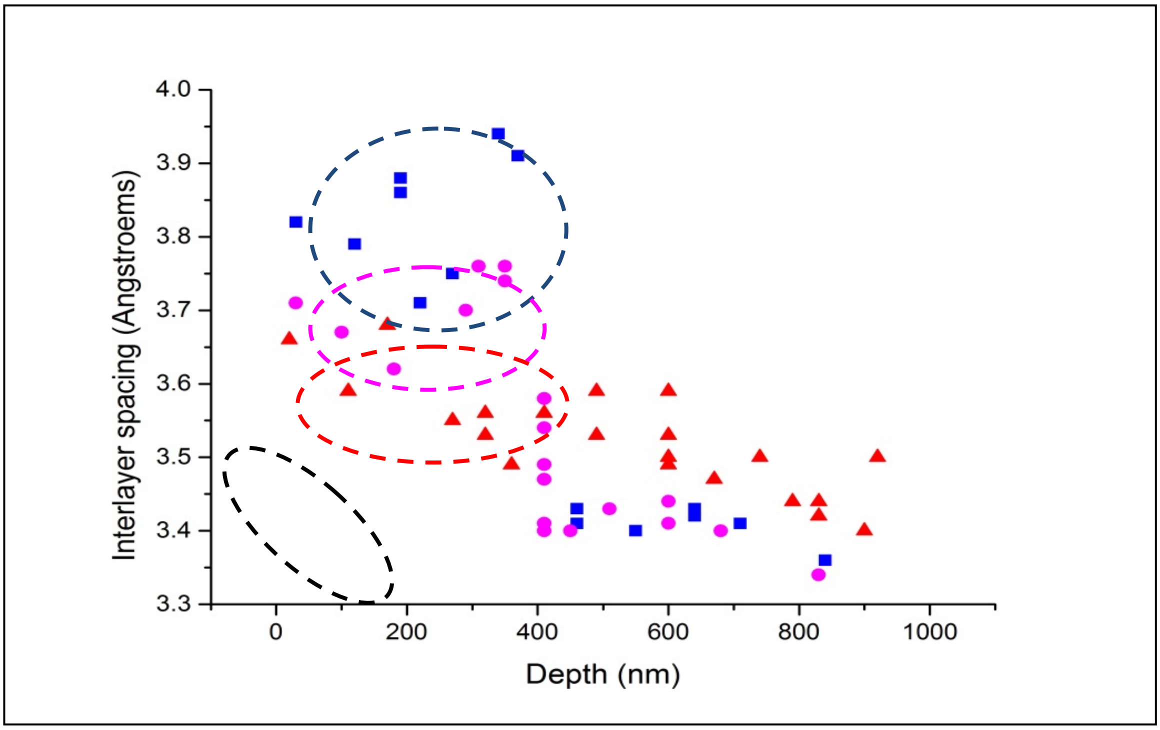


Figure 2.1.5: Interlayer spacing of the irradiated samples compared to the as implanted one measured by HRTEM. The keys of this figure are the same as for the Figure 2.1.4.

2) When the HOPG graphite structure is less damaged through preliminary (less than 0.1 dpa):

In this case the samples have been previously implanted either with ^{13}C (at a low fluence of 4x10^{14} ions.cm^{-2}) or with ^{37}Cl (at a low fluence of 5x10^{13} ions.cm^{-2}).

Ballistic regime:

Figure 2.1.6 compares the Raman spectra obtained on HOPG samples implanted a low fluence. HOPG is therefore less damaged than the previous ones (as can be seen from the Raman spectrum of the as implanted one in blue) that have been irradiated with 800 keV argon ions at different temperatures. The just annealed samples are also represented for comparison. The argon irradiation fluence was chosen in order to induce around 4 dpa in the implanted zone. The figure shows that temperature and ballistic irradiation seem to have antagonist effects in this case because irradiation disorders the structure whereas temperature tends to reorder the structure. The spectra of the sample irradiated at 1000°C is close to the one just annealed at 500°C.

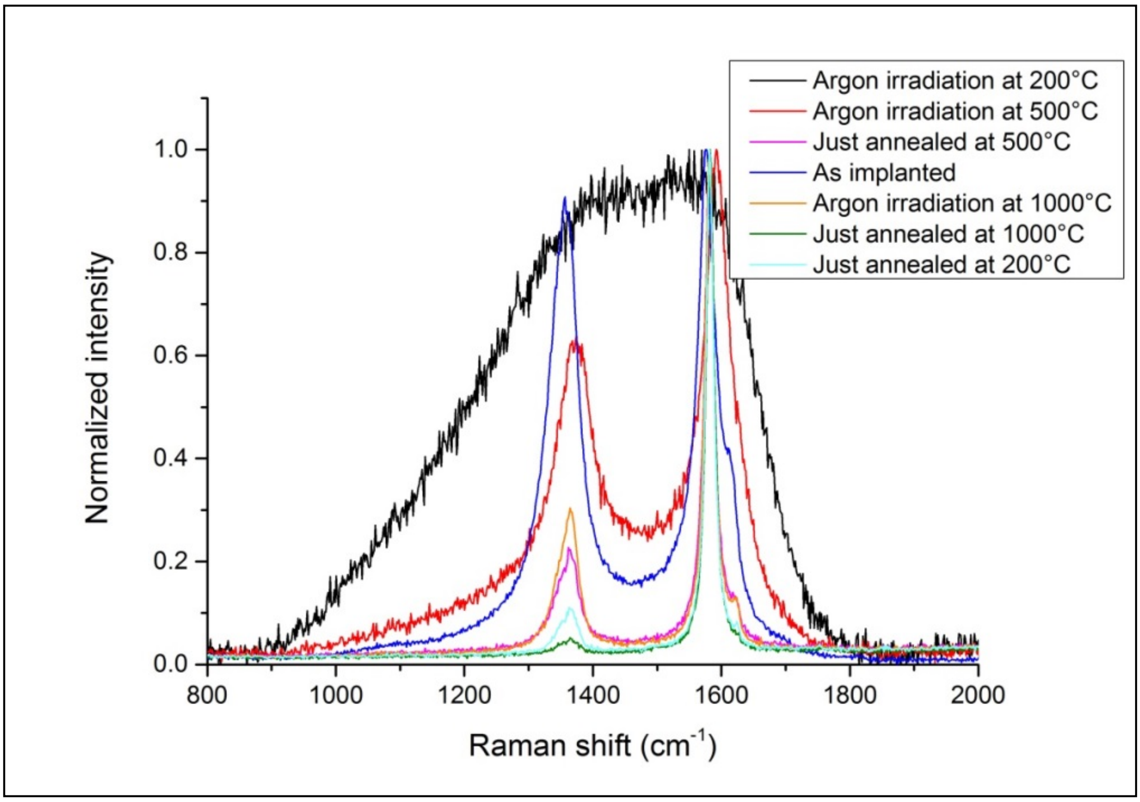


Figure 2.1.6: Raman spectra measured for the argon irradiated at different temperatures, as implanted and just annealed samples

Electronic regime compared to ballistic regime:

Figure 2.1.7 resumes the Raman results for the virgin HOPG, the as-implanted sample and for (as-implanted + carbon + sulfur) irradiated samples carried out at 500°C. This figure shows that irradiation in an electronic regime at 500°C induces structure reordering. At 500°C the reordering is about of the same order that for carbon irradiation carried out at 500°C.

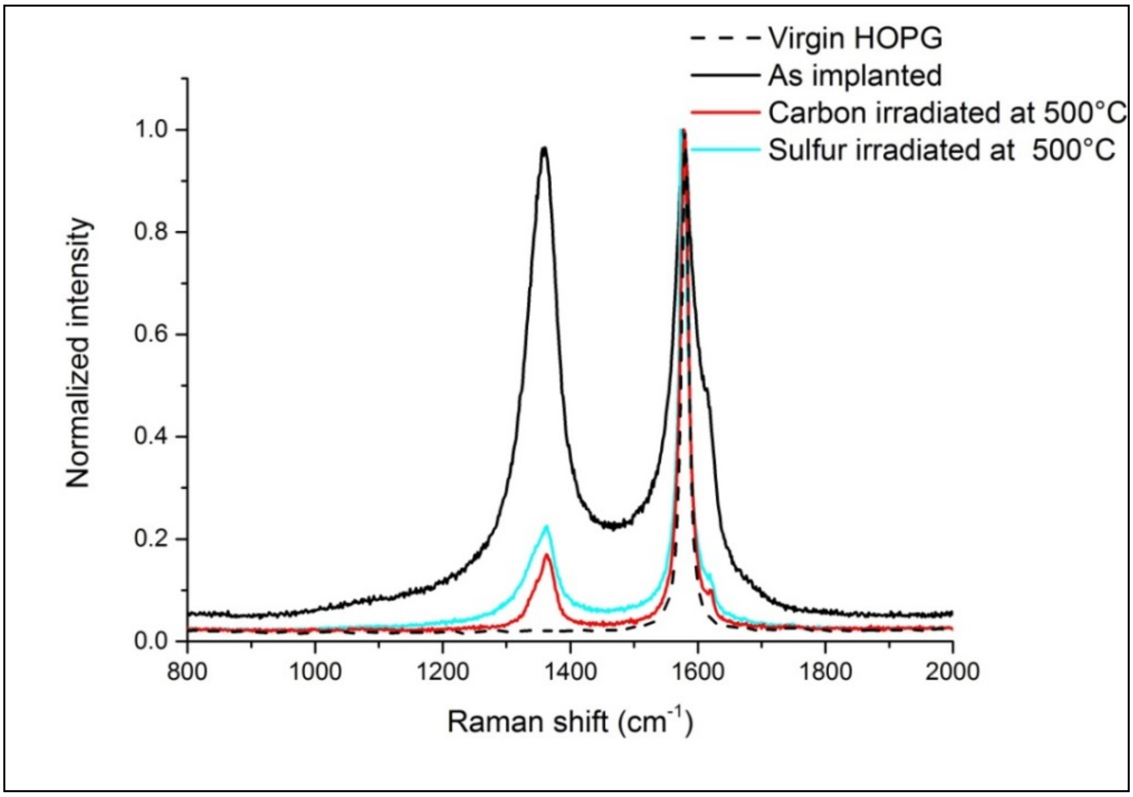


Figure 2.1.7: Raman spectra of the carbon and sulfur irradiated samples compared to the virgin and as implanted one

This is also illustrated in Figure 2.1.8 and 2.1.9 representing respectively the values of the interlayer spacing and the angular dispersion FWHM_{α} around a mean value FWHM_{m}, measured at different depths along the ion path, and obtained by HRTEM for the as implanted samples and the irradiated ones. The values of the irradiated samples are close to the as-implanted ones. Two sets of implanted samples have been analyzed, represented by the black squares and blue triangles. They correspond to samples implanted at two facilities (respectively, the 400 keV implanter of IPNL, Villeurbanne, or the 200 keV implanter of ICUBE laboratory, Strasbourg).

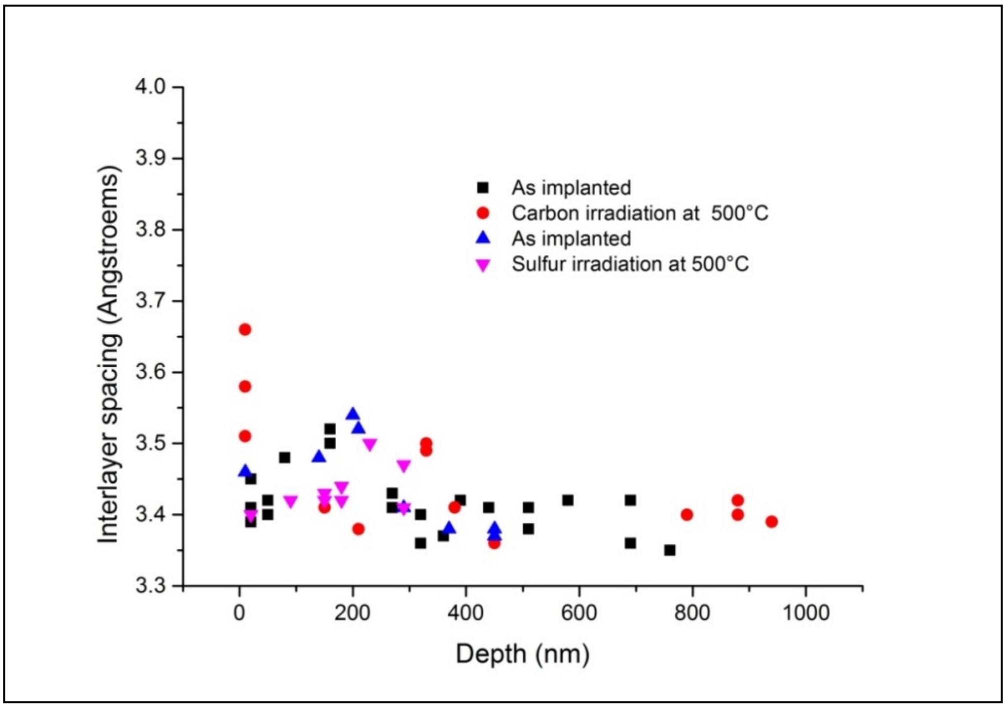


Figure 2.1.8: Interlayer spacing of the 500°C irradiated carbon and sulfur samples compared to the as implanted one measured by HRTEM.

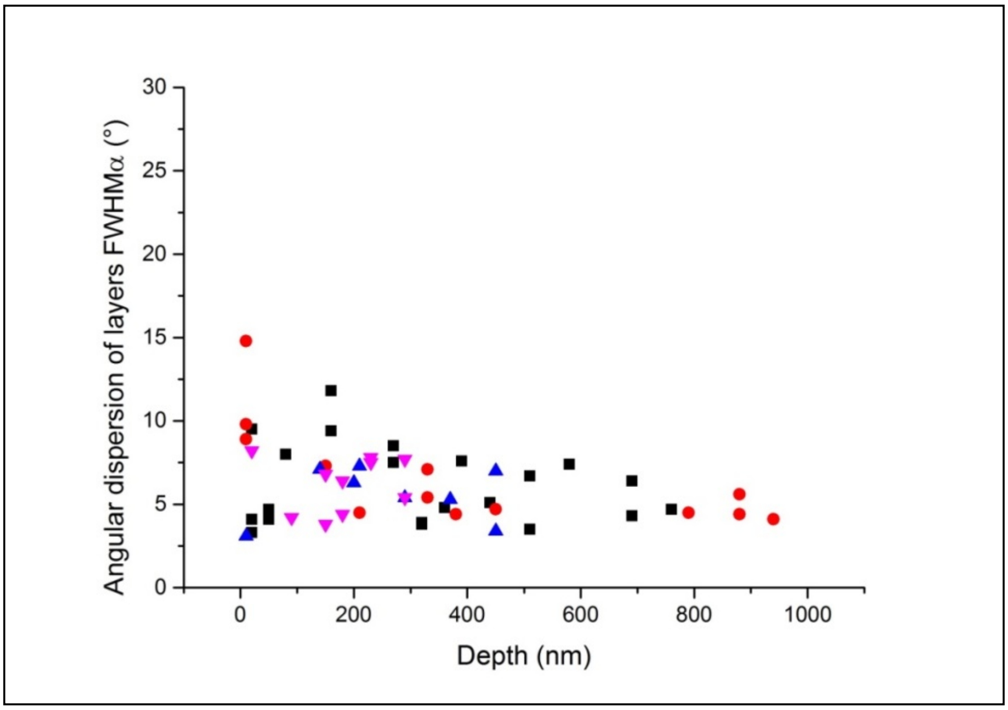


Figure 2.1.9: Angular dispersion of the 500°C irradiated carbon and sulfur samples compared to the as implanted one measured by HRTEM (key as per Figure 2.1.8)

Figure 2.1.10 summarises the Raman results for ID_1/IG variation for different samples: virgin HOPG, HOPG implanted at low ^{37}Cl or ^{13}C fluences, and the implanted and irradiated samples at different temperatures where D_1 and G are respectively the defect and graphite bands. This figure shows that, whatever the irradiation regime, the graphite structure reorders with increasing temperature. However, at high ballistic damage (argon irradiation inducing around 4 dpa), the reordering is worse than at lower ballistic damage (carbon irradiation inducing around 1 dpa) or in the electronic excitation regime.

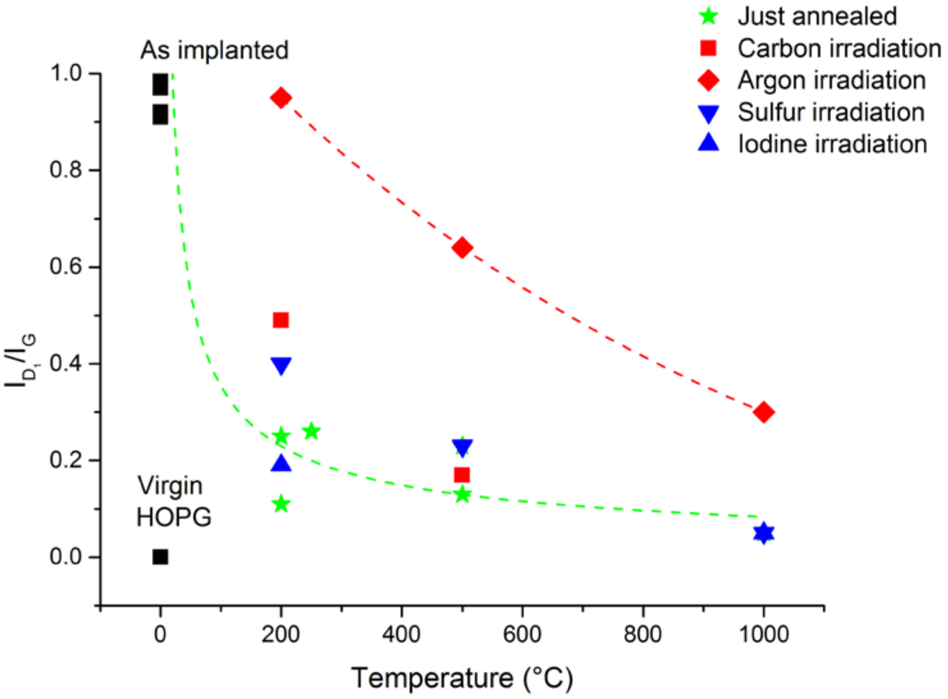


Figure 2.1.10: I_{D1}/I_G variation for virgin HOPG, as implanted HOPG and implanted HOPG irradiated at various temperatures with different ions

Concluding remarks:

1. Whatever the irradiation regime, implanted ^{13}C is always stabilized into graphite (sometimes into “new” carbon structures). The proportion of carbon stabilized into sp2 or sp3 structures depends on the irradiation regime and temperature.

2. The structure modification due to irradiation is strongly dependent on the initial graphite structure. i) When the initial graphite structure is already highly disordered

(more than 1 dpa), it seems that the mobility of the pre-existing and created vacancies and interstitials during irradiation is enhanced by the temperature increase, thereby allowing the graphite restructuring. Therefore, it seems that ballistic irradiation and temperature have synergistic effects favouring graphite reordering. This is not the case for the electronic irradiation regime for which the structure is scarcely reordered whatever the temperature; ii) When the initial graphite structure is only slightly disordered (less than 0.1 dpa), ballistic irradiation and temperature have antagonist effects because irradiation has a strong disordering effect while temperature reorders the structure. The higher the irradiation temperature, the higher the reordering of the structure. The electronic regime has a disordering effect but it is compensated by the reordering effects of temperature. However, at high ballistic damage (argon irradiation inducing around 4 dpa), the reordering is worse than at lower ballistic damage (carbon irradiation inducing around 1 dpa) or in the electronic excitation regime.

3. Thus, if we try to extrapolate our results to reactor conditions, following conclusion can be inferred:

   - the main graphite structure modifications are linked to ballistic damage;
   - when the graphite structure is already strongly disordered (for instance moderator coke grains that have been irradiated for several years in a high neutron flux region of the reactor), subsequent irradiation will have a low impact on its reordering because typical UNGG reactor temperatures of 200-500°C will not be able to reorder the already damaged structure. On the contrary, when the structure is only weakly damaged (for instance coke grains located in a low neutron flux region), the reordering possibilities will strongly depend on the following neutron flux and temperature conditions: if the graphite is irradiated at low flux in a hot zone (500°C) of the reactor, the structure should be far better ordered than if the graphite is irradiated at high flux in a cold zone (200°C).

- Thus, our results show that, according to the initial structure and the irradiation conditions, the graphite should display significant structural heterogeneities. Concerning ^{14}C, except from ^{14}C located close to open pores that might be removed through radiolytic corrosion, it should generally be stabilized in into sp2 or sp3 structures at varying proportions depending on the irradiation conditions.

2.2 Lithuanian Energy Institute (LEI) summary

LEI participates in Tasks 5.1, 5.2 and 5.5 within Work Package 5 (WP5) of the CAST Project.

During the first three years 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 ^{14}C from i-graphites" and Task 5.2 – "Characterisation of the ^{14}C inventory in i-graphites". Task 5.5 "Data interpretation and synthesis – final report" is a future activity. For Task 5.1, LEI reviewed the outcome of CARBOWASTE Project in the national context and based on that, provided input for deliverable D5.5 "Review of current understanding of inventory and release of ^{14}C from irradiated graphites". For the Task 5.2, LEI is modelling the ^{14}C inventory in a RBMK-1500 reactor core using new data and is preparing deliverable D5.17 "Report on modelling of ^{14}C inventory in RBMK reactor core", which is scheduled for the month 42 of the Project (next reporting period). The Task 5.5 "Data interpretation and synthesis – final report" is the last Task of WP5 that will summarise and synthesise in a final report the work undertaken in the previous Tasks by all participants. The outcome of this Task will be deliverable D5.19 "Final report on results from WP5", which is scheduled for the month 46 of the Project (next reporting period).

For the Task 5.1, LEI activities are completed. The outcomes from the CARBOWASTE Project were reviewed and summarised for the RBMK-1500 reactor. Based on that, the draft input for deliverable D5.5 "Review of current understanding of inventory and release of ^{14}C from irradiated graphites" was produced and sent to the NDA for the incorporation into the draft deliverable in the end of the first Project year. Some comments regarding LEI input were received during the second Project year. The LEI input then was updated based on the comments, and revised input for deliverable D5.5 was produced and sent to the NDA for the incorporation into the final deliverable. The final version of deliverable D5.5 was issued on 2015-07-15 and is available from CAST Project public website.

For the Task 5.2, LEI activities are ongoing. Following the knowledge gained in the CARBOWASTE Project, IAEA Co-ordinated Research Project, etc., new models for numerical estimation of RBMK-1500 graphite activation are further being developed (SCALE and MCNP software). Sampling of the Ignalina NPP Unit 1 RBMK-1500 reactor graphite stack (blocks and rings/sleeves) has been already done by the NPP staff. It is expected that radiological characterisation of the taken samples (activity of ^{14}C is of most importance for CAST Project) will be made in the near future and at least some results will be made publicly available. Combining these experimental data and numerical modelling for induced activity of ^{14}C, the inventory of ^{14}C in i-graphite of the whole core of Ignalina NPP Unit 1 reactor could be estimated more precise and with more confidence. For this, new models for numerical estimation of induced activity are further developed and results are scheduled for the next reporting period.

Gathering of new information relevant to the RBMK graphite activation issues is continuously ongoing during the course of the Project. Some recent results of ^{14}C activity in Ignalina NPP graphite were published in 2015 [Mazeika et al. 2015]. This paper presented experimental studies of ^{14}C activity in GRP-2-125 grade graphite rings, among the others. It revealed the following results: for the inner part of the rings ^{14}C specific activity was 2.6×10^5 Bq/g, while for the outer part of the rings – 3.9×10^6 Bq/g. This gave the outer / inner activity ratio of 15 for ^{14}C. Furthermore, several graphite sub-samples, attributed to the same sample of the reference bushing segment of the temperature channel made of GR-280 graphite, were investigated for the content of ^{14}C. Based on the statistical analysis of the sub-samples activity, the average value of the ^{14}C specific activity in this graphite was 1.67×10^5 Bq/g.

All the modelling results, obtained using aforementioned models and data, will better reflect real situation for RBMK-1500 reactors and contribute to the general knowledge of ^{14}C generation in graphite.

For the Task 5.5 “Data interpretation and synthesis – final report” LEI will prepare the Lithuanian input to deliverable D5.19 “Final report on results from WP5”, addressing the work LEI has performed in WP5. D5.19 is the last deliverable of WP5, and it will summarise and synthesise the work undertaken in WP5 tasks by all participants.

2.3 RATEN ICN summary

The thermal column of the TRIGA[2] reactor consists in a block of 96 rectangular bricks of graphite encased in aluminium. The thermal column is placed on a stainless steel frame fixed in the reactor pool, in the northern part of the steady state zone. It was built up in 1985 and it was mainly used for several experiments in thermal flux conditions.

The graphite was imported in the '50s from a UK producer but documents of origin were lost. No information on its characteristics and especially on the impurity content could be found. Since its installation in the reactor pool, a few changes in the column structure - consisting of the replacement of some bricks - have occurred, but no record of these changes exists. Only one brick has been extracted from the thermal column (and subsequently dismantled). This occurred in 2000, but no reference to its position in the thermal column was recorded.

Samples collected from this brick were used for radionuclide content measurements and leaching studies.

Long term leaching tests on TRIGA irradiated graphite samples in <u>aerobic</u> conditions

Under CAST WP5, RATEN ICN proposed to carry out long term leaching test on TRIGA irradiated graphite samples and to measure the total ^{14}C release in the liquid phase and its partition between inorganic and organic species.

The leaching tests started at the end of 2015, right after CAST Deliverable D 5.4 (Petrova et al, 2015) containing the definition of harmonized leaching parameters, was issued.

Two solid specimens of irradiated TRIGA graphite were obtained for use in this study. The i-graphite samples had been cut from one cylindrical piece (200 mm length, 50mm diameter) (Figure 2.3.1) taken from the brick that was removed from TRIGA reactor in 2000.

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[2] Training, Research, Isotopes, General Atomics

Figure 2.3.1. Physical appearance of the i- graphite cylindrical bar from TRIGA thermal column

Also powdered samples from the same sample have been used for this study. Two of these sub-samples were subject to leaching tests in order to investigate also the enhanced geometrical surface effect on ^{14}C release rate in solution.

Powdered sub-samples from the outer and inner surfaces of two of the segments (Figure 2.3.2) were analyzed for their radionuclide content to provide an estimate of the radionuclide inventory in each experiment.

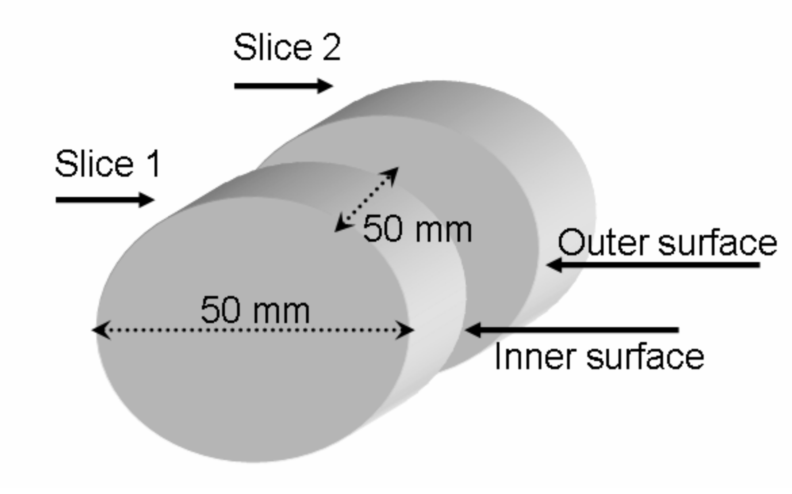


Figure 2.3 2. Mechanical cuts made to obtain the intact samples and powdered samples

The segments were given names 1 and 2, for the intact blocks respectively P1 and P2 for the powdered ones, with sample masses given in the Table 2.3.1.

Sample code	Sample mass [g]
1	172,72
2	168,24
P1	0,49
P2	0,50

Table 2.3.1. Graphite sample masses

The leaching approach is a long term semi-dynamic test, with a precise time scale sampling/replacement of the leachate, until equilibrium is reached. The leaching test is performed in Pyrex glass vessels at room temperature, in aerobe conditions. The samples from both powdered graphite and intact test specimens (length to diameter of cylindrical samples: 50x50 mm) were leached in a volume of 1118 cm^3 0.1M NaOH solution, with high pH (~13).

The ratio of solution volume to exposed surface area of the cylindrical samples is held constant and does not exceed the value 0.1 m. After the sampling step, in which a volume of 30 ml of leachate was sampled and replaced with the same volume of fresh leachant, ^{14}C activity in the leachates is measured via Liquid Scintillation Counting (LSC) method. For the intact test specimens no filtration step of the leachates solutions was necessary.

Leaching of ^{14}C from TRIGA intact irradiated graphite samples was quantified both as cumulative leaching fraction of ^{14}C (it correlates the total ^{14}C leached amount over the leaching time) and by incremental leaching rate. The values obtained were corrected with the dilution factor, reported to the initial ^{14}C content determined. These results will be reported at the end of the study, in the Final Deliverable (D5.10).

For the powdered samples, 0.5 grams of graphite were tested in 50 ml of NaOH leachant. The testing methodology for this type of samples was adapted to IAEA standard for ‘Semidynamic leach test’, whereby 5ml of leachant sample is removed according to the time intervals stated in Petrova et al. (2015) and replaced with the same volume of leachant. For the powdered samples, filtration of the leachates was performed prior to analysis of the solutions. The ^{14}C release rates in solution have been calculated as the cumulative fraction released as a function of time and takes into account the sum of ^{14}C release taken to reach equilibrium. Each sample pair was accompanied by a baseline test of virgin graphite in NaOH solution.

^{14}C measurement in irradiated graphite samples involved in the leaching tests

The ^{14}C activity measurement methodology consists in a complete combustion of the i-graphite samples (powder type) in an oxygen-enriched atmosphere with a continuous flow of oxygen using Sample Oxidizer, Model 307 PerkinElmer® .

The protocol for graphite oxidation conditions is as follows:

- ➢ 0.14 – 0.16 g of graphite powder
- ➢ 10 ml CarbosorbE
- ➢ 10 ml PermafluorE+.

The recovery yield was assessed by combustion of a known standard, Spec-Chec, in the presence of 0.14 g virgin graphite powder, to simulate sample loading. Also virgin graphite samples were combusted, for background measurements. The average combustion recovery by this method was 97% .

Further, four samples of irradiated graphite powder (masses 0.14-0.16 g) were combusted in an oxygen-enriched atmosphere with a continuous flow of oxygen:

- ➢ 2 samples from the outer surface area of the initial i-graphite piece;

- ➢ 2 samples from the inner surface.

Sample code	Sample type	Sample mass [g]	Spec-Chec [ml]	Reagents [ml]	
				Carbo-Sorb®E	Permafluor®E
1	Virgin graphite	0,16		10	10
2	Virgin graphite labelled	0,14	0,1	10	10
3	Virgin graphite labelled	0,14	0,1	10	10
4	I-graphite from outer surface	0,13		10	10
5	I-graphite from outer surface	0,14		10	10
6	I-graphite from inner surface	0,14		10	10
7	I-graphite from inner surface	0,16		10	10

Table 2.3.2. Powdered graphite samples subject to combustion process

The ^{14}C activity in the resulting solutions after each combustion cycle was measured by liquid scintillation method using a Tri-Carb® 3110TR analyzer, which allows for ultra low level counting mode with typical count rate in the range of 1 – 20 CPM above background.

The complete set of results for ^{14}C activity measurements from irradiated graphite powder are presented in Table 2.3.3.

Sample code	^{14}C Net activity [dpm]	^{14}C Specific activity [Bq/sample]	^{14}C specific activity [Bq/g]
1	31	5.17E-01	3.23E+00
2	72	1.20E+00	8.57E+00
3	75	1.25E+00	8.93E+00
4	3707.216	6.18E+01	4.75E+02
5	3710.309	6.18E+01	4.42E+02
6	3696.907	6.16E+01	4.40E+02
7	4285.567	7.14E+01	4.46E+02

Table 2.3.3. ^{14}C analysis of irradiated graphite powder

The results obtained show good consistency between the subsamples from the inner surface and from the outer surface of the graphite bar. The mean value was used to calculate the ^{14}C inventories in the samples involved in the leaching study.

Gamma spectrometry of the i-graphite powder was also carried out. Counting vials (Figure 2.3.3) were filled with graphite powder, up to a calibration line (2-3 mm), so that a standard counting geometry is obtained.

Figure 2.3.3. Irradiated graphite sample subject to gamma spectrometry analysis

The result obtained show that the only gamma emitting radionuclides, above the detection limit, present in this piece of irradiated TRIGA graphite are Eu-152 and Eu 154.

The mean values were calculated taking into account the values obtained for all sub-samples. For ^{14}C the uncertainty is given by the variation of the results for all subsamples, while the activity for the gamma emitting radionuclides comes from one measurement and the given errors correspond to the analysis method. In Table 2.3.4, the mean specific activities for ^{14}C activity measurement as well as the gamma emitting radionuclides activity, are given. In Table 2.3.5, the initial experimental conditions for leaching activities of graphite, under aerobic conditions are summarized.

Radionuclide	Mean specific activity [Bq /g]
Eu-152	89,7±0.48
Eu-154	4,92±0,16
C-14	451±16,5*

* the uncertainty is one standard deviation of the calculated mean.

Table 2.3.4. Mean specific activities of measured radionuclides in irradiated graphite

Sample code	Sample mass [g]	Leachate volume [ml]	C-14 total calculated activity [Bq]
1	172,72	1118	7.79E+04
2	168,24	1118	7.58E+04
P1	0,49	50	2.21E+02
P2	0,50	50	2.25E+02

Table 2.3.5. Experimental conditions for graphite leaching in aerobic conditions

Long term leaching tests on TRIGA irradiated graphite samples in anaerobic conditions

Although in the description of work, RATEN ICN Piteşti did not undertake to perform any leaching test on irradiated TRIGA graphite under anaerobe conditions, in order to evaluate ^{14}C longer-term release in solution, under conditions relevant to a cement-based geological disposal facility, we have recently started a new leaching test.

The leaching test is running under N_2 atmosphere in closed Pyrex glass vessels, placed on a magnetic stirrer and adapted to allow N_2 purging in order to ensure anaerobe conditions. Figure 2.3.4 shows the laboratory set-up for the irradiated TRIGA graphite leaching study under anaerobe conditions. The samples (length to diameter: 50x60 cm and masses 250.09 g respectively 249.69 g) were leached in a 1500 cm^3 volume of 0.1M NaOH solution.

Figure 2.3.4. Photograph of leaching set-up for anaerobic conditions

The sampling and renewal of the leachant, time intervals and evaluation of the result is also done as stated in Petrova et al. (2015).

The total ^{14}C partition between inorganic and organic species are foreseen to be carried out by the end of 2016 (this activity was postponed due to a delay in purchasing the catalytic furnace needed to measure the organic ^{14}C content).

In each tests the ^{14}C release in the liquid phase will be measurement by LSC using a TRICARB 3110 TR counter allowing ^{14}C measurements in ultra-low levels with typical count rate in the range of 1-20 CPM (counts per minute) above the background. To measure the inorganic and organic ^{14}C a combination of acid stripping and wet oxidation method will be used.

2.4 Agence Nationale pour la gestion des Déchets RAdioactifs / EDF (Andra / EDF) summary

Andra and EDF were involved in the review of CARBOWASTE and are now involved in 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 disposal.

Andra and EDF are more especially in charge of reviewing the data on ^{14}C release and on the speciation of ^{14}C in French i-graphites. During the first year of the CAST project, the available data on ^{14}C release in French i-graphite were reviewed and presented in deliverable D5.1.

During the second year, the data on the speciation of released ^{14}C in French i-graphites were reviewed. The associated CAST Deliverable 5.8 (Catherin, 2016) has been issued at the beginning of this third year. This deliverable is focused on two French reactors, SLA2 (Saint Laurent A2, EDF) and G2 (CEA). The studied leaching tests are the same as for Deliverable D5.1 (Petit et al., 2014). These tests have been realized with the following parameters:

- semi-dynamic sampling: Due to very low concentration of the leachate a semi-dynamic methodology has been used in order to increase the ^{14}C concentration as much as possible.

- the use of graphite powder has been chosen in order to increase the contact between the leaching solution and the graphite.

- a high quantity of i-graphite has been used. As a consequence, the tests have been carried out in CEA, in a laboratory which can handle such a quantity of radioactive material.

- the pH of the solution has been chosen in order to be representative of the future disposal, i.e. pH 13 (NaOH 0,1 M).
- the tests have been carried out with continuous agitation.

The gas phase and the leaching solution have been analyzed, and the results are presented in the Deliverable D5.8 (Catherin, 2016).

The experimental procedure gives the possibility to identify the mineral fraction and the organic fraction in the liquid. As a consequence, Deliverable D5.8 (Catherin, 2016) shows the release of these two fractions.

Due to the pH of the liquor, the assumption is that the gas phase can contain only organic molecule or CO. It was not possible to separate CO and organic molecules.

Deliverable D5.8 (Catherin, 2016) also gives an overview of the influence of some parameters, i.e. water chemistry and specific surface area of the samples. Some other parameters can have an impact but these were not studied yet.

2.5 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, as per all the graphite coming from moderators exposed to a neutron flux (Latina NPP flux reached $5x10^{22}$ n/cm^2), presents a wide range and amount of activation products such as ^{3}H, ^{14}C, ^{36}Cl, ^{55}Fe, ^{60}Co, ^{63}Ni, ^{134}Cs, ^{154}Eu and ^{155}Eu.

This distribution of activated elements concerns the bulk of the samples, mainly in the closed porosity or between the typical graphite layers; chemical bonds are not usually involved. 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 the solvent to reach the inner layers/areas (i.e. closed pores, crystallites, etc.) and extract contaminants in solution.

The main idea of the current ENEA work is to apply an exfoliation-like process to 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. 2011, Choi et al. 2011, Hernandez et al. 2008 and Bourlinos et al. 2009). This process, helped by mild sonication, consists in separating the individual layers in a more or less regular manner. Such a separation is sufficient to remove all the inter-planar interactions, due to the dipole-induced/dipole interactions between graphene layers and organic solvents, and results in a dispersion of the graphite in a workable media. This facilitates processing, treatment and characterization for the contaminants recoveries (Figure 2.5.1).

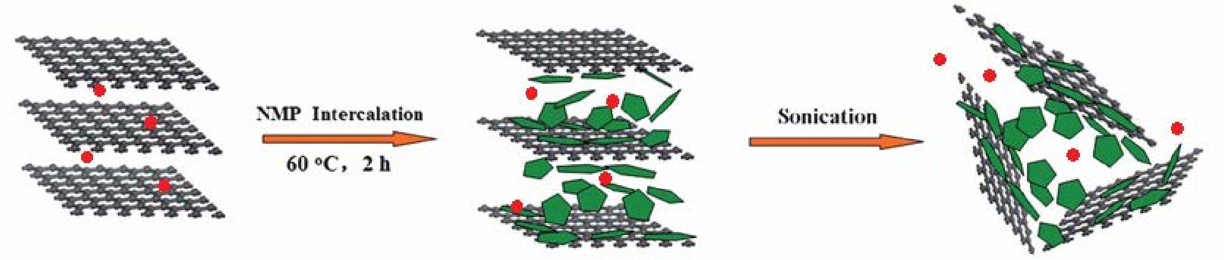


Figure 2.5.1: Representation of the main steps for the graphite exfoliation process promoted by organic solvents and ultrasound assisted

Moreover, the oxidation process is not performed by super-strong acid actions, as this would lead to non-oxidized products, and the graphite would be completely recovered, without alteration, at the end of the treatment (no chemical transformation would have been performed, only a physical one, so at the end of the process recovery of graphite, albeit in a different physical form - graphene layers - would be possible).

During this last year, the exfoliation-like process on the graphite by organic solvents (liquid-phase exfoliation) helped by mild sonication has been widely studied to establish the best process parameters in order to obtain graphene layers in a stable homogeneous dispersion. This will result in a dispersion of the graphite in a workable media. In this way it should be allowed by the solvent to reach the inner layers/areas (i.e. closed pores, crystallites, etc.) and extract contaminants.

This facilitates processing, treatment and characterization for the contaminants recoveries when applied on i-graphite. The overall process has been tested on some samples of nuclear graphite from Latina NPP. The improvements to the process and the related results are described herein.

Experimental Procedures: preliminary considerations

As it has been stated in the previous reports, the main steps in this process are:

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

For the first point, in order to overcome the van der Waals-like forces between graphite layers to yield a good exfoliation and dispersal of the resultant graphene sheets in a liquid media, highly polar organic solvents have to be used:

- 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.

For the second point a sonication power of 30W and a frequency of 37kHz has been assessed as it arises from the experiments made in the last year.

Although the right centrifugation rate should also be widely tested in order to remove all large aggregates to be reprocessed by following exfoliation step, in this work a low centrifugation rate (500 rotations per minute, rpm) followed by a filtration step has been chosen in all the experiments already performed, because of the good results obtained. The supernatant liquid phases coming from the centrifugation are filtered on polyvinylidene fluoride (PVDF) filter membranes of 0.10 µm of pore size.

For the last point, the process has been applied on three samples of nuclear graphite coming from the decommissioning of the Italian NNP in Latina. Previously, on these i-graphite samples, a characterisation of ^{14}C contents has been performed. Then, the radiocarbon measurement by Liquid Scintillation Counting (LSC) on the extracting solutions has established the Removal Efficiency values.

Experimental Procedures: description of the process on irradiated graphite

Preliminary measurement of ^{14}C on i-graphite samples

Works previously done during the last two years has been performed on virgin nuclear graphite; this work has proved the validity of the overall process on the exfoliation of the nuclear graphite as well as for HOPG. From this point forward, work will be based on the trial use of the process for extracting radiocarbon from irradiated nuclear graphite, and, having assessed the best parameters, suggestions for improving the process will be made.

First a characterisation on the i-graphite samples in term of ^{14}C content has been performed. For this purpose, 13 samples of the 15 available have been processed. For each of the 13 samples, 0.1 g of powder has been taken and added to 100mL of a mixture of H_2SO_4-HNO_3-$HClO_4$ 8:3:1 v/v/v for the determination of ^{14}C by Wet Oxidation Acid Digestion. The system for the graphite samples digestion consist in a hot acid digestion in a closed apparel under N_2 flow and a series of Drechsel bottles for trapping the ^{14}C as CO_2 in 3-MPA (3-methoxypropylamine). The system is shown in Figure 2.5.2.

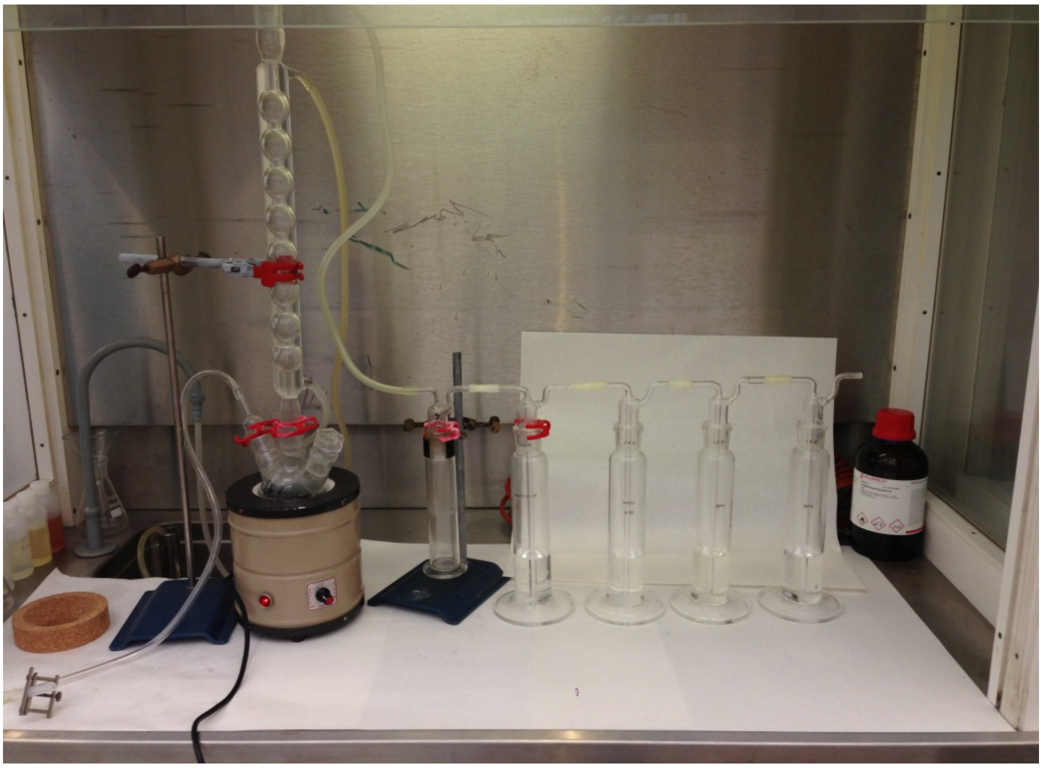


Figure 2.5.2 – Apparel for the wet oxidation acid digestion of the graphite sample for the ^{14}C determination.

The solutions of 3-MPA obtained from graphite samples dissolution are then measured by Liquid Scintillation Counting with a LSC HIDEX 300SL TDCR. The concentrations of activity for each sample analysed are illustrated in Table 2.5.1.

	iGF1	iGF3	iGF4	iGF5	iGF6	iGF7	iGF8	iGF9	iGF10	iGF12	iGF13	iGF14	iGF15
kBq/g	**8508**	**12886**	**8552**	**37769**	**4650**	**7315**	**4370**	**9520**	**49489**	**68583**	**6042**	**80704**	**76744**

Table 2.5.1 – ^{14}C concentration of activity of irradiated graphite samples before treatment

Solvent treatment Ultrasound assisted on i-graphite samples

The test for applying the organic solvent treatment by exfoliation has been performed on 3 of the 13 characterised samples.

For each different sample, for 10 mg of i-graphite powder, 5 mL of solvent was added (DMF, DMA and NMP).

The time of sonication is set on 3, 5 and 10 hours for each group of the same sample but different solvent, in a sonication bath at the power of 30W – 37 kHz.

The solutions obtained have then centrifuged at 500 rpm for 90 minutes followed by filtration on PVDF 0.1 μm filters. These filters were then dried in a vacuum oven and weighed.

The filtrated solution then is supposed to contain the ^{14}C extracted by mean of this process. In order to confirm this, each organic solution coming from the process above-described (3 for each of the 3 different organic solvent, corresponding to the 3 organic solvent used and 3 different time of sonication) has been analysed in order to measure the ^{14}C content.

The results are shown in Table 2.5.2; values of the Removal Efficiency in percentage (RE%) for each test are also shown. The Removal Efficiency (in %) is defined as a percentage that represents the activity removed from the original matrix relative to the activity before the applied process.

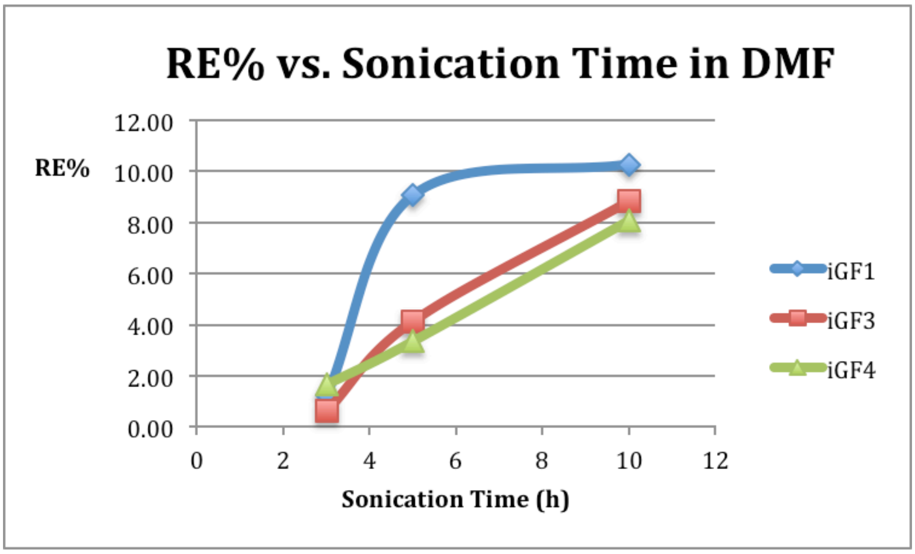
Sample ID	weight (g)	solvent (5 mL)	time (h)	Initial Activity (Bq)	Removed Activity (Bq)	RE%
iGF1	0,0108	DMF	3	91.89	1.12	**1.22**
	0,0100		5	85.08	7.71	**9.06**
	0,0113		10	96.14	9.87	**10.26**
	0,0111	DMA	3	94.44	0.21	**0.23**
	0,0112		5	95.29	4.27	**4.48**
	0,0110		10	93.59	11.49	**12.28**
	0,0112	NMP	3	95.29	0.85	**0.89**
	0,0107		5	91.04	2.02	**2.22**
	0,0104		10	88.49	8.47	**9.57**
iGF3	0,0109	DMF	3	140.46	0.87	**0.62**
	0,0107		5	137.88	5.69	**4.13**
	0,0111		10	143.03	12.63	**8.83**
	0,0102	DMA	3	131.44	1.34	**1.02**
	0,0114		5	146.90	11.11	**7.56**
	0,0102		10	131.44	19.01	**14.46**
	0,0101	NMP	3	130.15	3.14	**2.41**
	0,0110		5	141.74	5.59	**3.95**
	0,0109		10	140.46	14.01	**9.98**
iGF4	0,0103	DMF	3	88.08	1.45	**1.65**
	0,0113		5	96.63	3.26	**3.37**
	0,0114		10	97.49	7.89	**8.10**
	0,0112	DMA	3	95.78	0.37	**0.39**
	0,0103		5	88.08	1.10	**1.25**
	0,0107		10	91.50	3.72	**4.07**
	0,0109	NMP	3	93.21	1.73	**1.85**
	0,0120		5	102.62	3.80	**3.70**
	0,0120		10	102.62	13.68	**13.33**

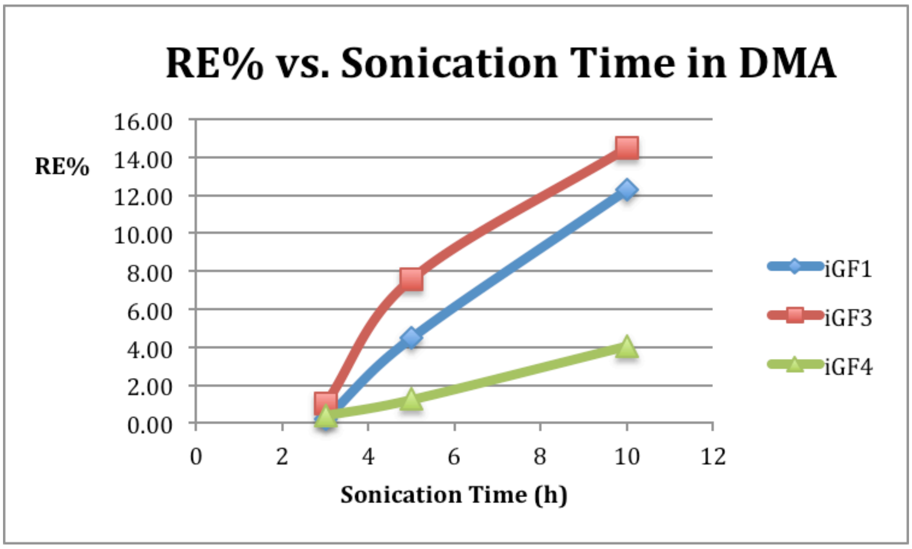
Table 2.5.2 Summary of the tests performed on i-graphite samples and relative results

Results and Discussion

In order to have an idea on the efficiency of this exfoliation-like process for the treatment of the irradiated graphite and in particular with respect to the radiocarbon, these preliminary and first results, as shown in Table 2.5.2, can be represented by plotting the values of removal efficiency RE% for each solvent used towards the sonication time, for each iGF sample.

This is illustrated in Figure 2.5.3.





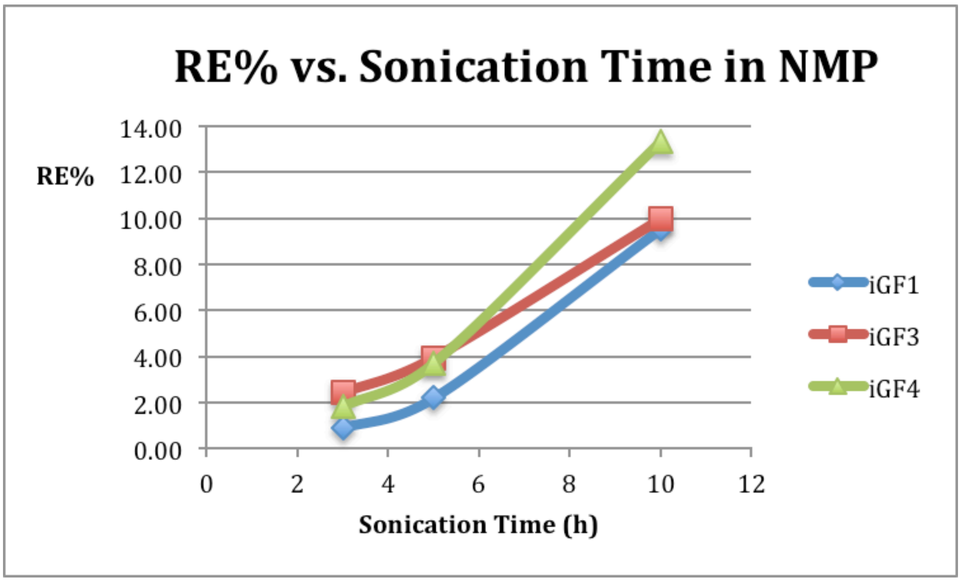


Figure 2.5.3 ***(from ttop to bottom)*** **Removal efficiency in % for each organic solvent (DMF, DMA and NMP) with respect to different sonication times for 3 different irradiated graphite samples.**

At the first glance what comes out is that the efficiency of removal of the activity in terms of ^{14}C increases with the respect to the sonication time. This is well explained by the fact that, as already demonstrated in the previous report, the exfoliation of the graphite increases with respect to the sonication time. So, this allows to the solvent to easily reach the target radiocarbon in the closed porosity and extract it.

Moreover, no solvent seems to be better than another as all of them play the same property in solvating the radiocarbon without particular capacity.

The yields in extraction (RE%) obtained range from 0.2 to about 15 %; although these values are relatively low, they can be considered the first ones obtained with this kind of treatment since no other value are produced in the literature by the same process to be compared. These results should be considered promising to keep on by this route.

Future activities

At this point, after having considered the results obtained, it seems clear that the next parameters of the process to focus on are the solvent choice and/or the improvements in extracting/solvency properties of these in order to enhance the degree of removal for the ^{14}C.

For this route the attention will be moved on the addition of particular chemicals able to enhance the extraction of the ^{14}C taking into account the speciation of the radiocarbon in the graphite. For this purpose, alkaline salts as NaOH, KOH, etc will be tested.

From literature works it has been also suggested that solvents like 1-propanol, water and surfactants seem to play a fundamental role in improving exfoliation. This gives a suggestion on how a better exfoliation could improve the extraction of radiocarbon for the aim to allow to the solvent to reach inner porosity and extract more ^{14}C.

2.6 Forshungzentrum Juelich GmbH (FZJ) summary

Progress in Task 5.2

Pre-leaching examination was performed for the irradiated nuclear graphite sampled from the block 4 of the head part of thermal column (TC) of RFR (Rossendorfer Forschungsreaktor). The block was cut in plates of 3 cm thick (10 plates in total). The plate No. 5 was chosen for further sampling, which corresponds to the 15cm distance from the reactor core. The samples for leaching were taken in the form of cylinders of 30 mm long and 25 mm in diameter (for more details see CAST Deliverable D5.6, Toulhoat et al, 2015).

For characterization of sampled graphite, the γ-spectrometry was performed using a semiconductor coaxial detector with beryllium window (Model Gr3018 by Canberra). Acquired spectra were evaluated using GammaVision software (ORTEC). For measurement, a sample of graphite was placed 20cm over the detector, therefore the evaluation was performed assuming the sample as a point source. The results of γ-spectrometric analysis, summarized in the Table 2.6.1, demonstrate that the main source of gamma-radiation is ^{60}Co. The results also show the presence of ^{137}Cs and europium isotopes, however the isotopes ^{134}Cs and ^{133}Ba normally present in irradiated graphite are completely decayed. An overall activity of gamma-emitting isotopes was relatively low and didn't exceed 200 Bq/g.

Sample No.	mass, g	^{152}Eu	^{154}Eu	^{155}Eu	^{137}Cs	^{60}Co	^{133}Ba
1	23.481	1.11	0.99	bdl	2.05	25.63	bdl
3	23.569	1.08	1.72	bdl	2.15	28.55	bdl
4	23.760	0.72	1.37	bdl	1.92	27.11	0.34
5	23.630	0.93	1.97	bdl	3.93	15.32	bdl
6	23.409	1.45	0.99	bdl	2.52	11.91	0.07
7	23.629	0.42	1.97	bdl	2.38	27.42	0.30
8	23.249	0.63	2.02	bdl	5.67	11.93	bdl
9	23.254	0.71	2.10	bdl	3.32	7.41	0.10
10	23.459	0.21	1.90	bdl	2.40	27.62	0.30
11	23.257	0.55	1.95	bdl	4.56	16.56	0.38
12	23.170	1.06	3.84	bdl	7.28	43.96	0.23
13	23.164	0.37	2.08	bdl	0.77	37.90	0.34
14	23.076	0.79	3.15	bdl	2.20	20.16	0.65
15	22.451	0.27	2.92	bdl	1.41	24.61	1.03
16	22.999	5.49	4.73	bdl	0.81	65.39	bdl
17	23.092	2.69	3.38	bdl	1.07	50.20	bdl
18	23.282	2.44	2.60	bdl	0.75	48.73	bdl
19	22.735	4.21	5.85	bdl	4.03	67.56	0.57
20	22.750	2.01	3.39	bdl	2.50	31.36	bdl
21	22.933	1.58	2.66	bdl	1.08	22.87	bdl
22	22.670	3.58	6.61	bdl	5.20	63.05	0.35
23	22.698	1.43	4.23	bdl	3.34	26.48	bdl
24	22.699	1.43	3.77	bdl	0.99	13.31	0.64
25	22.548	2.52	8.46	0.81	3.17	90.78	0.51
26	22.259	1.63	4.95	bdl	3.28	30.56	0.46
27	22.149	2.09	8.79	0.74	1.71	112.77	0.41
28	21.949	0.99	6.79	0.80	2.25	36.16	0.36
29	22.188	0.84	4.81	0.59	2.78	39.68	0.58
30	21.990	2.09	10.79	1.42	2.70	141.28	1.55
31	21.926	0.90	6.93	0.83	1.74	46.89	0.99

*bdl – below detection limit: DL(^{155}Eu)=0.5 Bq/g, DL(^{133}Ba)=0.1 Bq/g

Table 2.6.1: Results of γ-spectrometric characterization of irradiated graphite (TC) from RFR (in Bq/g): block 4, plate 5.

It should be noticed that activity distribution of the graphite is not uniform. Mainly, it is due to the neutron flux deviation. As an example, Figure 2.6.1 demonstrates the distribution of ^{60}Co specific activity over the graphite plate. Here the ^{60}Co activity increases in a direction from up to down (vertically) and from left to the right (horizontally), corresponding to the neutron flux deviation. As the distribution of ^{14}C in graphite linearly depends on the neutron flux, the ^{60}Co-mapping was used for selection of the samples, presumably more enriched in ^{14}C, e.g. samples 22, 25, 27 and 30.

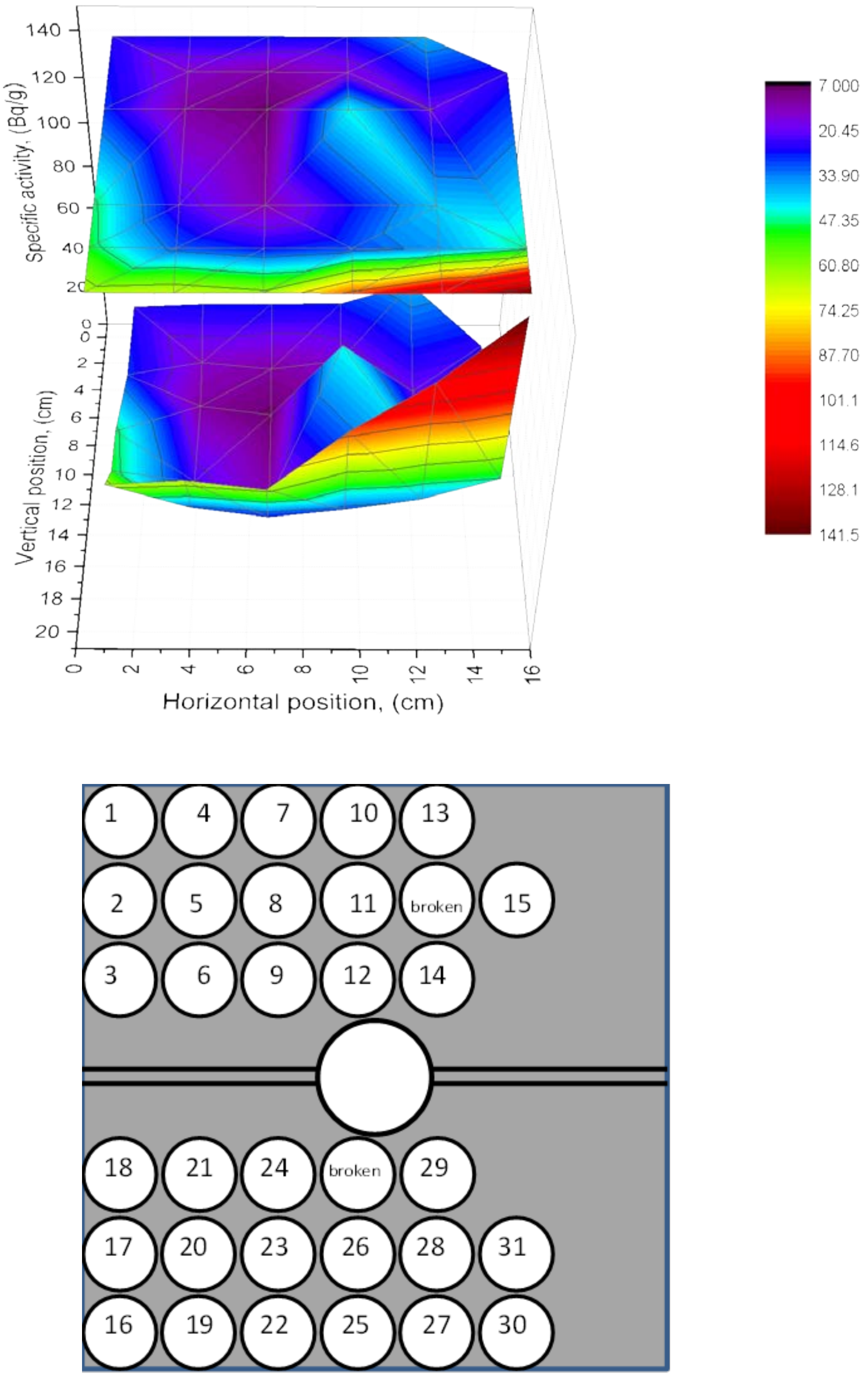


Figure 2.6.1: Distribution of ^{60}Co specific activity over the irradiated nuclear graphite from RFR correlated to the sampling positions (block 4, plate 5, ca. 15 cm from the reactor core).

Former studies demonstrated that distribution of activation products (APs) in nuclear graphite is inhomogeneous and APs are usually present in the form of hot-spots (Kuhne et al., 2015). For more detailed investigation of AP distribution in RFR graphite a few samples were analyzed by autoradiography method. This non-destructive method allows for rather quick identification of activity spatial distribution and hot-spots. The method is sensitive to the radioactive components, however it does not allow the qualitative or quantitative analysis of the hot-spot composition in a voluminous samples. Therefore an SEM equipped with EDX was used for investigation of hot-spots with the higher precision. The analyses have been performed with use of a sensitive plate followed by the plate scanning with CR-35 image scanner (Raytest, Germany). The image data analysis program AIDA (Raytest, Germany) was used for data evaluation. The contact time varied from 3.5 to 5 hours, which allows for a scan resolution of 50 microns. The analyzed samples (e.g. 7, 11, 17, 5 and 29) were selected in the way that graphite from the center as well as the periphery of the plate exposed to the different neutron fluxes is characterized. The results of autoradiography, given in Figure 2.6.2, demonstrate the presence of hot-spots on every graphite sample selected. The contrast of background indicates the degree of activation. White inclusions on the images are shielded areas from a copper tape, used for an indication and localization of the hot-spots.

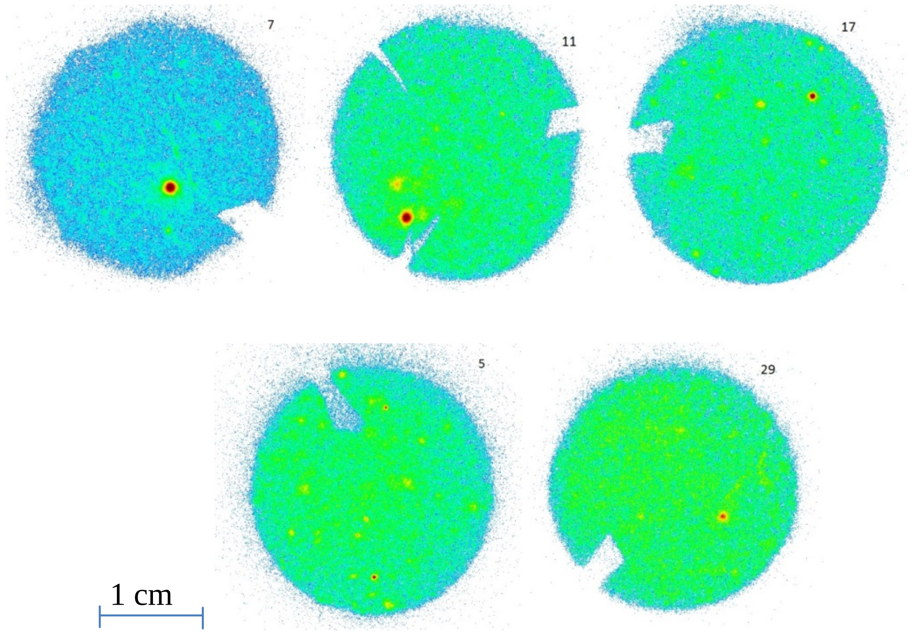


Figure 2.6.2: Autoradiography images irradiated graphite samples from RFR; colours other than blue correspond to activity above the background; red corresponds to the regions with the highest activity.

Following an autoradiography the SEM/EDX was performed for the revealed hot-spots. The results are shown in Figure 2.6.3, demonstrating autoradiography and SEM images of the hot-spot area.

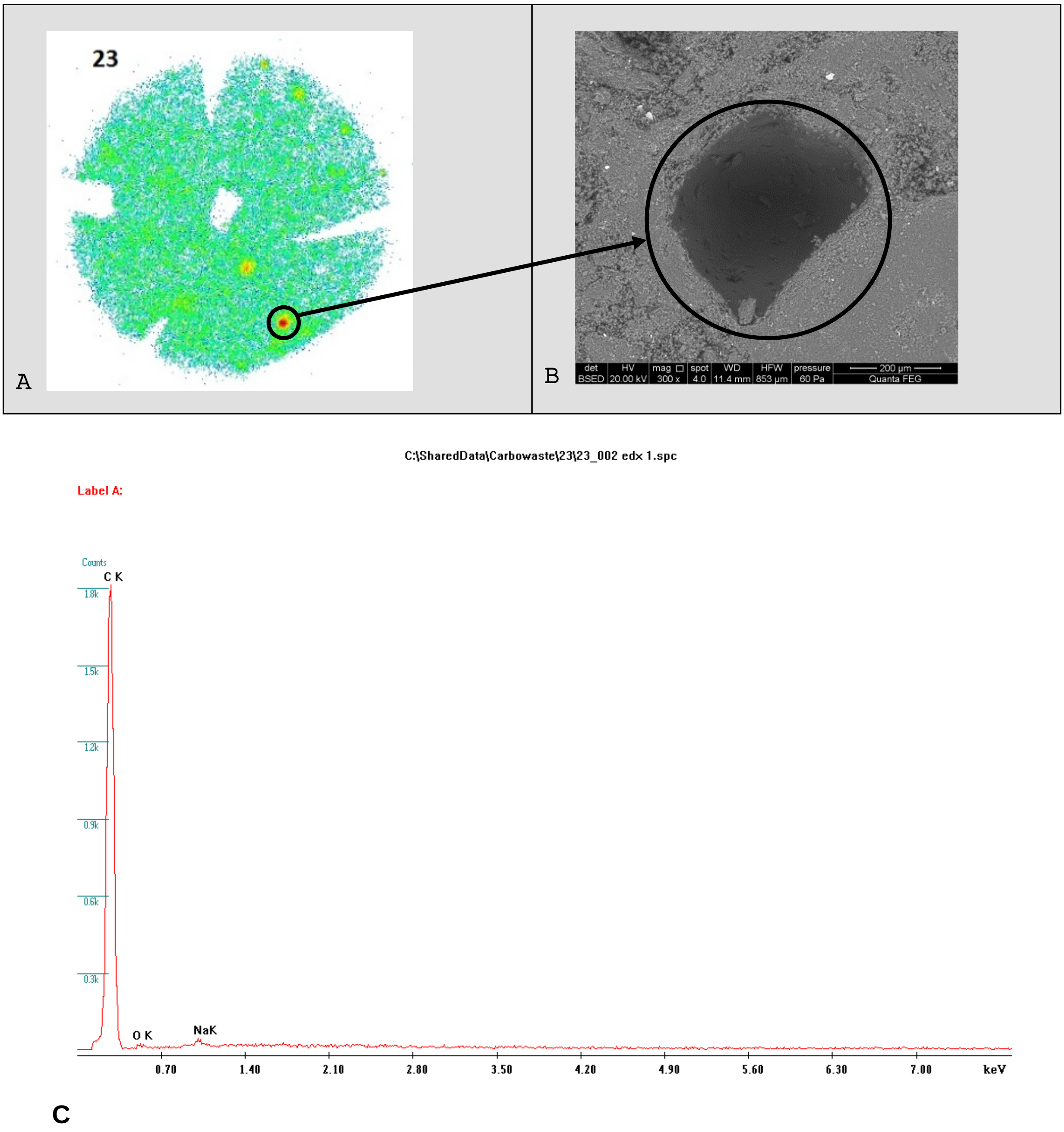


Figure 2.6.3: Graphite hotspots characterization with autoradiography/SEM/EDX: (A) – autoradiography image, (B) - SEM image of the hotspot area, (C) - EDX spectrum.

From the EDX spectrum, it is clearly seen there is almost no impurity in the hot-spot vicinity, mainly the carbon X-lines and traces of oxygen and sodium. No significant amounts of impurities around hot-spots may indicate that the increased activity in these areas was due to radioactive ^{14}C. This result was consistently observed for all graphite samples and is in a good agreement with an assumption that the highest fraction of ^{14}C inventory is activated from ^{14}N, accumulated in the pores or on the pore surface. The ^{14}C activated from ^{13}C is uniformly distributed in the graphite, and therefore cannot be the reason of hot-spots, but rather contributes to the background on the autoradiography images.

Given that a significant amount of ^{14}C is accumulated in the pores, the information about the graphite porosity and surface area of the pores is important parameter needed for a proper evaluation of ^{14}C release rate. Until now the porosity was estimated by accounting for a difference of nuclear graphite density from its theoretical once. For better precision, an experimental measurement of graphite porosity is in progress.

Progress in Task 5.3

The first leaching test on nuclear graphite has been started. Figure 2.6.4 demonstrates assembled equipment used for leaching tests. Within this reporting period the test with inactive nuclear graphite from RFR was performed. The experiment with the blank (i.e. not irradiated) sample is meant for establishing a proper sampling technique for gas and liquid samples, as well as obtaining the background composition for carbon species in the gas and liquid phase.

Figure 2.6.4:An assembled reactor vessel (Berghof GmbH) for leaching test with nuclear graphite.

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

Progress in Task 5.3

During this third year of the CAST project CIEMAT's efforts concerning WP5 have been focused on the need to adapt our knowledge on leaching cemented wastes, based on the use of the ISO 6961 standard, to the irradiated graphite powder samples available in our laboratories.

After some preliminary tests, and a thorough review of the ISO norm mentioned above and the associated leaching rates that could have been obtained using powder samples, the use of graphite in this form was finally discarded, mainly because of the following reasons:

- Due to the static electricity of the reactor PFTE inserts, a variable amount of the powder graphite got retained or stuck to the walls; moreover, a thin layer of powder was observed floating on the leachant. Therefore, it is considered that this graphite is not under the same leaching conditions as the rest of the sample, and the leaching results may not be representative of the whole sample.
- The complete renewal of the leachate (static leaching), according to CIEMAT's procedure (Carpentiero et al., ENTRAP Report WG-B-02, Abril 2004), implies the recovery of the powder suspended in the liquid by filtering. Testing with samples of around 1 – 2 grams, a loss of mass of approximately 1 – 2 % was observed in every leaching step.
- Dubious suitability to powder samples of a method (ISO 6961) intended for monolithic waste forms, mainly in terms of the surface or volume of the sample that had to be considered, and that can yield questionable leaching rates figures expressed as incremental leaching rates as a function of leaching time.

Because of the reasons previously mentioned, a procedure to obtain monolithic specimens with regular shape from the small graphite pieces from Vandellós-I NPP (UNGG reactor) had to be created.

Leaching samples manufacturing process

The method chosen to prepare the leaching specimens consisted on:

- First of all, the biggest fragments of graphite available (stone-like material of around 2 - 3 cm. Ref. GC-2) were selected and wrapped in plastic (Figure 2.7.1).
- The selected pieces were put into a weighting bottle of 60 x 35 mm (Ø x h) containing fresh cement for at least 48 hours or until the mixture becomes set (Figure 2.7.2).
- Into a portable glove box, graphite core samples of about 11 mm x 12 mm (Ø x H) were obtained using a diamond core drill of 14 mm Ø (Figures 2.7.3 and 2.7.4).
- The upper and lower surfaces of the cylindrical blocks were polished with P120 grit paper.
- All the samples obtained were weighed and by means of a caliper with ± 0.02 mm accuracy, the diameter "Ø" (average of the values obtained in the middle and both ends of the cylinder) and the height "H" (average of two measures taken at points separated 90°) of the sample were determined, and therefore the specimen volume and its surface area (the physical properties of samples obtained this way are provided in Table 2.7.1).
- The most of the graphite powder produced after each drilling was contained into the weighting bottle. In this way, it could be easily collected for its radiological characterization by gamma spectrometry and, prior to its total incineration, by LSC (Table 2.7.2).

Figure 2.7.1. GC-2. Selected graphite.

Figure 2.7.2. Cemented graphite sample.

Figure 2.7.3 (Above). Graphite core 11 mm x 12 mm (ØxH) and diamond core drill 14 mm Ø.

Figure 2.7.4 (Left). Vise clamp, drill and cemented sample.

Sample Ref.	Mass (g)	H_{avg} (mm)	$Ø_{avg}$ (mm)	S (cm^2)	V (cm^3)	$Ø_{avg}$ / H_{avg}	ρ (g/cm^3)
V-I-1	1,9688	12,68	11,28	6,49	1,27	0,89	1,55
V-I-2	2,0222	12,51	11,09	6,29	1,21	0,89	1,67
V-I-3	2,1861	14,07	11,11	6,85	1,36	0,79	1,60
V-I-4	1,8077	12,15	11,08	6,15	1,17	0,91	1,54
V-I-5	1,9102	11,70	11,07	5,99	1,13	0,95	1,70
V-I-6	2,0964	12,51	11,05	6,26	1,20	0,88	1,75

Table 2.7.1. Specimens 1 to 6 - physical properties.

	Activity (Bq/g)								
Sample	**C-14**	**Am-241**	**Ba-133**	**Co-60**	**Cs-137**	**Eu-154**	**Na-22**	**Nb-94**	**Zr-95**
V-I-1	1,22E+04	3,97E+02	1,67E+01	5,56E+01	2,03E+03	1,51E+02	2,18E+01	1,14E+01	1,17E+01
V-I-2	1,35E+04	1,14E+02	1,27E+01	4,98E+01	3,98E+02	4,41E+01	6,86E+00	8,22E+00	3,63E+00
V-I-3	1,08E+04								
V-I-4	1,13E+04								
V-I-5	1,12E+04								
V-I-6	1,10E+04								

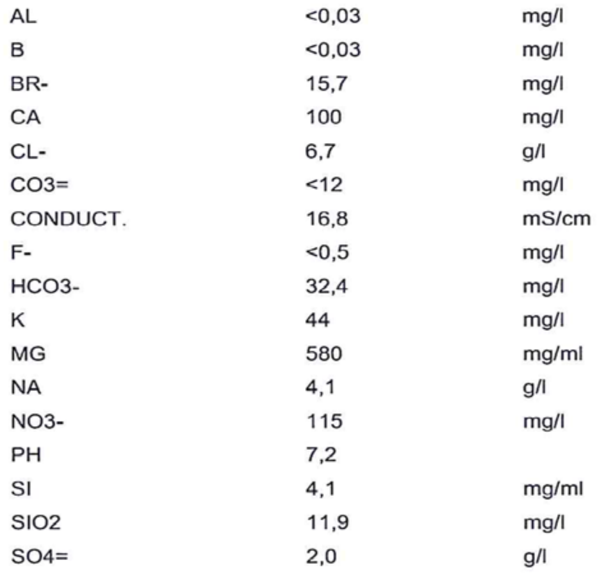
Table 2.7.2. Radiological characterization of graphite cylinders 1 to 6.

Leaching procedure

Once graphite cylindrical samples were obtained, the leaching process was carried out on the basis detailed below.

Specimen, leachant, leachant container and temperature

Leaching experiments started on June 2016 with the V-I-1 and V-I-2 core-drilled samples whose main characteristics are depicted in Tables 2.7.1 and 2.7.2. As leachant, Milli-Q® water type 1 (pH = 5.8, EC = 0.05 µS/cm) for V-I-1 and granite-bentonite water (synthetic) for V-I-2 has been used (see Table 2.7.3 for granite-bentonite water composition).



AL	<0,03	mg/l
B	<0,03	mg/l
BR-	15,7	mg/l
CA	100	mg/l
CL-	6,7	g/l
CO3=	<12	mg/l
CONDUCT.	16,8	mS/cm
F-	<0,5	mg/l
HCO3-	32,4	mg/l
K	44	mg/l
MG	580	mg/ml
NA	4,1	g/l
NO3-	115	mg/l
PH	7,2	
SI	4,1	mg/ml
SIO2	11,9	mg/l
SO4=	2,0	g/l

Table 2.7.3. Granite-bentonite water composition.

The leachant container is made of PTFE (material recommended for its chemical inertness) and the value of the ratio provided by dividing the volume of leachant by the exposed geometric surface area of specimen is 0.2 m. This geometric surface area is calculated from measurements of the overall macroscopic dimensions of the specimen. During the leach tests carried out up to now, although the tests have been conducted at room temperature, the losses of leachant by vaporization are negligible.

Leach container preparation and leachant renewal

The specimen is suspended in 120 ml of leachant by means of a PFTE thread and surrounded by at least 1 cm of liquid in all directions (Figure 2.7.5). The total volume of the vessel is 150 ml and prior to its first use it was cleaned up with deionized water.

Figure 2.7.5. Leaching containers for deionized water and granite-bentonite water.

The initial gas phase composition consists on synthetic air (21 % oxygen, 79 % nitrogen) supplied from a 5 litre compressed air cylinder.

The leachant changing frequency has been chosen depending on the material, its radioactivity levels and the availability for measurements of the different equipment needed. Based on that, it was planned to renew both the gas and the leachate after 14, 28, 56, 90, 180 and 360 days from the start of the test. The periods corresponding to 14, 28, 56 and 90 days have been already covered.

After each interval, first of all the gas sample (volatile species) is collected through the gas sample extraction valve by means of a gas tight syringe and immediately injected into the GC-MS system. Once completed the previous step the container is opened, the specimen is withdrawn from the leachant, and the leachate is filtered using Schleicher & Schuell white ribbon filter paper and finally transferred to a PEHD bottle. Both, the filter paper and the liquid are conveniently stored for later analysis.

Once stored the leachate, the PFTE is cleaned up with deionized water, refilled with fresh leachant, the specimen immersed in the liquid and the reactor closed with its headspace purged with synthetic air.

Analyses and preliminary results

The pH and electrical conductivity of leachant and leachate are determined before and after each leaching period (see Table 2.7.4).

		pH		**EC (µS/cm)**	
		Initial	**End**	**Initial**	**End**
Deionized Water	Leaching Period 1 (15 days)	5,52	7,1	0,05	16,3
	Leaching Period 2 (28 days)	5,7	6,13	0,05	6,8
	Leaching Period 3 (56 days)	5,37	6,21	0,05	10,79
	Leaching Period 4 (90 days)	6,29		0,05	
Granite-Bentonite Water	Leaching Period 1 (15 days)	7,31	6,87	21200	21700
	Leaching Period 2 (28 days)	7,32	6,93	21400	21000
	Leaching Period 3 (56 days)	7,09	7,21	20400	21300
	Leaching Period 4 (90 days)	7,27		20500	

Table 2.7.4. pH and EC control of leaching solutions.

The filter paper and the filtered leachate have been taken to analyze its activity of ^{14}C with a Packard Tricarb 3110 TR/LL LSC or/and Quantulus LSC system (this last one currently in the process of setting up), and gamma emitters with a Canberra BEGe 3830 HPGe Detector.

The gas and leachate volatile species are being measured with an Agilent GC-MS 7890B system (Agilent DB624UI 60m column type for liquid samples and Molsieve 5A Porabond Q column for permanent gases and CO_2) and the organic dissolved species (carboxylic acids) with an IC Dionex ICS-900 Ion Chromatography System with Ionic Reagent Free Controller (RFC) with an AS11-HC column.

To date, although all the gas phases have been analyzed, and the leachate samples extracted, GC-MS, IC and LSC conclusive results are pending.

Progress in Task 5.4

IGM SAMPLES

Graphite is a geologically stable material proven by its natural occurrence but its porous structure enables the penetration of aqueous phases into the graphite and therefore radionuclides can be leached. However, i-graphite could be transferred into a long term stable impermeable graphite matrix (IGM) which would inhibit ingress of water and disable the release of any radionuclides, resulting in a safer final disposal. Crushed graphite mixed with a suitable glass powder has been pressed at elevated temperature under vacuum. The vacuum is required to avoid gas enclosures in the obtained product. The obtained products, IGM samples, have densities above 99% of theoretical density. The amount of glass has been chosen with respect to the pore volume of the former graphite parts (20% glass, 80% graphite). The method allows the production of encapsulated graphite without increasing the disposal volume.

As the glass may interact with aqueous phases and could be dissolved, a leaching resistant glass is required for the IGM in order to obtain a long term stable material. For this purpose leaching experiments of inactive IGM samples were performed with 5 different glass types used as inorganic binder material.

The first studies investigate the behaviour of IGM without radioactive contamination. Two leachants, deionized water and granitic-bentonitic water, have been selected to simulate the Spanish final disposal conditions. Deionized water is the worst case (the conservative conditions) for final disposal because it has no ions in its composition and the leaching rate will be greater than other types of water. The granitic-bentonitic water simulates the conditions for deep geological disposal.

Leaching experiments are performed with virgin graphite and 5 types of glasses. In these experiments, the corrosion progress is determined by mass loss, and the corrosion behaviour of glass is determined by chemical analysis of the leachant, studying if the components of the glass matrix - Al, B, K, Na and Si - are leached. The corrosion rate is a key parameter for determining the applicability of IGM as waste matrix and must be studied before using irradiated graphite in experiments.

Once which glass matrix has less corrosion in contact with the leachant is determined, it is necessary to establish the best formula in the hot vacuum press, which allows manufacture of the IGM samples. For these tests, non-irradiated graphite has been used.

Once the best formula for making the samples had been established, they were then manufactured with irradiated graphite.

Manufacture IGM samples by hot vacuum press

The system for manufacturing the samples, a hot vacuum press is in Figure 2.7.6:

Figure 2.7.6. Hot Press

Procedure

To prepare the samples it is necessary to grind the graphite. The obtained graphite powder will be mixed with the glass in the correct proportion (usually 80% graphite- 20% glass). It is necessary to manufacture samples with a density around 2,2 g/cm^3.

The two powders that are to be mixed are introduced in the pressing tool (Figure 2.7.7). Previously the tool wall will be covered with graphite foiled to avoid the mixture baking together with the wall of the tool.

Figure 2.7.7. Pressing Tool with 2 cm diameter.

Now the tool is mounted in to the furnace, Figure 2.7.8, and the door is closed.

Figure 2.7.8. Inner Furnace.

The work temperature is 1270 ºC, the force 10 kN and the duration 12 hours. When the cycle is finished, the sample is demolded with a small hydraulic press. Now the sample is weighed with the graphite foil. Than the graphite foil is removed by a cutter and by sandpaper.

The samples obtained are shown in the following picture (Figure 2.7.9).

Figure 2.7.9. IGM samples

For irradiated IGM samples, the procedure is the same but the work with the i-graphite was performed in a flexible glove box which was set up in a hood (Figure 2.7.10).

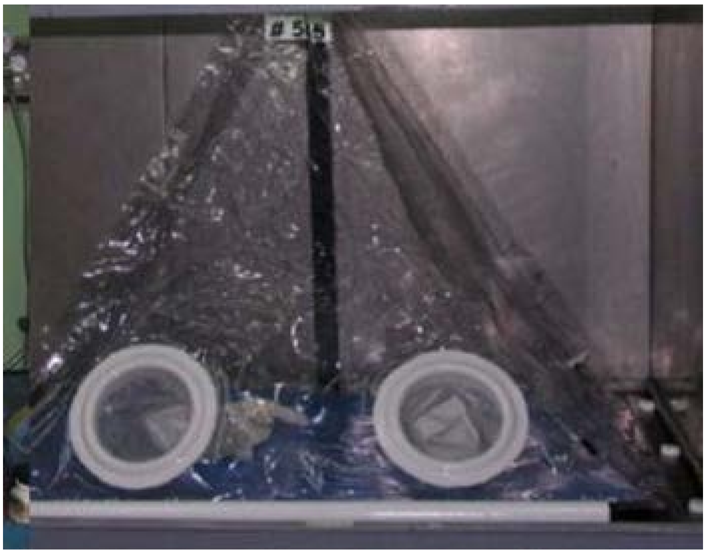


Figure 2.7.10. Glove box.

With this methodology two IGM samples have been manufactured for this project. The same graphite used for cylindrical blocks, Ref. GC-2, was selected. The density was measured by Archimedes balance.

The leaching methodology has been described in CAST Deliverable D5.4 (Petrova et al., 2015); only one change was necessary because Teflon beakers induce contamination of leachant with low dose rates: little amounts of fluoride come from beaker's walls and act as a complexant of certain nuclides (as demonstrated at Forschungszentrum Jülich GmbH (FZJ) with Th (IV)).

To solve the problem of Teflon, containers of polyether ether ketone (PEEK) have been bought and used with the IGM samples. The volume of these containers is less than the PTFE containers so only 100 ml of leachant was used.

Leaching experiments started on July 2016 with the IGM samples. As leachant, Milli-Q® water for IGM-4 and granite-bentonite water for IGM-5 has been used.

Analyses and preliminary results of IGM samples

The size and weight of the samples are shown in Table 2.7.5:

Sample Ref.	Mass (g)	H_{avg} (mm)	$Ø_{avg}$ (mm)	ρ (g/cm^3)
IGM-4	7,6949	11,50	20,67	2,04
IGM-5	7,8156	11,01	20,70	2,01

Table 2.7.5. Physical properties

The initials activities of the samples are indicated in Table 2.7.6:

	Activity (Bq/g)								
Sample	**C-14**	**Am-241**	**Ba-133**	**Co-60**	**Cs-137**	**Eu-154**	**Eu-155**	**Nb-94**	**Zr-95**
IGM-4	1,13E+04	2,90E+01	3,71E+00	8,39E+01	1,14E+02	3,83E+01	4,91E+00	1,33E+00	2,12E+00
IGM-5	1,13E+04	2,93E+01	3,79E+00	8,49E+01	1,19E+02	2,98E+01	1,68E+00	1,32E+00	2,75E+00

Table 2.7.6. Activity (Bq/g)

The pH and electrical conductivity of leachant and leachate are noted in Table 2.7.7:

		pH		EC (µS/cm)	
		Initial	**End**	**Initial**	**End**
Deionized Water IGM-4	Leaching Period 1 (13 days)	5,72	8,99	3,55	46,5
	Leaching Period 2 (28 days)	6,04	8,08	2,68	18,88
	Leaching Period 3 (59 days)	5,87	8,03	3,85	19,5
	Leaching Period 4 (90 days)	5,73		1,57	
Granite-Bentonite Water IGM-5	Leaching Period 1 (13 days)	7,06	8,13	21400	22000
	Leaching Period 2 (28 days)	7,24	7,04	20400	21300
	Leaching Period 3 (59 days)	7,31	7,11	21900	21900
	Leaching Period 4 (90 days)	7,01		21900	

Table 2.7.7. pH and EC control of leaching solutions

THERMAL TREATMENT

There are 3680 tons of i-graphite, mainly from Vandellós I, in Spain to be managed as radioactive waste. This i-graphite contains long lived nuclides as ^{14}C in such amounts that disposal in ENRESA's El Cabril near surface repository facility for intermediate and low level radioactive waste is not permitted. It is therefore necessary to undertake the R&D in decontamination methods that, once implemented, would allow i-graphite to fulfil the relevant Waste Acceptance Criteria (WAC). This is the origin of the necessity of extracting this radionuclide from the graphite.

It is demonstrated for other i-graphite types that thermal treatment is effective in the selective decontamination of radiocarbon (J. Fachinger et al. 2008, R. Holmes et al., L. Babout et al. 2005, D. Labrier (thesis), S. McCrory (thesis), J. Cleaver (thesis)). Chemical behaviour of ^{14}C is not different of ^{12}C, only different bonds of activated forms or different positions in the structure of i-graphite can be distinguished, and for this reason the release of ^{14}C also implies the release of ^{12}C and consequently a corrosion of the treated matrix.

The release of ^{14}C through thermal treatment without significant mass loss is being investigated by a partial oxidation.

$$C+O_2 \rightarrow CO_2$$

$$C+1/2\ O_2 \rightarrow CO$$

To perform the thermal treatment the system elements (see also Figure 2.7.11) are:

- A rotating furnace manufactured by Cremer Thermoprozessanlagen GmbH.
- A particle filter
- A mass flow controller system,
- A pneumatic sample injector
- A single quadrupole mass spectrometer by Pfeiffer Vacuum.
- A catalytic oxidizer furnace by Nabertherm that contains a nickel dioxide catalyser
- Four washing bottles (special design for trapping the gases of interest (with the elements /nuclides to be studied).

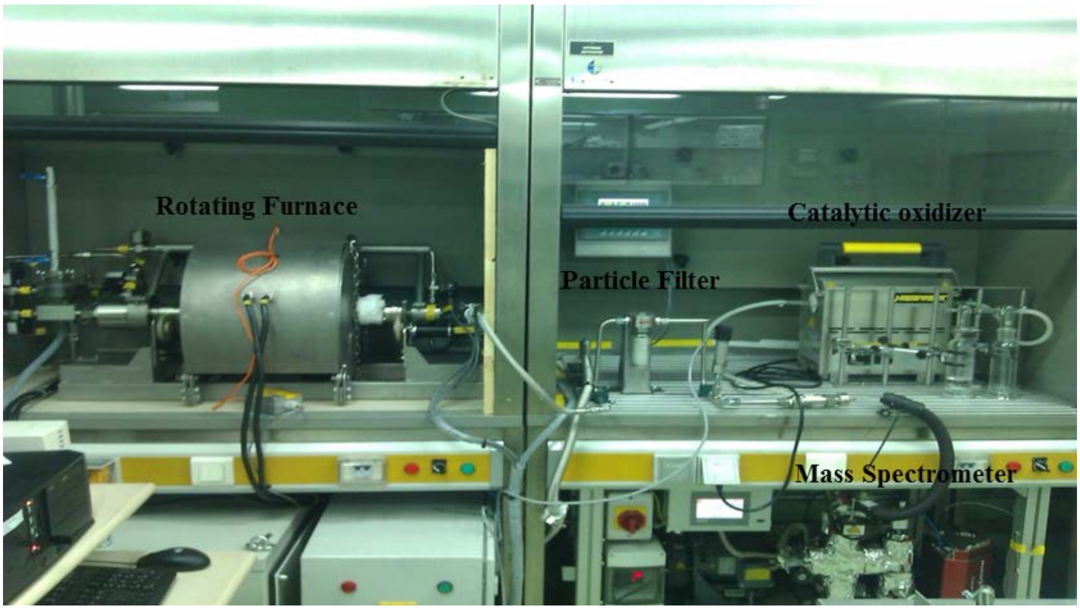


Figure 2.7.11. Thermal Treatment Facility

To carry out an experiment with graphite, the following must be taken into account:

- The gas flow has to be constant, in order to has no influence in the mass spectrometer background;
- The washing bottles have to have the same liquid level, in order not to have an influence on the total pressure of the system;

- The laboratory room temperature has to be constant, in order to has no influence in the amplifier signal of the mass spectrometer;
- The system stabilization time has to be higher if the system is not intended for operation for a long time;
- The spectrum signal has to be maintained stable after every experiment step.

Procedure

To perform the experiments to calculate the recovery rates for different parameters, first it is necessary to establish what parameters have influence in the oxidation of graphite and must be studied. These parameters are the temperature, the oxidizer agent, the gas flow and the grain size. Once established, it is necessary to study each one separately. The amount of the oxidizing agent, the temperature and gas flow will be varied. The procedure consists of introducing in the rotating furnace an inert atmosphere (Ar), followed by an oxidizing atmosphere (O_2). The temperature in the furnace will be under study. The off-gases are passed through a particulate filter and a catalytic furnace where the CO will be oxidized to CO_2, which is the substance to be measured at the end of the experiment due to ^{14}C release as $^{14}CO_2$. CO_2 will be trapped in the NaOH and the recovery rate of carbon was calculated precipitating with barium nitrate. The mass spectrometer allows a qualitative monitoring of the experiment.

Recovery Rates

The tests with virgin graphite were performed with a sleeve of Pechiney graphite from Vandellós I supplied by ENRESA. The graphite was crushed and milled to obtain a graphite-powder, similar to the physical conditions as the irradiated graphite available from Vandellós I.

The pneumatic injector, Figure 2.7.12, was used to introduce the virgin powder graphite into the glass tube. The amounts of carbon processed in the initial experiments were smaller than the injected amounts, which was caused by static charges of graphite powder, avoiding the full injection of the sample.

Figure 2.7.12. Pneumatic Injector

The injector was tapped until whole graphite sample fell into the box situated in the bottom. So, the irradiated graphite was introduced directly in the glass tube in order to minimize the mass losses in the experiments.

The experiments with virgin graphite have been used to obtain the information about the behaviour of Vandellós I graphite under thermal treatment conditions and to adjust the process parameters to optimize the operational condition for a maximum efficiency of the system or the possible problems as the total pressure control of the process.

Table 2.7.8 summarised the main data of the inactive experiments for different temperatures and 5%-10% of oxygen.

Experiment	Mass (g)	T(ºC)	O_2 (L/h)	Recovery Rate (% C)
TR-7-10-1	2,0058	700	10	39,93
TR-7-10-2	2,0029	700	10	89,57
TR-9-5-1	2,0129	900	5	71,55
TR-9-5-2	2,0021	900	5	97,76
TR-9-10-3	1,9907	900	10	6,03
TR-9-10-4	2,0163	900	10	45,83
TR-11-10-1	2,0043	1100	10	87,71
TR-11-10-2	2,0161	1100	10	67,93

Table 2.7.8. Experiments with virgin graphite at 700ºC, 900ºC and 1100ºC

The volume of NaOH in the washing bottles was increased after the first experiments to ensure an excess of NaOH for trapping the complete CO_2 generated, reducing the uncertainty in the mass balance of the process and further more avoiding the release to the atmosphere of CO_2 and especially $^{14}CO_2$ in case of experiments with i-graphite.

The static charge problem in the injector showed up in the experiments TR-7-10-1, TR-9-10-3, TR-9-10-4. For this reason, the mass balances in these experiments are much lower than the other experiments.

To establish the minimum volume of O_2 necessary to carry out the complete oxidation, some experiments with the three temperatures were carried out where oxygen was completely consumed with a flux of 2 litres per hour and an excess of oxidant existed using a flux of 10 litres per hour. An oxygen flux of 3 litres per hour was fixed for the following experiments and to fulfill the objective to reduce the consumption of O_2.

On the basis of recovery rates obtained and in some cases a negative mass balance between the consumed and the gasified carbon, it was decided to add an extra washing bottle with CO_2 trapping agent (as Carbosorb® or similar) in order to ensure the retention of all generated CO_2 in the process.

Experiments with irradiated graphite

The irradiated graphite used came from sample GC-2 (coarse grain size) from fuel element The activity was determined as: $3{,}50 \cdot 10^4$ Bq/g of tritium and $1{,}42 \cdot 10^4$ Bq/g for radiocarbon.

New washing bottles were used in the system and their inlets were modified in order to by-pass the first washing bottle in the case of precipitation appears, and can continuing the experiment without losses of information or release of ^{14}C.

As the graphite is into the furnace when the temperature of the experiments is reached, it is possible to observe an increase of the production of CO and CO_2 when the furnace temperature is around 400 ºC.

The first step was to study the release of ^{14}C in inert atmosphere (Ar) and the second one the release with a low amount of oxidizing agent (O_2)

Experiment 1 (EXP-1)

Procedure

The graphite was treated with Ar for 4 hours at 100 litres per hour and 700ºC, after that the flux was changed to 97 litres per hour of Ar and 3 litres per hour of oxygen for 4 hours in order to oxidise the graphite. To calculate recovery rates total combustion of graphite was performed increasing the temperature up to 1100ºC.

The aliquots were taken for radiocarbon determination by LSC and the scintillation cocktail was Hionic Fluor which avoids the chemo-luminescent effect of NaOH media.

Results

The amounts of ^{12}C in each experimental step were determined by MS and the final amount was obtained by gravimetric method, getting 94.20% of the initial mass of graphite which was 1.0060 g.

Tritium recovery from the first HCl washing bottle was 13% (relative to initial inventory). This low recovery rate leads to increasing the volume of HCl (from 100 mL to 200 mL) and adding a second HCl washing bottle. Results are collected in Table 2.7.9:

Sampling time*	**Temp (°C)**	**O_2 (L/h)**	**Ar (L/h)**	**^{14}C (Bq)**	**^{14}C %**	**^{12}C g**	**^{12}C %**	**^{14}C/^{12}C**
10 min	700	0	100	0.00	0.00	0.0248	2.63	0.00
30 min	700	0	100	0.00	0.00	0.0248	2.63	0.00
1 h	700	0	100	0.00	0.00	0.0248	2.63	0.00
2 h	700	0	100	0.00	0.00	0.0248	2.63	0.00
3 h	700	0	100	0.00	0.00	0.0248	2.63	0.00
4 h	700	0	100	0.00	0.00	0.0248	2.63	0.00
10 min	700	3	97	1127.64	8.53	0.0796	8.45	1.01
30 min	700	3	97	4252.29	32.16	0.1983	21.06	1.53
1 h	700	3	97	6785.70	51.31	0.3409	36.19	1.42
2 h	700	3	97	8933.86	67.56	0.5474	58.11	1.16
3 h	700	3	97	10928.43	82.64	0.6928	73.55	1.12
4 h	700	3	97	11015.71	83.30	0.7955	84.45	0.99
Final Sample	1100	0	100	3224.03	100.00	0.9420	100.00	1.00

* Time when a sample is taken in each washing bottle

Table 2.7.9. Release ratios of ^{14}C and ^{12}C at 700°C.

Figure 2.7.13 shows the experimental data obtained in EXP-1. It is observed that there are no releases of ^{14}C in inert atmosphere nevertheless when oxygen is injected at this temperature the ratio ^{14}C /^{12}C is around 1.5 and after one hour treatment 51% of ^{14}C was release with a corrosion rate of 36%.

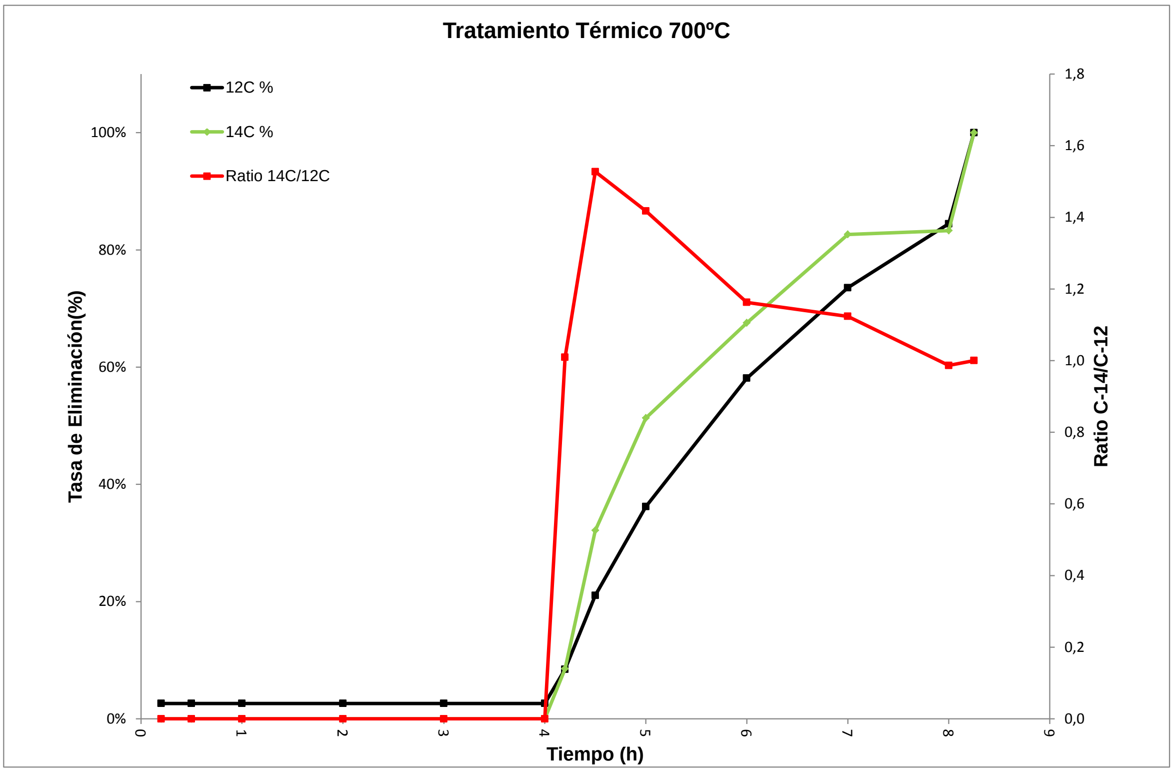


Figure 2.7.13. ^{14}C and ^{12}C release rate by thermal treatment at 700ºC

Experiment 2 (EXP-2)

Procedure

The graphite was treated with Ar for 1 hour at 100 litres per hour and 1100 ºC, holding the gas flux the temperature was reduced to 300 ºC. The flux was changed to 95 litres per hour of Ar and 5 litres per hour of oxygen for half an hour after 300 ºC was reached. Temperature was raised again until 1100 ºC and the gas flux was changed to 100 litres per hour of Ar for half an hour. Finally, a gas flux of 95 litres per hour of Ar and 5 litres per hour of oxygen was applied until total oxidation of the graphite sample.

Results

The temperature and gas fluxes in EXP-1 and 2 tried to saturate the graphite surface with oxygen at low temperature (≈400 ºC) chemisorbed on it and when the temperature increases the superficial and more labile ^{14}C reacts with the chemisorbed oxygen and produces these amounts of CO and CO_2 registered.

The results of EXP-2 are in Table 2.7.10:

Sampling time	**Temp. (ºC)**	**O_2 (L/h)**	**Ar (L/h)**	**^{14}C(Bq)**	**^{14}C(%)**	**^{12}C(g)**	**^{12}C(%)**	**$^{14}C/^{12}C$**
10 min	1100	0	100	87.45	0.84	0.0089	0.98	0.8607
30 min	1100	0	100	80.11	0.77	0.0094	1.03	0.7481
Decreasing to 300ºC 95 L/h Ar 5 L/h O_2								
30 min	300	5	95	128.94	1.24	0.0104	1.14	1.0950
Increasing to 1100ºC 100 L/h Ar								
10 min	1100	0	100	192.19	1.86	0.0107	1.18	1.5766
30 min	1100	0	100	318.25	3.07	0.0109	1.20	2.5629
Final Sample	1100	0	100	10356.65	100	0.9110	100.00	1.0000

Table 2.7.10. Release ratios of ^{14}C and ^{12}C at 1100ºC

Amounts of ^{14}C and ^{12}C were determined as in EXP-1 described before. The mass of carbon obtained in this experiment was 91.1% regarding initial graphite mass (m_0 =1.0139 g). Additionally, a 32% of ^3H was recovery in this process.

It is observed that, once oxygen is chemisorbed, in treatment process at 1100º C in inert atmosphere, the depletion of ^{14}C in relation to that of ^{12}C has a ratio of 2.6 at 30 minutes. That indicates chemisorption is higher at low temperature and reaction (and consequently corrosion) is produced at higher temperature.

Data obtained are plotted in Figure 2.7.14:

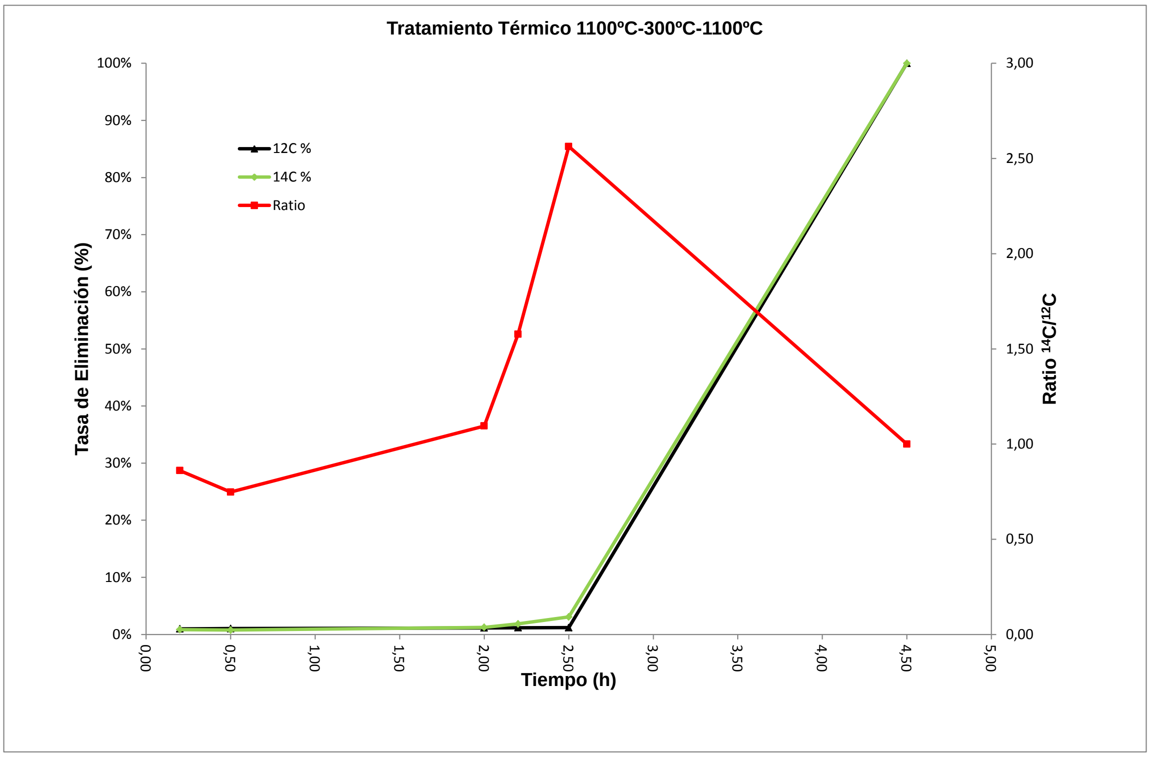


Figure 2.7.14. ^{14}C and ^{12}C release rate by thermal treatment at 1100ºC-300ºC-1100ºC

Experiment 3 (EXP-3)

Procedure

The graphite was treated with Ar for 4 hour at 100 litres per hour and 1100 ºC, after that gas flux was changed to 97 litres per hour of Ar and 3 litres per hour of oxygen until total oxidation of the graphite sample.

Results

The amounts of ^{12}C and ^{14}C were determined as in EXP-1 and 2. The obtained mass of carbon, in this case, by precipitation as carbonate was 97% (relative to the initial mass m_0= 0.9801 g). Release of ^{3}H was 24%. Obtained data are shown in Table 2.7.11:

Sampling time	**Temp. (ºC)**	**O_2 (L/h)**	**Ar (L/h)**	**^{14}C(Bq)**	**^{14}C(%)**	**^{12}C(g)**	**^{12}C(%)**	**$^{14}C/^{12}C$**
10 min	1100	0	100	5.14	0.03	0.0011	0.12	0.2866
30 min	1100	0	100	7.14	0.05	0.0012	0.13	0.3633
1h	1100	0	100	11.46	0.07	0.0014	0.14	0.5140
2h	1100	0	100	24.52	0.16	0.0017	0.17	0.9041
3h	1100	0	100	35.39	0.23	0.0019	0.20	1.1295
4h	1100	0	100	45.66	0.29	0.0022	0.23	1.3021
10 min	1100	3	97	2739.36	17.58	0.1702	17.55	1.0017
30 min	1100	3	97	9674.70	62.07	0.6822	70.33	0.8826
1h	1100	3	97	14367.22	92.18	0.9694	99.94	0.9223
Final Sample	1100	0	100	15586.48	100.00	0.9700	100.00	1.0000

Table 2.7.11. Release ratios of ^{14}C and ^{12}C at 1100ºC.

There is not a selective release of ^{14}C regarding ^{12}C (or total carbon) when 1100ºC is applied for thermal treatment. ^{14}C released came from graphite corrosion instead of decontamination after 2 hours of treatment.

Obtained data are represented in Figure 2.7.15:

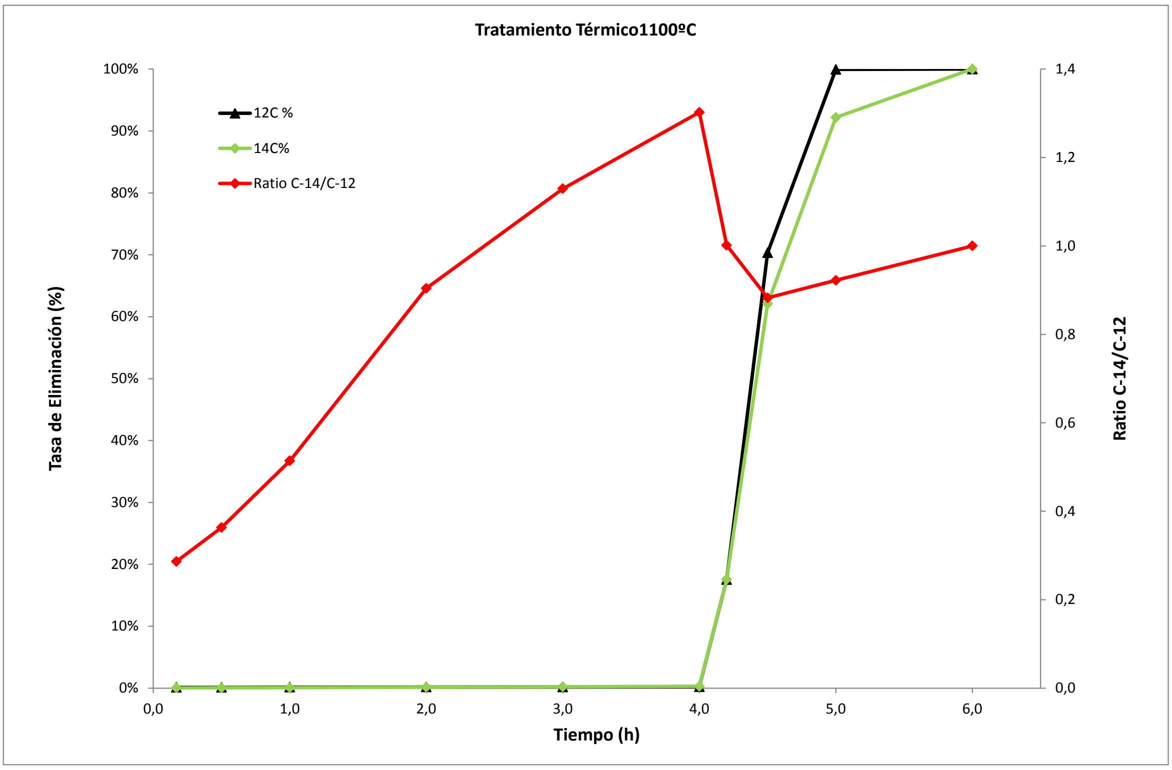


Figure 2.7.15. ^{14}C and ^{12}C release rate by thermal treatment at 1100°C

Experiment 4 (EXP-4)

Procedure

Conditions of EXP-4 are the same than EXP-1. The graphite was treated with Ar for 4 hours at 100 litres per hour and 700° C, after that the flux was changed to 97 litres per hour of Ar and 3 litres per hour of oxygen for 4 hours in order to oxidise the graphite. For total combustion of graphite the temperature was increased to 1100°C.

Results

In this case the results are shown in Table 2.7.12:

Sampling Time	**Temp. (ºC)**	**O_2 (L/h)**	**Ar (L/h)**	**^{14}C(Bq)**	**^{14}C(%)**	**^{12}C(g)**	**^{12}C(%)**	**$^{14}C/^{12}C$**
10 min	700	0	100	4.5887	0.04	0.0003	0.03	1.2118
30 min	700	0	100	4.1423	0.04	0.0004	0.05	0.7830
1h	700	0	100	7.1765	0.06	0.0006	0.07	0.9617
2h	700	0	100	6.9875	0.06	0.0009	0.10	0.6212
3h	700	0	100	12.6135	0.11	0.0012	0.13	0.8515
4h	700	0	100	17.2056	0.15	0.0014	0.16	0.9478
10 min	700	3	97	1242.8190	11.16	0.0459	5.30	2.1043
30 min	700	3	97	3970.2059	35.65	0.1459	16.87	2.1133
1h	700	3	97	6414.0260	57.59	0.2694	31.15	1.8491
2h	700	3	97	8426.0609	75.66	0.4609	53.29	1.4197
3h	700	3	97	9523.7668	85.51	0.6060	70.06	1.2206
4h	700	3	97	10093.2378	90.63	0.7102	82.10	1.1038
Final Sample	1100	0	100	11137.2725	100.00	0.865	100.00	1.0000

Table 2.7.12. Release ratios of ^{14}C and ^{12}C at 1100ºC

Release of ^{14}C in inert atmosphere is very low at this temperature, as was obtained in EXP-1. On the other hand, in an oxidizing atmosphere, ratios of $^{14}C/^{12}C$ close to 2 were observed, getting a ^{14}C release of 11% versus a release of 5% for ^{12}C 10 minutes after oxygen flux started. This percentage became 58% for ^{14}C and 31% for ^{12}C in 1 hour. Data of this experiment are plotted in Figure 2.7.16.

Determinations of ^{14}C and ^{12}C were performed in the same way that is described for the other experiments. In EXP-4 the mass of graphite obtained by precipitation was 86.5% of an original mass of m_0 = 1.0169 g. The recovery of ^3H was 32%.

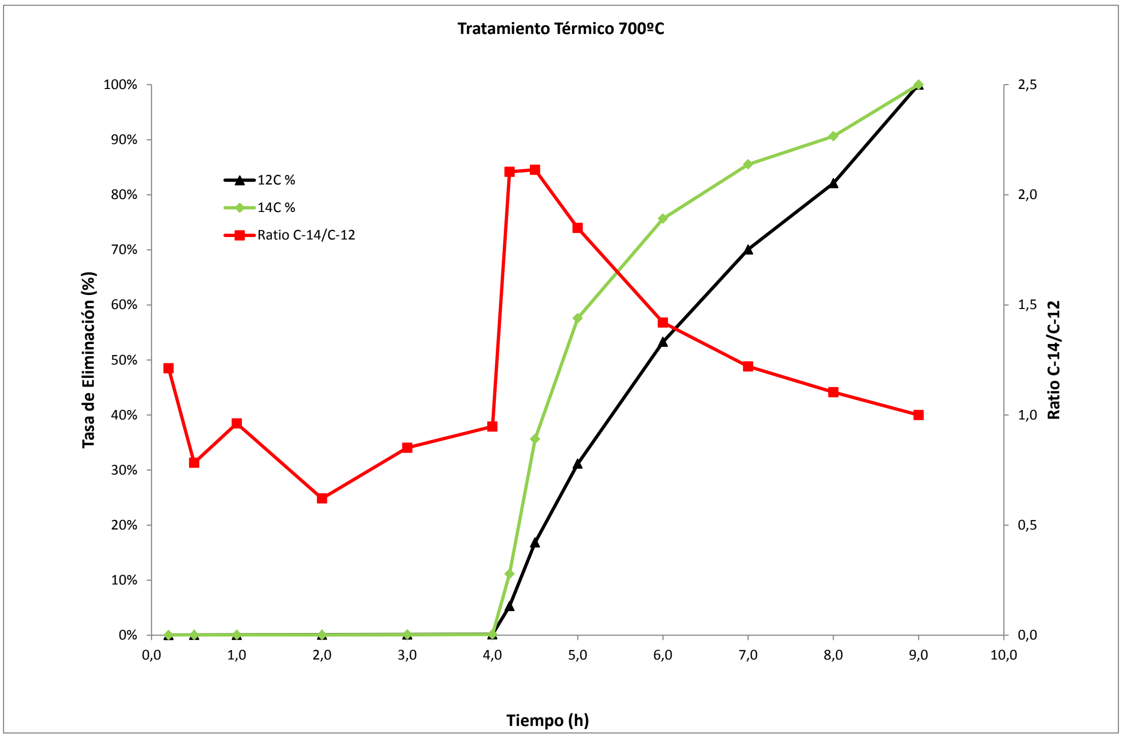


Figure 2.7.16. ^{14}C and ^{12}C release rate by thermal treatment at 700ºC

To study the influence of the total flow and the flow of the oxidant agent in the recovery rate, some experiments were performed. The temperature was established in 700ºC and the flows selected were 20, 50 and 100 litres per hour. The results are in the following Table 2.7.13:

PRECIPITATION				
Graphite Mass (g)	**Flow**	**Recovery 700ºC (%)**	**Recovery 1100ºC (%)**	**Recovery Total (%)**
1,0091	100 L/h 82,4 L/h Ar+17,6 L/h O_2	31	68	78
1,004		12	75	78
1,0136		21	78	83
1,0119		30	77	84
1,0126	50 L/h 41,2 L/h Ar+8,8 L/h O_2	41	134	120
1,0233		32	122	115
1,0115		32	86	91
1,0152		24	93	95
1,0903	20 L/h 17 L/h Ar+3 L/h O_2	29	122	116
1,0195		42	140	123
1,0158		24	93	95
1,0018		25	98	99

Table 2.7.13. Recovery Rates by Precipitation

The results show that the total recovery rate is lower with a flow of 100 litres per hour. That means some amount of CO_2 is not trapped in the washing bottles and goes out due to the rate of the flow: it is necessary for a greater amount of NaOH to be present in each washing bottles, or for more bottles to be used, to overcome this issue. It is therefore possible to conclude that the rate of the total flow has a very important influence in the recovery rate. If the total flow is low, higher amounts of CO_2 will be trapped with NaOH because the gas is in contact with the solution more time.

It is possible to observe that the recovery rate at 700 ºC is between 25-30% in all experiments regardless of the amount of oxygen. In some cases, the recovery rate is above 100% due to the time between taking the sample and the measurement being higher than one day: it is possible that the NaOH solution has taken CO_2 from the air.

The influence of temperature is very important in the oxidation of graphite, so for a low temperature it is better for there to be a lower flow. The recovery rate with 20 litres per hour at 700ºC is in general lower than the others flow, but at a temperature of 1100ºC is higher.

It was observed in all experiments that CO_2 and CO concentrations increased during some minutes in inert atmosphere starting from 400ºC, (reaction temperature of O_2). The explanation is that both O_2, chemisorbed in the surface and pore system, and the labile C which is also in the graphite surface (probably as CN groups), react in the following way:

$$C_{(s)} + \frac{1}{2} O_{2\,(chs)} \rightarrow CO_{(g)}$$

$$CO_{(s)} + \frac{1}{2} O_{2\,(chs)} \rightarrow CO_{2\,(g)}$$

Summary

The main efforts of the CIEMAT in the third year of its input to Work Package 5 were focused in the design and implementation of the leaching experiments on irradiated powder graphite and on IGM graphite. After some preliminary tests, the use of powdered graphite was discarded and a method to obtain cylindrical graphite samples of about 11 mm x 12 mm (Ø x H) was developed. Up to date four leaching periods on graphite cylinders and IGM has been completed using two different media (deionized water and granite bentonite water).

A complete description of the leaching experiments carried out has been described. The periods corresponding to 14, 28 56 and 90 days have been already covered. Process parameters such as sample weight, volume, surface area or leachant pH and electrical conductivity have been reported. CIEMAT has characterized the ^{14}C and gamma emitters inventory of each irradiated sample.

The set-up of different equipment intended for speciation studies (GC-MS and IC) has been completed (Quantulus setting-up ongoing) and the analysis method of gas and liquid samples has been stablished. The data analysis of both the gas and the liquid samples are in progress.

Regarding thermal treatment, the data obtained with virgin graphite experiments have allowed elements of the experimental system to be adjusted, devices and methods which will be the base of the system at pilot plant scale.

Virgin graphite experiments lead to establishing and optimizing the thermal treatment procedure for:

- Collecting the nuclides of interest and allowing for the mass balance of every experiment performed; this allows the decontamination factors to be determined in an accurate way.
- Establishing the working temperature.

Some important details have been concluded with the experiments in relation to scaling-up the procedure at industrial or semi-industrial level:

- Overpressure is an important factor to be taken into account. This shows up in the system due to evaporation in the washing bottles with NaOH that promotes precipitation that blocks the gas fluency. It will be necessary to install a first deposit before the ^{14}C trapping system or injection of new solution in the trapping washing bottles.

The obtained data indicate that thermal treatment can decontaminate selectively ^{14}C from Vandellós I irradiated graphite.

Ratio ^{14}C/Total C results are neither definitive nor conclusive and they have to be improved because the corrosion rate of the graphite is higher than the one desired. Reasons for this behaviour are assumed to be due to use of powdered graphite, which increases the surface area and the corrosion kinetic due to the higher availability of ^{12}C. Further experiments can demonstrate the influence of the grain size in the corrosion kinetic.

More experiments with irradiated graphite will be programmed to optimise the decontamination factors ($^{14}C/^{12}C$) without significant mass loss, starting from the valuable results already obtained. In this sense a decontamination ratio around 58% of ^{14}C versus 31% of ^{12}C in 1 hour treatment at 700ºC in a 3 litres per hour of oxygen flux was obtained.

In the case that such a decontamination factor were not enough to meet the waste acceptance criteria to dispose the graphite in a near surface repository (as El Cabril L&ILW Repository), thermal treatment can reduce ^{14}C by a significant factor and condition it in a IGM (as is mentioned) demonstrating the low leaching rate of this waste form.

The smallest amount of ^{14}C in the inert atmosphere obtained in Experiment 1 is in contrast with the experiment performed with other graphite type reactors such as Merlin and AVR (Fachinger et al., 2008). The different behaviour can be explained by the loss of ^{14}C of the graphite surface during reactor operation. UNGG reactors use graphite as the moderator and CO_2 as coolant, with an average operation temperature of 400º C. In these conditions CO_2 reacts with graphite producing ^{14}CO. The radiocarbon comes from the graphite surface, more probably from the activation of ^{14}N impurities of coolant and/or nitro-derivatives in the graphite. Due to the release of majority of ^{14}C in the surface, the source in the graphite comes from the activation of the ^{13}C and forms part of the structure.

Although the release of surface ^{14}C of Vandellós I graphite took place during operation, Experiment 2 demonstrates that oxygen saturation of the surface at 300º C, and allows ^{14}C without high corrosion rate ($^{14}C/^{12}C = 2.6$) to be obtained with a thermal treatment in an inert atmosphere. This indicates that ^{14}C not released during operation needs an oxidant agent chemisorbed in the surface to be decontaminated. There is a lack of oxygen in the surface of Vandellós 1 irradiated graphite. An experimental line was opened in which at the experiment beginning surface saturation with oxygen is performed following by a partial oxidation.

The set of experimental data indicates that a lower treatment temperature and lower reactivity of the oxidant agent increase the $^{14}C/^{12}C$ ratio. A series of experiments in which a reduced oxygen flux of under 2 litres per hour is used, or in which CO_2 as oxidant agent is used (H_2O is not included in order to avoid steam reforming treatment interference) – all to be undertaken with an increased treatment time at 700º C - are planned.

2.8 Institutul National de Cercetare-Dezvoltare pentru Fizica si Inginerie Nucleara “Horia Hulubel” (IFIN-HH) summary

Irradiated graphite at IFIN-HH

The irradiated graphite grades, which are investigated in IFIN-HH, have been taken from the thermal column of the VVR[3]-S Research Reactor. The reactor was permanently shut down in 1997. The mobile thermal column (Figure 2.8.1) is made of 6 graphite discs placed on a mobile truck. Graphite discs are installed into a 20 mm wall thickness aluminium cylinder. Initially, the thermal column was provided with a cooling system that axially penetrated the graphite plate connected to the water-cooling system. On the basis of subsequent operational experience, it was concluded that this system is not necessary; it was not used any further. Therefore, 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. Samples have been collected from these graphite rods and the surrounding graphite sleeve of the central graphite rod (Figure 2.8.2).

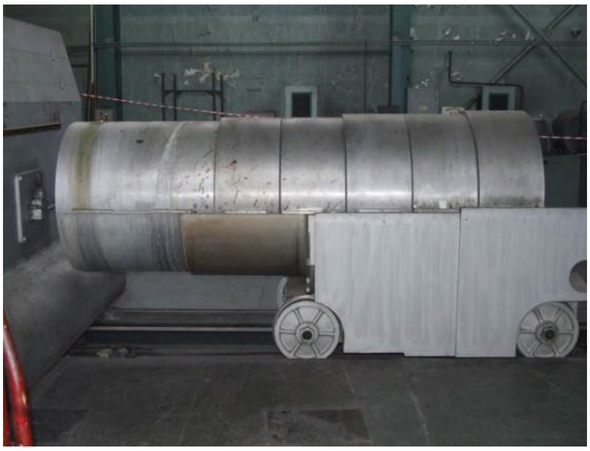


Figure 2.8.1: Thermal column

Figure 2.8.2: Thermal column disc 6

The nearest disc to the reactor core is number 6. During reactor operation the central tube of the cooling system was filled with a graphite rod (8 cm diameter) covered by a 1 cm thick

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[3] Water-Water Energetic Reactor

cylindrical graphite sleeve for column discs 1-4 and a graphite rod (diameter 10 cm) for column discs 5 and 6, which sealed the entire central opening. The other horizontal tubes of the cooling system have been filled (only for discs 5 and 6) with graphite rods of 4.4 cm diameter.

The graphite samples were collected from the inner and the outer surface of the graphite sleeve of the rod's edge near to the reactor vessel for the column discs no 1-4, (**Sample code: D2.1, D3.1, D4.1, D5.1**) and the others from the opposite part (**Sample code: D1.2, D2.2, D3.2, D4.2, D5.2**) and from small graphite rods located around the central graphite rod for discs 5 and 6. For the disc 6, two pieces of i-graphite have been cut from the graphite rods, to facilitate easier handling in the radiochemical laboratory. One piece was cut from rod's edge nearer the reactor vessel (**Sample 6.1**) and the other piece from the opposite part of the rod (**Sample 6.2**). From each piece collected from graphite rod located inside the disc 6, two separate samples have been taken (Sample 6.1-1, Sample 6.1-2, Sample 6.2-1 and Sample 6.2-2) (Figure 2.8.3).

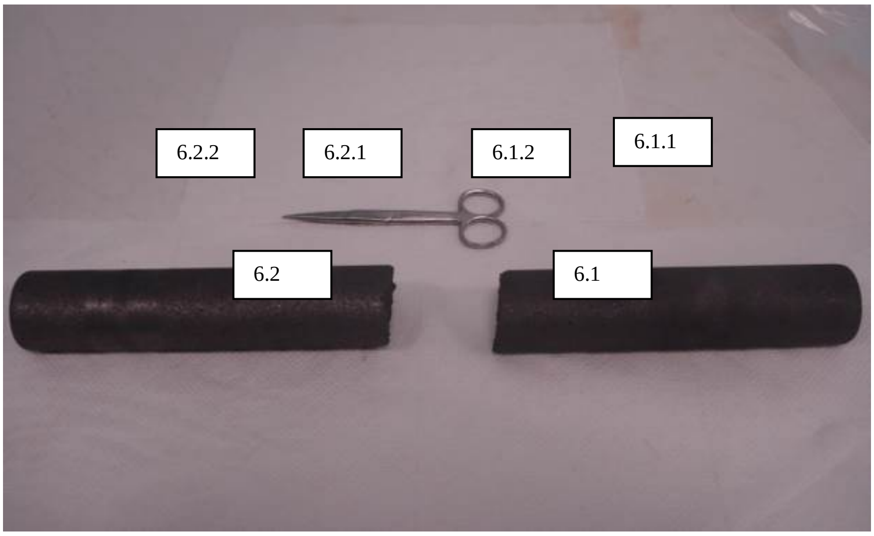

Figure 2.8.3:Irradiated graphite samples collected from small rod in disc 6

Table 2.8.1 records mass and dimension data for the 6 graphite discs.

Disc	Diameter (cm)	Length (cm)	Graphite mass(kg)
1	115	40	715
2	110	40	660
3	110	40	670
4	105	40	595
5	105	40	610
6	100	100	1360

Table 2.8.1:Graphite discs masses and dimensions

8.1 Materials and Methods

8.1.1 Accelerator Mass Spectrometry based on the 9 MV and 1 MV accelerators of IFIN-HH for measurements of 14C concentration in irradiated graphite

The goal of the present research study is to measure ^{14}C accumulations and possible contaminations in nuclear materials from the VVRS-2 reactor in IFIN HH. The ^{14}C has a half-life of 5370 years. It is produced in the Earth's atmosphere and in the nuclear reactors by the reaction of high energetic neutrons with nitrogen. ^{14}C concentrations in different materials and components of the reactor may vary on a large scale with distance from reactor core and also may depend with the depth in a sample from a particular location. Therefore, in this project and depending on the expected concentrations of^{14}C, two different AMS facilities are used, as follows:

1) The AMS facility of the 9 MV Tandem accelerator: for ^{14}C exceeding the natural level of 10^{-12} for the ratio$^{14}C/^{12}C$ and for performing the depth profiling of the concentration in materials.
2) The AMS facility at 1 MV Tandetron: for ^{14}C concentrations below the natural level of 10^{-12} for the ratio$^{14}C/^{12}C$

The measurements at 1 MV AMS machine were performed on samples collected from disc numbers 1, 2, 3, 4, 5 and 6. The samples were collected from inside and outside the graphite coating of the rod's edge nearer to the reactor vessel for (**Samples D2.1, D3.1, D4.1, D5.1 and D6.1**) and the other samples from the opposite part of the graphite coating the rod (**Sample D1.2, D2.2, D3.2, D4.2, D5.2, D6.2**). In the case of disc 6, the samples were collected from the inside and outside of the graphite rods' edge. About 20 mg of material from the samples (from both face of the samples) were transformed to powder and loaded and pressed into 8 sample holders (2 mg/sample)-of the ion source, together with reference and blank carbon samples (reference sample HOxII: 18.40 dpm/g (0.31Bq/g).

Due to the high concentration of ^{14}C, samples collected from the discs 5 and 6 were diluted 100 times using ultrapure graphite (^{14}C / ^{12}C atoms ratio= $6x10^{-15}$ (Alpha Aesar Johnson Matthey, Germany). Since the two powders that were to be mixed had different grain sizes, dilution was made using a mortar agate in which 1 ml ultrapure water was added.

To ensure optimum measurement (provided by a given current source sufficiently large), all samples (diluted or undiluted) were mixed in a mass ratio of 1: 5 with Metals (^{14}C free; source - Alpha Aesar Johnson Matthey, Germany). The mixture obtained was loaded into holders of the ion source and measured.

8.2 Determination of total ^{14}C and tritium (T) in graphite samples collected from graphite column of the VVR-S reactor using a separation technique, based on silica gel columns coupled with oxidation at high temperature over a CuO catalyst bed coupled with LSC device.

Based on the experience acquired during the second year of the CAST, IFIN-HH modified the experimental apparatus in order to collect separately ^{14}C and T released from irradiated graphite. The combustion apparatus is presented in Figure 2.8.4, Figure 2.8.5 and Figure 2.8.6.

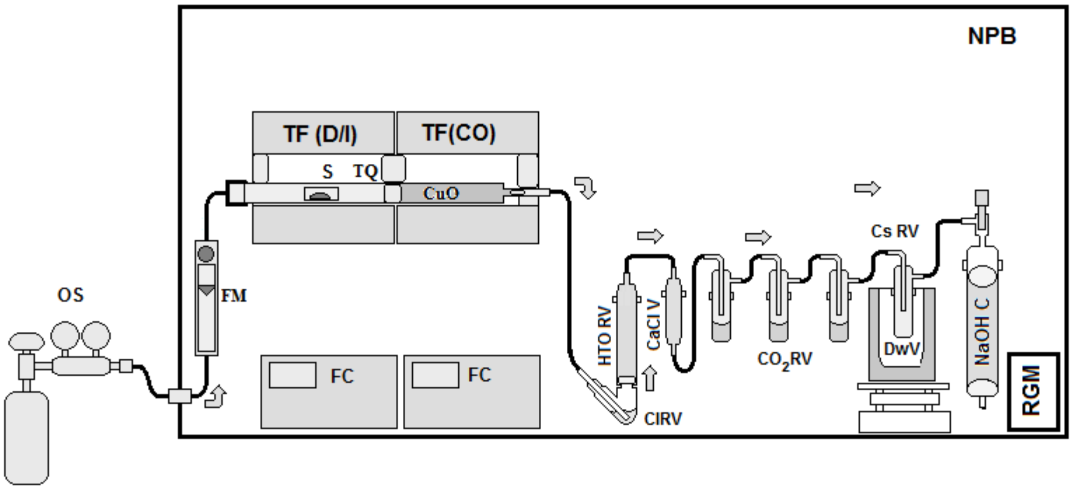

Figure 2.8.4: Combustion apparatus for^{3}H and ^{14}C determination in irradiated graphite

Schematic view of the combustion apparatus with separate retention of radionuclides of interest. QS- Oxygen supply; FM-Flow-meter; TF (D/I)-Tube furnace (Degassing/incineration); TF (CO)-Tube Furnace (catalytic oxidation); TQ- Quartz tube; S- Sample; CuO - CuO wire oxidation bed; ClRV – ^{36}Cl retention vials and saturator; HTORV- HTO retention cartridge; CO_2RV-ansembly with 3 CO_2 retention vials; CSRV- CARBOSORB retention vials ; DwV- Dewar vessel; NaOH C- retention cartridge with NaOH, RGM- Radioactive gas monitor

Figure 2.8.5. Pictures of the experimental apparatus. (left) - tubular furnace tandem; (right) – ^{3}H and ^{14}C retention system

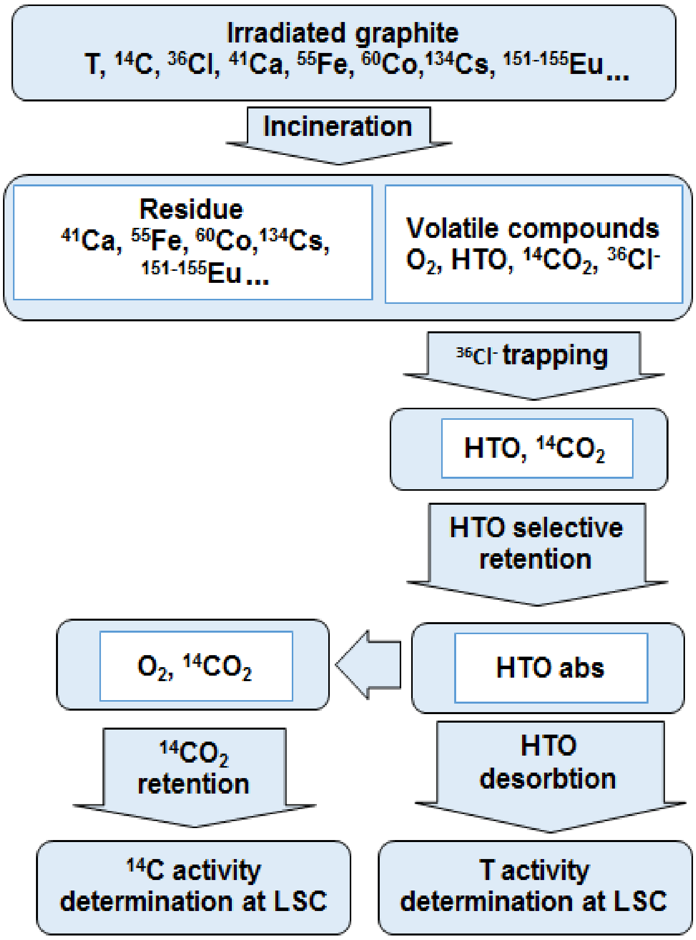

Figure 2.8.6 Experimental method for simultaneous determination of ^{3}H and ^{14}C in irradiated graphite

Sample preparation

Graphite samples were collected from the thermal column of the VVR-S reactor by cutting small pieces from each disc. Assigned sample codes were: D1.2, D2.2, D2.1, D3.2, D3.1, D4.2, D5.2, D5.1, D6.2.2, D62.1 D61.2, D61.1 (as mentioned before) and D6.3 (sample collected from the middle of the rod).

An inactive graphite (virgin graphite) sample was also prepared from the same type graphite type as that used in the VVR-S reactor. The weight of the samples was: 150-200 mg.

Sample combustion

The samples were oxidized initially at a temperature of 850°C (combustion temperature) in the first furnace, followed by exposure in the second furnace with the catalytic bed to a temperature of 750°C[4]; both furnaces had a stream of oxygen. The oxidation compounds containing ^{36}Cl were trapped in a cartridge with $AgNO_3$.

Oxidation compounds retention and activity measurement

The retention reagent used for HTO was Silica gel (15-30 g) / $CaCl_2$ (4-8 g). After the complete combustion of the sample, the silica gel was immersed for 24 h in 50 ml distilled water. 4 ml of the solution were mixed with 16 ml ULTIMA GOLD L.S. and the activity was measured using LSC TRICARB TR2800. In the case of ^{14}C the retention reagent used was CARBOSORB E+ (3 vials with 1-5 ml each) and CARBOSORB E+ vapours were trapped in a vial immersed in liquid nitrogen. An aliquot of each solution (two millilitres of retention solution) was transferred to a 20 ml LSC vial, and 10 ml of Permafluor cocktail was added. ^{14}C activity was measured by a TRICARB TR 2800 liquid scintillation counter. The activity of the graphite virgin sample was considered as background level

Determination of HTO and $^{14}CO_2$ retention yields

Virgin nuclear graphite powder was contaminated in a controlled manner with a known activity of ^{3}H (Testosterone-1,2-T) or ^{14}C (1-ocatdecanol-^{14}C). The samples were incinerated at a temperature of 850°C (750°C catalytic bed) and the combustion compounds were trapped. ^{3}H and ^{14}C activities were measured and compared with initial sample activity.

8.3. Experimental results

8.3.1 Determination of ^{14}C in graphite samples collected from graphite column of the VVR-S reactor using AMS 1 MV facility

The AMS experiments results are shown in Figure 2.8.7.

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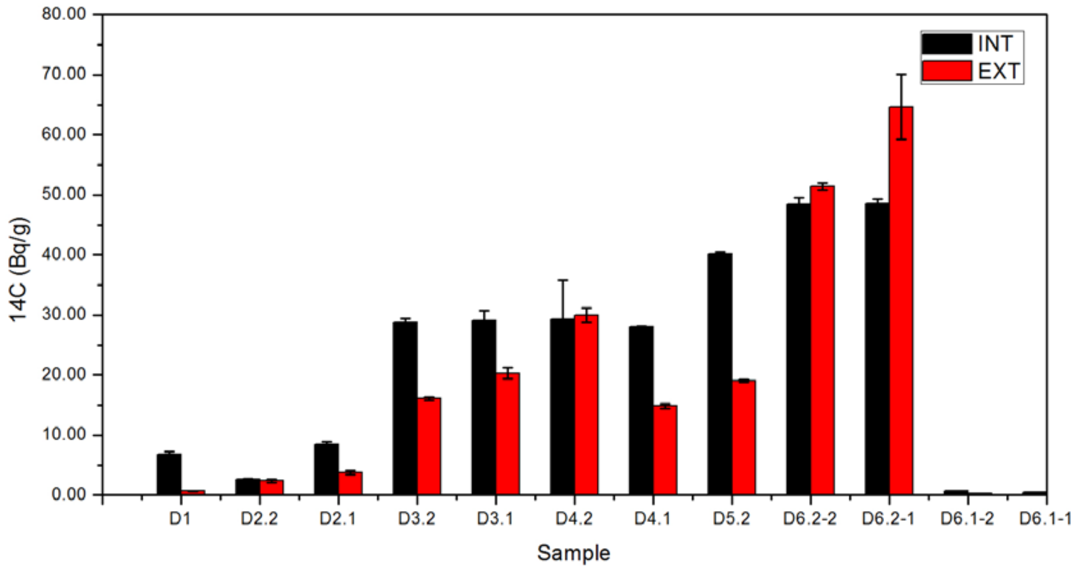
[4] Hereafter "850°C (750°C catalytic bed)"



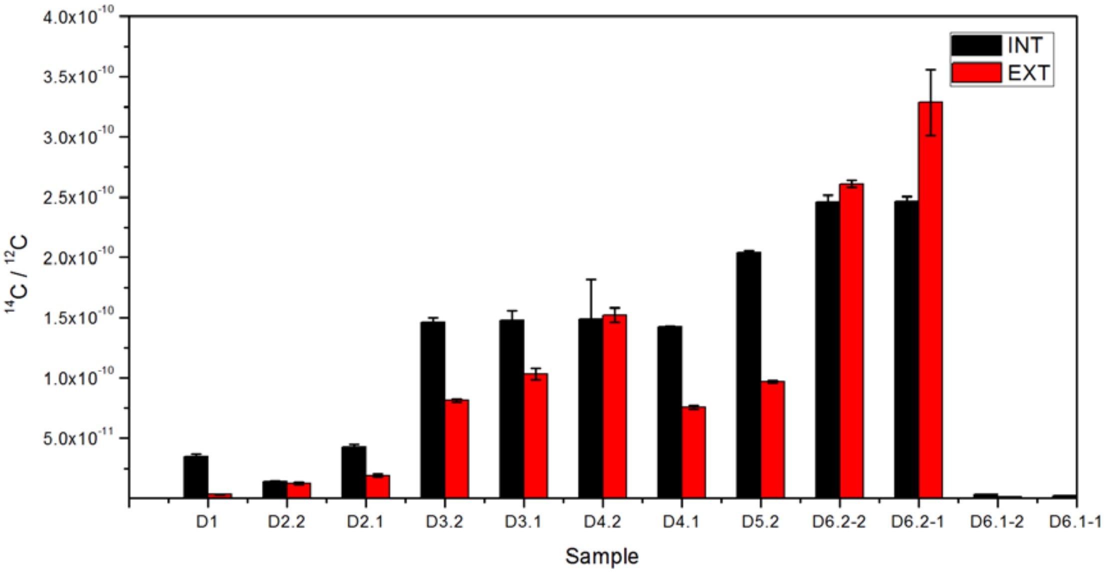


Figure 2.8.7: Results of the AMS experiments determining the ^{14}C concentration accumulated in the thermal column of the VVR-S reactor

Unfortunately, radiocarbon concentration for disc 6 could not be measured, due to limitation of the 1MV AMS machine to concentrations exceeding the natural level of radiocarbon.

For high concentration (samples collected from disc numbers 5 and 6) of ^{14}C the deviations are very large and such results are subject to a new experiment appropriate for higher radiocarbon concentrations. These samples need to be measured at the AMS facility with the 9 MV accelerator, which possesses calibrated beam attenuators and is able to measure higher concentrations (by about a factor of 10^3).

Due to the failure of the Wien Filter power supply, the experiments had to be rescheduled for the end of this year or the beginning of 2017. The numerical results of the AMS measurements are listed in Table 2.8.2.

Sample	**Outer side**		**Inner side**		**Weighted Average**[5]
D1.2	0.64	0.04	6.85	0.45	0.69 ± 0.04
D2.2	2.39	0.24	2.71	0.08	2.68 ± 0.08
D2.1	3.73	0.3	8.48	0.43	5.29 ± 0.25
D3.2	16.04	0.27	28.74	0.72	17.56 ± 0.25
D3.1	20.28	0.95	29.13	1.61	22.55 ± 0.82
D4.2	29.92	0.37	29.33	6.42	29.92 ± 0.37
D4.1	14.88	0.22	27.95	0.13	24.67 ± 0.11
D5.2	19.07	0.59	40.16	0.31	35.69 ± 0.27
D5.1	Not	measured			
D6.2-2	51.38	5.37	48.43	1.06	48.54 ± 1.04
D6.2-1	64.76	0.02	48.62	0.72	64.74 ± 0.02
D6.1-2	Not	able	to	measured	
D6.1-1	Not	able	to	measured	

^{14}C concentration results for samples collected from disc 5 and 6, even if they are presented in the table, are not trusted.

Table 2.8.2: ^{14}C concentration (Bq/g) in graphite samples

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[5] Weighted average of a N measurements x_1, x_2, … x_n with uncertainties σ_1, σ_2, … σ_n is:

$$x_{avg} = \frac{\sum_{i=1}^{N} xi_i w_i}{\sum_{i=1}^{N} w_i}$$

where the weights w_i are $1/\sigma_\iota^2$. The uncertainty on x_{avg} is:

$$\sigma_{avg} = \frac{1}{\sum_{i=1}^{N} w_i}$$

8.3.2 Determination of the experimental retention yields of HTO and $^{14}CO_2$ released by the graphite samples during incineration

The experimental retention yields obtained for ^{14}C and T are presented in Table 2.8.3.

Compounds	Samples activity [Bq]	Measured activity [Bq]		Retention yields [%]
		In HTO retention vial	In CO_2 retention vials	
Testosterone-1,2-T	35647 ± 328	35024 ± 588	87 ± 17	98.25
	5432 ± 56	5358 ± 98	32 ± 11	98.64
1-Octadecanol-^{14}C	15287 ± 143	57± 12	12231 ± 182	80.01
	1792 ± 19	36 ± 8	1412 ± 35	78.79

Table 2.8.3. ^{14}C and T retention yields for ^{14}C standards

8.3.3 Determination of total ^{14}C and ^{3}H specific activity in graphite samples collected from graphite column of the VVR-S reactor

The results regarding the total activity of ^{14}C and ^{3}H activity in graphite samples collected from graphite column discs are showed in Table 2.8.4. The activities of ^{14}C and ^{3}H for each graphite samples were calculated based on LCS activity measurements, sample weight and retention yield (98% for T and 80% for ^{14}C) (Hou. 2007).

Sample code	Distance from reactor core (cm)	Activity C-14 (Bq/g)	Standard deviation	Activity T (Bq/g)	Standard deviation	T/C activity ratio
D6.1.1	2	82518	6178.6	336124	31451.1	4.07
D6.1.2	20	59075	4284.3	183126	19502.9	3.10
D6.3	45	21532	1856.1	86342	8945.1	4.01
D6.1.2	80	9670	811.6	41330	4645.5	4.27
D6.2.2	98	3645	269.1	20132	1886.4	5.52
D5.1	102	3862	307.4	12687	1176.1	3.28
D5.2	138	1468	127.1	7868	862.3	5.35
D4.1	142	864	78.8	2867	279.0	3.31
D4.2	178	234	20.9	968	112.1	4.13
D3.1	182	117	10.3	521	62.5	4.43
D3.2	218	43	4.6	187	23.1	4.29
D2.1	222	21	2.4	112	13.4	5.22
D2.2	258	11.3	1.1	69	9.9	6.09
D1.2	300	6.9	1.3	39	6.7	5.74

Table 2.8.4 Specific activity of **^{14}C and T in the samples collected from graphite column**

8.4. Conclusions

a) IFIN-HH developed a method, based on the use of Accelerator Mass Spectrometry (AMS) based on the 1 MV accelerator to characterize the distributions of ^{14}C inventory in irradiated graphite from VVR-S Reactor.

b) Samples extracted from discs 4, 5 and 6 of the thermal column will be re-measured at 9 MV Tandem accelerator for a more accurate determination of ^{14}C concentration. The measurements will be performed on irradiated graphite samples during this year, when the beam time at 9 MV tandem accelerator will be assigned.

c) An apparatus based on silica gel/ $CaCl_2$ column and oxidation at high temperature over a CuO catalyst was designed and built for T and ^{14}C determination in irradiated graphite.

d) An experimental protocol for the combustion of irradiated graphite samples and separate retaining of T and ^{14}C was established with a retention yield of 98% for T and 80% for ^{14}C.

e) The results of the specific activity variation of ^{14}C and T along the length of the graphite The difference between the specific activity of ^{14}C samples obtained using AMS method and separation technique could be explained by the fact that the samples analyzed were crushed or powder graphite.

f) During the third year of the CAST project, IFIN-HH delivered project report D5.7 (Fugaru, 2016).

2.9 Radioactive Waste Management Limited (RWM) summary

Over Year 3 of Work Package 5 of the CAST project, RWM undertook its role as Work Package 5 leader. No other contributions to WP5 were scheduled in Year 3.

3 Summary

Work Package 5 of the EC CAST project considers irradiated graphite and related ^{14}C behaviour. The objective of this Work Package is to understand the factors determining release of ^{14}C from irradiated graphite under disposal conditions (to include surface disposal facilities and geological disposal facilities). This is the third annual report of Work Package 5, and details, on an organisation by organisation basis, progress in the Work Package over its Year 2. The achievements of each organisation are noted below:

1. The aim of work undertaken by IPNL is to simulate the behaviour of ^{14}C during reactor operation and evaluate the independent or synergistic effects of temperature and irradiation on ^{14}C migration. ^{14}C is mainly formed through the activation of ^{13}C but a certain amount may also be generated through the activation of ^{14}N. In this study, ^{13}C is mainly used to simulate ^{14}C release from the matrix carbon.

   Irradiation in both ballistic and electronic regimes disorders the graphite structure, promoting the formation of sp3 bonds. On the contrary, temperature has reordering effects in both regimes, resulting into the formation of new sp2 structures. Moreover, in the ballistic regime, graphite reordering is even more pronounced as temperature increases, because it enhances the mobility of vacancies and interstitials created during irradiation. Therefore, the synergistic effects of ballistic irradiation and temperature favour graphite reordering.

   Whatever the irradiation regime and even for temperatures as high as 1000°C, the implanted ^{13}C is not released from the graphite matrix. It stabilizes into sp3 or sp2 structures, whose relative proportions depend on the irradiation regime and temperature. In disposal conditions, the stabilization of ^{14}C into sp3 or sp2 structures should lead to reduced leaching rates in comparison to ^{14}C present in degraded and porous graphite.

2. Previously, 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

further developed. Sampling of the Ignalina NPP Unit 1 RBMK-1500 reactor graphite stack (blocks and rings/sleeves) has been already done by the NPP staff and it is expected that some radiological data of the samples will be publically available soon, including data on ^{14}C. Combining these experimental data, data available from other sources and numerical modelling for induced activity of ^{14}C, it should be possible to estimate the inventory of ^{14}C more precisely and with more confidence in i-graphite of the whole core of Ignalina NPP Unit 1 reactor. For the Task 5.5 "Data interpretation and synthesis – final report" LEI will provide the required input during the next reporting period.

3. The main objective of the RATEN ICN in WP5 is to update the inventory of ^{14}C in the irradiated graphite arising from TRIGA 14MW reactor thermal column and to define the associated source term, not only as total amount of ^{14}C 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 ^{14}C releases from TRIGA thermal column irradiated samples in order to establish the design parameters of the leaching experimental set up. RATEN ICN 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 ^{14}C 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 ^{14}C releases in hyperalkaline environment, both in liquid and gas phases.

4. Andra and EDF are in charge of reviewing the data on ^{14}C release and on the speciation of ^{14}C in French i-graphites. During this third year, the data on the speciation of released ^{14}C in French i-graphites were reviewed, and associated work was reported in Deliverable D5.8.

5. Work undertaken by ENEA considers i-graphite from Latina NPP. During this last year, the exfoliation-like process on the graphite by organic solvents (liquid-phase

exfoliation) helped by mild sonication has been widely studied to establish the best process parameters so to obtain graphene layers in a stable homogeneous dispersion. This will result in a dispersion of the graphite in a workable media. In this way, the solvent should be allowed to reach the inner layers/areas (i.e. closed pores, crystallites, etc.) and extract contaminants. This facilitates processing, treatment and easy characterization for the contaminants' recovery when applied on i-graphite. The overall process has been applied on three samples of nuclear graphite coming from the decommissioning of the Italian NNP in Latina. Previously, on these i-graphite samples, a characterisation of ^{14}C contents has been performed. Then, the radiocarbon measurement by Liquid Scintillation Counting (LSC) on the extracting solutions has established the Removal Efficiency values. The yields in extraction (RE%) obtained range from 0.2 to about 15 %. Although these values are relatively low, they can be considered the first ones obtained with this kind of treatment since no other values are produced in the literature by the same process to be compared. These results should be considered promising to keep on by this route.

6. Within the last reporting period, the activity of FZJ was focused on the pre-leaching characterization of irradiated graphite from Rossendorf research reactor (RFR), This included porosity measurements, g-spectrometry and autoradiography analysis followed by SEM for detailed identification of the hot-spot composition. Besides this the leaching equipment was set up and test phase of leaching experiment using inactive nuclear graphite has been started. The leaching conditions were selected according to the harmonized leaching procedure summarized in D 5.4.

7. During the third year of the CAST project, CIEMAT has fulfilled the design and implementation of the leaching experiments on irradiated powder graphite and on IGM graphite. After some preliminary tests, the use of powder graphite was discarded and a method to obtain cylindrical graphite samples was developed. CIEMAT has characterized the ^{14}C and e-gamma inventory of each irradiated sample. Up to date four leaching periods on graphite cylinders and IGM has been completed using two different media (deionized water and granite bentonite water). The set-up of different equipment intended for speciation studies (GC-MS and IC)

has been completed (Quantulus setting-up ongoing) and the analysis method of gas and liquid samples has been stablished. The data analyses of both the gas and the liquid samples are in progress.

Regarding thermal treatment, the data obtained with virgin graphite experiments have allowed the devices and methods to be used in the system at pilot plant scale to be established. Different parameters have been studied to optimize the methodology, such as temperature, gas flow and the oxidizing agent. The behaviour of Vandellós irradiated graphite in inert atmosphere is different if it is compared with other graphite. The ratio ^{14}C/Total C results are not definitive or conclusive and it has to be improved because of undesirable higher corrosion rates; more experiments should be programmed to optimize the decontamination factors (^{14}C/^{12}C) without significant mass loss, and the obtained data indicates that thermal treatment can decontaminate selectively ^{14}C from Vandellós I irradiated graphite.

8. The main objective of the IFIN-HH in the third 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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