CArbon-14 Source Term

CAST

WP5 Annual Progress Report – Year 2 (D5.6)

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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 2 (D5.6)

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 14C 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. Under task 5.2 new models for the numerical estimation of RBMK-1500 graphite activation are under development. 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 soon. Combining these data, the data from the other sources and numerical modelling for the induced activity of C-14, it should be possible to estimate the inventory of C-14 more precisely in i-graphite of the whole core of Ignalina NPP Unit 1 reactor.

3. The main objective of the INR in Work Package 5 is to update the inventory of C-14 in the irradiated graphite arising from TRIGA 14MW reactor thermal column and to define the associated source term, not only as total amount of C-14 but also as inorganic/organic ratio. Data on the leaching rate presented in the literature have been analysed and the most appropriate kinetics used to predict the C-14 releases from TRIGA thermal column irradiated samples in order to establish the design parameters of the leaching experimental set up. Activities performed up to now consisted in the design of the experiments in order to ensure measurable C-14 releases in hyperalkaline environment, both in liquid and gas phases.

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 ^{14}C release in French i-graphite were reviewed and presented in deliverable D5.1. During this second year, the data on the speciation of released ^{14}C in French i-graphites were reviewed, and associated work towards deliverable D5.8 is in progress.

5. Work undertaken by ENEA considers i-graphite from Latina NPP. An exfoliation-like approach is studied for irradiated nuclear graphite by mean of non-oxidizing organic solvents extraction combined with prolonged ultrasound bath as a possible new decontamination method. The graphite 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 work of FZJ was involved in the development of a harmonized leaching procedure. For that the information on leaching approach was extensively reviewed, critically discussed (with input from CIEMAT and NDA[1]) and summarized. Previous experience of leaching tests with RFR graphite performed in the frame of CarboDisp project at FZJ is considered. It is anticipated that the developed leaching approach can be used by other project participants, to enable better inter-laboratory comparison of results from leaching of irradiated graphite, allowing systematic progress in the studies of ^{14}C leaching behaviour.

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[1] From April 2014 onwards, work previously undertaken by the UK Nuclear Decommissioning Authority (NDA) Radioactive Waste Management Directorate (RWMD) has been undertaken by Radioactive Waste Management Limited (RWM), a wholly-owned subsidiary of the NDA.

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

8. The main objective of the IFIN-HH in the second 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 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, the experimental 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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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 Limited (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 second annual report of Work Package 5 and details, on an organisation by organisation basis, progress in the Work Package over its second 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

Introduction

Our contribution aims at understanding better the inventory of ^{14}C in irradiated French UNGG nuclear graphite. In France, the irradiated graphite should be directly disposed of. However, leaching tests on irradiated graphite waste are still underway. According to the results of these tests, purification aiming at removing the most disordered and most ^{14}C contaminated parts of the irradiated graphite waste might be implemented before disposal.

The safety assessment calculations need reliable data related to ^{14}C quantity, location within the graphite and speciation. These data are not easily accessible on irradiated radioactive graphite but some information can be inferred through experiments made on virgin implanted samples.

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.

During the second year of this project, our study was devoted to the comparison of the respective roles of electronic excitations and ballistic damage on ^{13}C migration and structure evolution in Highly Oriented Pyrolytic Graphite (HOPG). In order to simulate the presence of ^{14}C, we have implanted the samples with ^{13}C (parallel to c axis). The HOPG samples (Grade SPI-1) are issued from SPI 4 Supplies via Neyco Company. The advantage of the model graphite is the absence of pores preventing the release through “shortcuts” due to the interconnected pores (as in nuclear graphite) thereby providing a better understanding of the release mechanisms.

The collisions of the impinging neutrons with the graphite matrix carbon atoms induce mainly ballistic damage. However, a small part of the recoil carbon energy is also transferred to the graphite lattice through electronic excitations. These effects coupled to temperature may strongly affect the graphite structure as well as the behaviour of the radionuclides during reactor operation. The respective ballistic or electronic excitation effects can be quantified according to the nuclear and electronic stopping power values (respectively S_n and S_e). Thus we have studied the behaviour of the implanted ^{13}C and the graphite structure modification induced by ion irradiation and temperature as a function of S_n/S_e using different irradiation facilities. Therefore, in the following, the results will be presented according to the ratio S_n/S_e.

The results presented in this document are issued from the PhD work of N. Galy that is still underway.

Experimental

The ^{13}C implantations have been performed at the 200kV Eaton implanter of the Icube laboratory in Strasbourg (by Y. le Gall) at depths around 300 nm and two respective fluences. A fluence of $6x10^{16}at.cm^{-2}$ (concentration at the projected range R_p around 5 at%) on one hand. This fluence allows analysing ^{13}C by SIMS before and after irradiation and induces around 5 dpa (displaced atoms) at the maximum projected range R_p. On the other hand, a lower implantation fluence of $4x10^{14}$ $at.cm^{-2}$ (concentration at the projected range R_p around 0.04 at.%) has been used. This fluence induces a very low damage level (around 0.04 dpa at the R_p) and allows following the structure modifications induced by both temperature and irradiation by *in operando* Raman spectrometry.

The implantation results in quasi Gaussian distribution profiles of the implanted ^{13}C. ^{13}C profiles have been analysed (before and after treatment) at the *Laboratoire Science et Surface* at Ecully using an IONTOF ToF-SIMS V (by J. Amalric and J. Brissot).

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

The irradiations experiments have been carried out with different ions such as C, Ar, S and He. The 4 MV Van de Graaff or the 400 kV IMIO accelerators at IPNL was used in order to study the ballistic effects. The electronic excitation effects to achieve high S_e levels have been studied using the 15 MV Tandem of IPN at Orsay. The CEMHTI cyclotron facility was used to achieve lower S_e levels (in collaboration with M.R. Ammar, P. Simon and T. Sauvage) using a dedicated irradiation cell allowing *in operando* sample structure monitoring. During irradiation, the samples could be heated in all cases (up to 500°C or 1000°C, depending on the cell). The irradiations were carried out in gas or secondary vacuum.

Results and discussion

Two main types of irradiation have been carried out: irradiations for which the ballistic impact is predominant ($S_n/S_e > 10^{-3}$) and irradiations for which the electronic effect is predominant ($S_n/S_e < 10^{-3}$). In this latter case, the ballistic damage was almost nil (Figure 2.1.1).

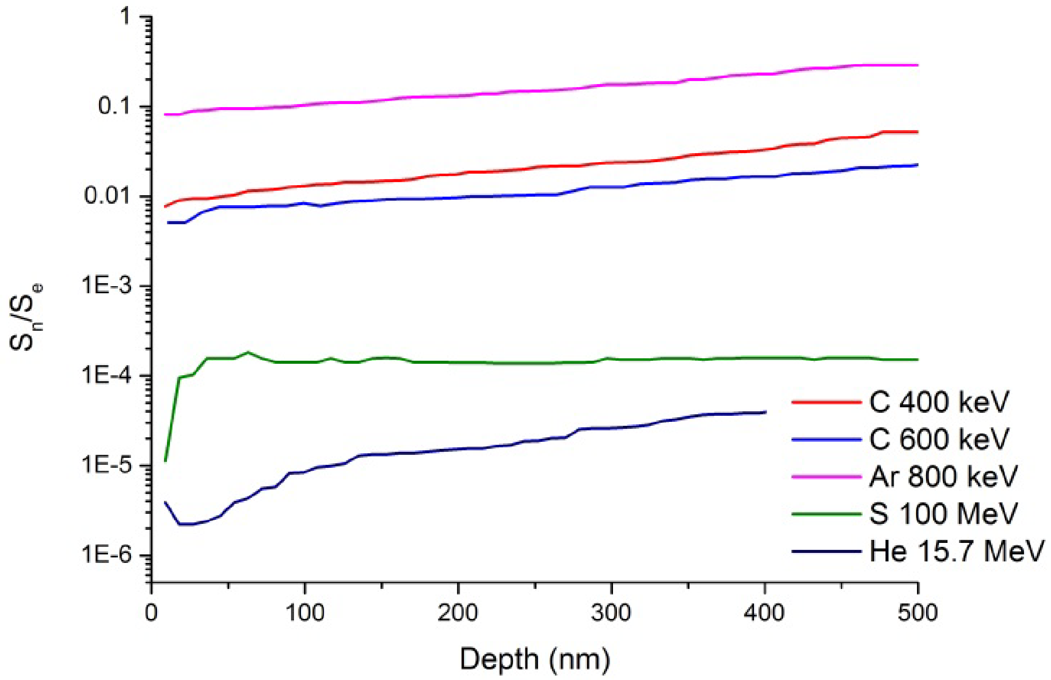


Figure 2.1.1: The stopping power ratio S_n/S_e in the implanted zone for different ions used for irradiation

Ballistic effects predominant:

- **Irradiation at** $S_n/S_e > 10^{-3}$

Whatever the nature and energy of the incident irradiating ion, C^+ (energies of 400 and 600 keV) and Ar^+ (energy of 800 keV) the range of the irradiating ion was greater than that of the implanted species. In other words the irradiating ion stopped beyond the implanted zone. The fluences were adjusted to allow creating respective ballistic damages around 1 dpa for C^+ ions and 4 dpa for Ar^+ ions in this zone.

Figures 2.1.2 and 2.1.3 show the evolution of the implanted ^{13}C concentration for C^+ irradiations respectively carried out at 200°C and 1000°C. These Figures show that ^{13}C is not released.

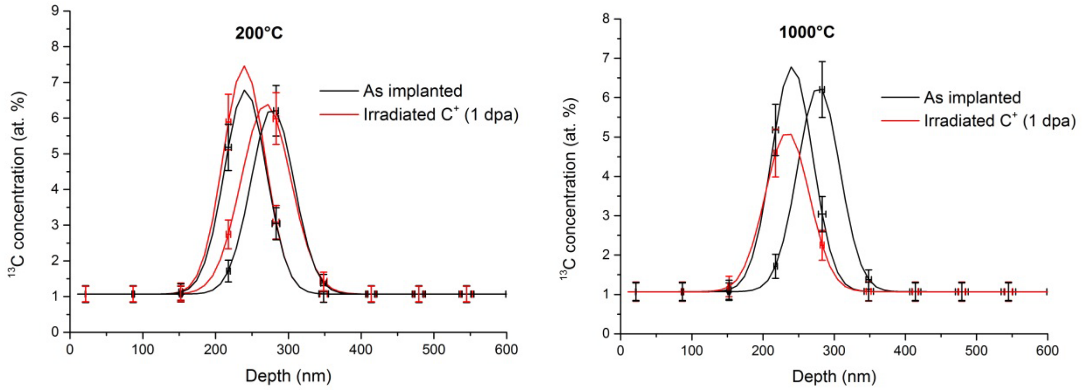


Figure 2.1.2 (left) and 2.1.3 (right): Evolution of the implanted ^{13}C concentration profiles for C^+ irradiations respectively carried out at 200°C and 1000°C

Same type of results has been obtained for the Ar^+ irradiations (not shown here). Figures 2.1.4 and 2.1.5 show the Raman spectra for the samples irradiated at different temperatures from RT to 1000°C respectively with C^+ and Ar^+ and compared to the as implanted sample as well as to a just annealed sample at 1600°C.

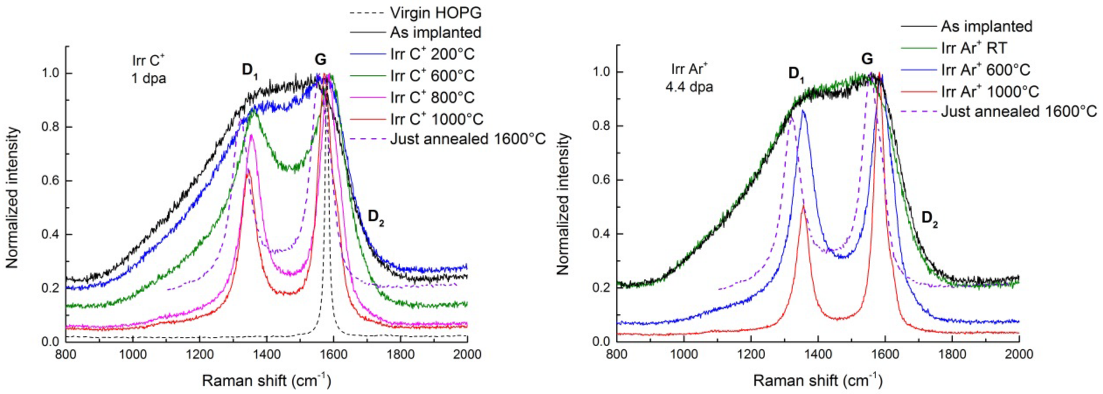


Figure 2.1.4 (left) and 2.1.5 (right): Raman spectra for the samples irradiated at different temperatures from RT to 1000°C respectively with C^+ and Ar^+

The comparison of the irradiated spectra with the as implanted one and the just annealed one shows that irradiation coupled to temperature favours graphite structure reordering all the more the temperature is high. Distinct bands emerge: the defect bands D_1 and D_2 and the graphitisation band G. This means that the proportion of sp^2 structures increases with respect to sp^3 structures. Therefore, even if the structure of the as implanted sample is already strongly damaged through implantation that has created sp^3 bonds, **the synergistic effects of irradiation in ballistic regime coupled to temperature strongly favour the graphite structure reordering,** thereby stabilising **the implanted ^{13}C into sp^2 structures.**

<u>Electronic excitation effects predominant:</u>

- **Irradiation at S_n/S_e <** 10^{-3} and **high S_e (3700 keV/µm in the implanted ^{13}C zone):**

Such high S_e levels are not reached in UNGG reactors but allow measuring the impact of **high energy transfer on the matrix evolution and implanted ^{13}C behaviour.**

S^{9+} ions at energy of 100 MeV were used. As previously, the irradiating sulphur ions stopped far beyond the ^{13}C implanted zone.

Figure 2.1.6 compares the implanted ^{13}C profiles of the irradiated samples at different temperatures to the as implanted sample. Whatever the irradiation temperature, the ^{13}C profile remains stable.

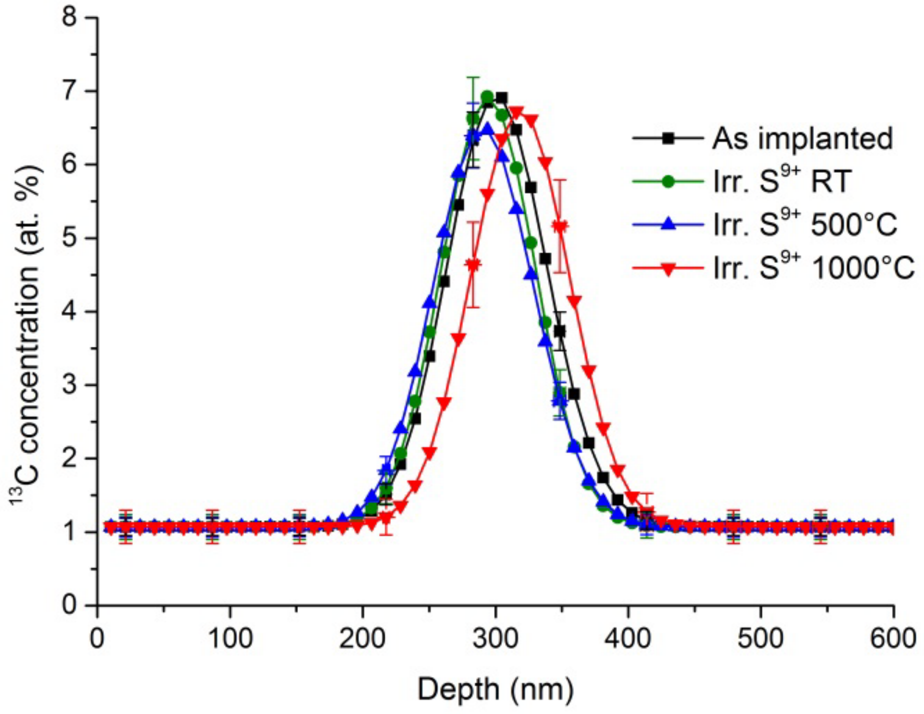


Figure 2.1.6: Evolution of the implanted ^{13}C concentration profile for S^{9+} irradiations carried out from RT to 1000°C

Figure 2.1.7 shows the Raman spectra of the irradiated samples compared to that of the as implanted one.

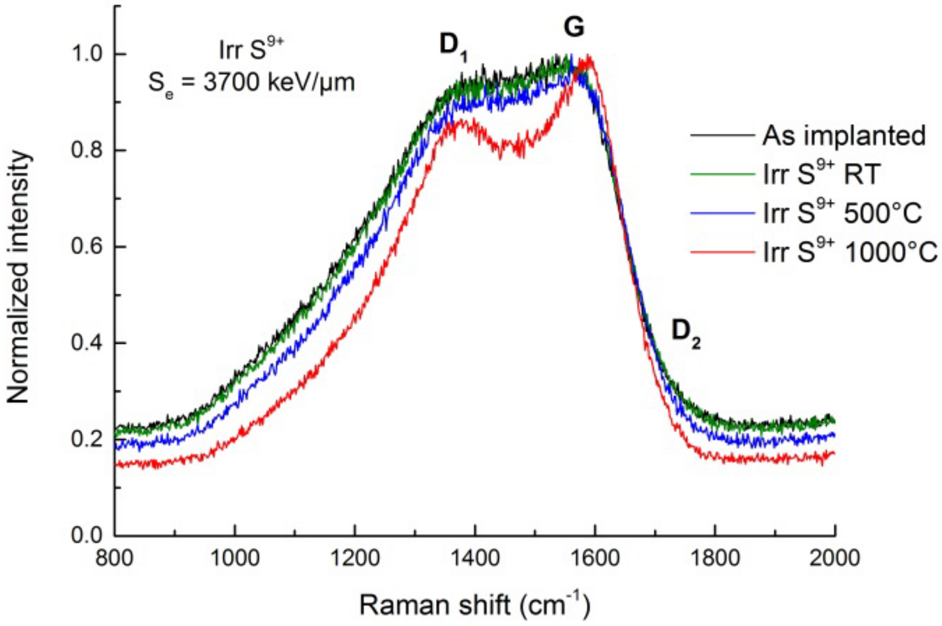


Figure 2.1.7: Raman spectra for the samples irradiated at different temperatures from RT to 1000°C with S^{9+}

Contrary to the ballistic regime, the electronic excitations do not favour the graphite structure reordering. Only a small recovery of the sp^2 structure is achieved at 1000°C. **This means that electronic excitation favour the formation of sp^3 bonds and that implanted ^{13}C probably stabilise into these structures.**

- **Irradiation at S_n/S_e** < 10^{-3} and **low S_e (80 keV/µm in the implanted ^{13}C zone):**

The irradiations were carried out with 15.7 MeV He^+ ions in order to create electronic excitations S_e around 80 keV/µm in the implanted ^{13}C zone **which is in the range achieved in UNGG reactors**. In order to follow the effect of this low S_e level on graphite structure modification, the samples had been previously implanted with ^{13}C at a fluence of $4x10^{14}at.cm^{-2}$. This fluence allows simulating a slightly damaged graphite structure (less than 0.1 dpa). Moreover, in order to simulate the UNGG reactor conditions, the irradiations have been carried out in UNGG simulating gas composed mainly of CO_2.

Figure 2.1.8 shows the Raman spectra recorded before irradiation at room temperature (RT) and during sample heating up to 500°C. The RT sample spectrum exhibits the signals due to CO_2 as well as the G, D_1 and D_2 bands of the implanted graphite. The 500°C sample shows the decrease of the D_1 and D_2 band intensities.

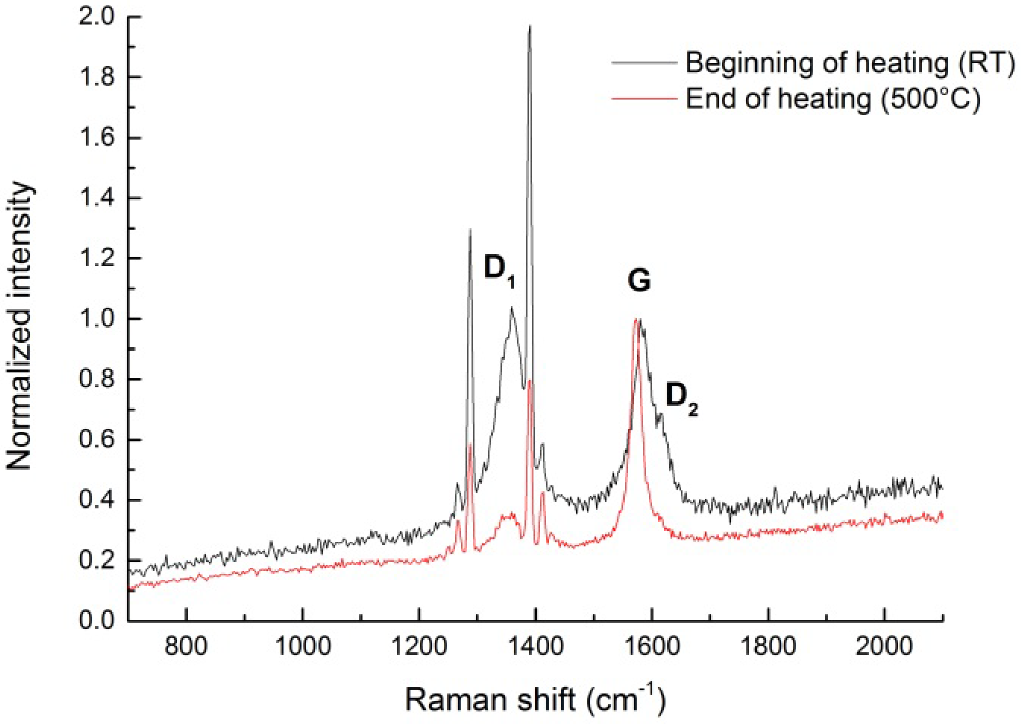


Figure 2.1.8: Raman spectra recorded before irradiation at RT and at the end of sample heating up to 500°C

Figure 2.1.9 represents the I_{D1}/I_G ratio, allowing quantifying the damage level, during sample heating.

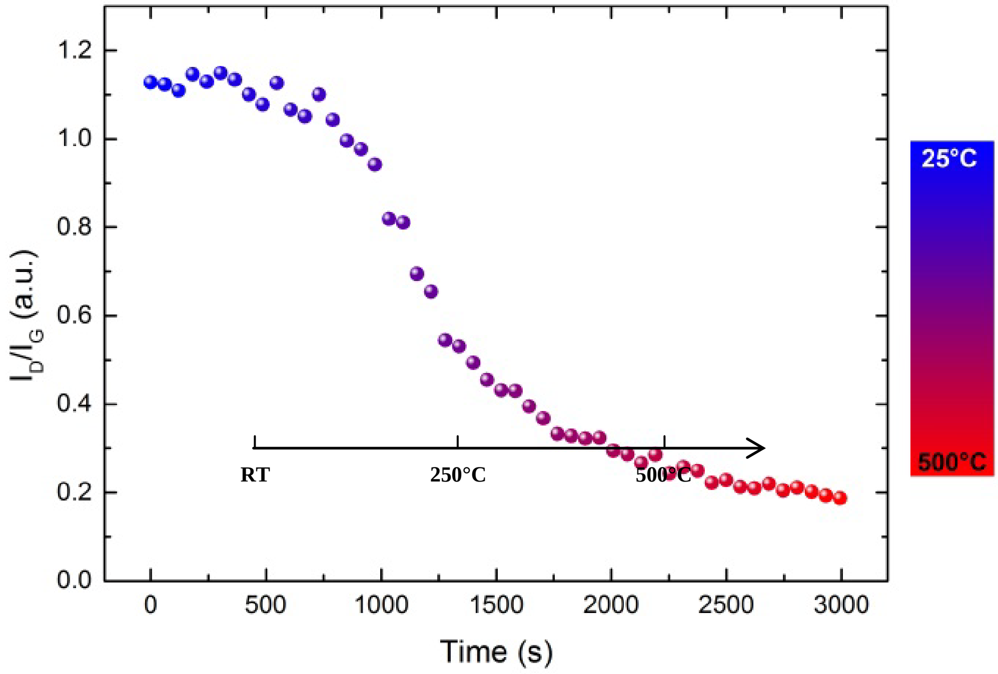


Figure 2.1.9: The I_{D1}/I_G ratio during sample heating

It is interesting to note that a strong decrease of the ratio is observed above 200°C – 250°C, temperatures for which the vacancies begin to be mobile, the interstitials being already mobile at room temperature. Thus, the graphite reordering with temperature is linked to the interstitial-vacancy recombination.

As soon as the sample has reached the temperature of 500°C, irradiation begins. Figure 2.1.10 displays the Raman spectra recorded on the heated sample at the beginning of irradiation and at the end of irradiation. This figure shows that D_1 band grows during irradiation, indicating the disordering induced effect of irradiation.

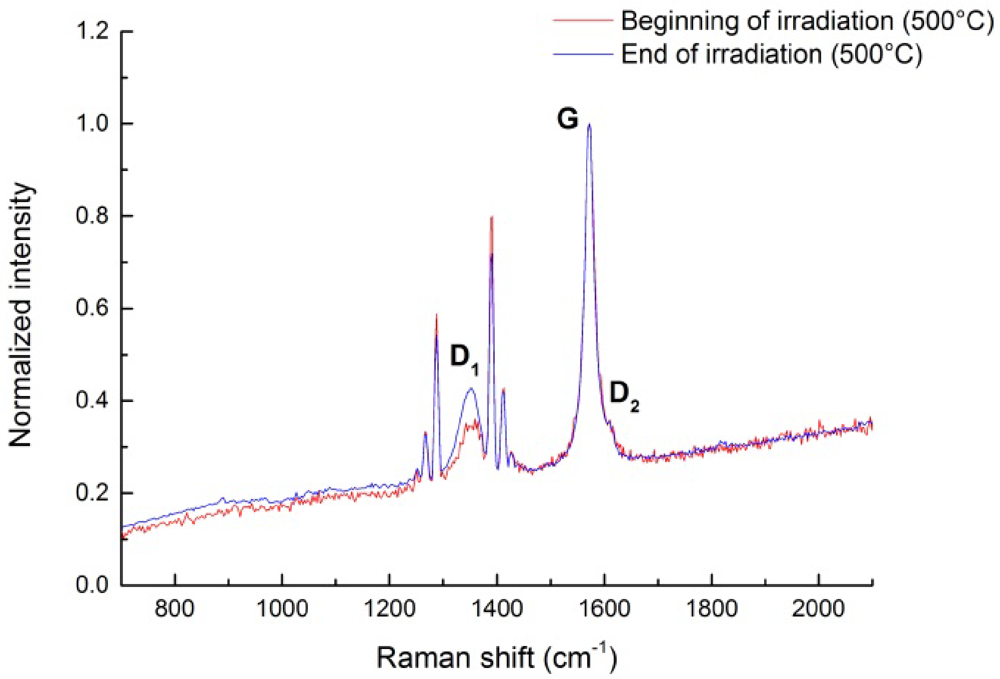


Figure 2.1.10: Raman spectra recorded at the beginning and at the end of irradiation

Figure 2.1.11 displays the I_{D1}/I_G ratio in function of time. This figure clearly displays the increase of the I_{D1}/I_G ratio until it stabilises at a value around 0.27.

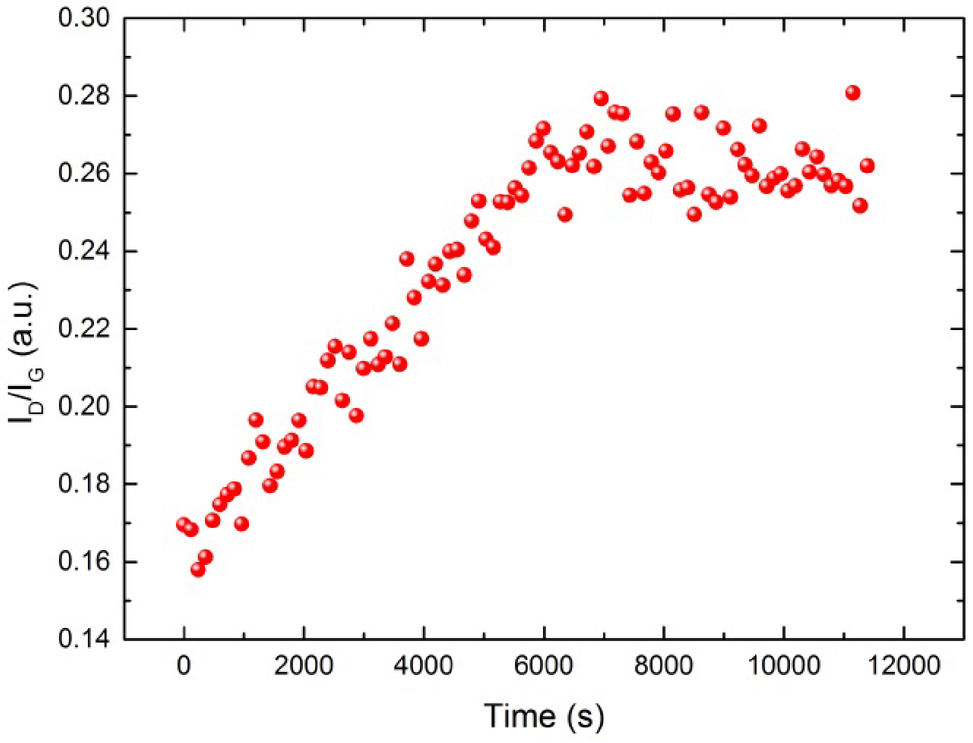


Figure 2.1.11: The I_{D1}/I_G ratio during sample irradiation

This experiment shows that electronic excitations disorder the graphite structure, even at low S_e levels and shows evidence for the opposing effect of temperature in tending to reorder the structure.

Conclusion

- 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.

- Trying to extrapolate the results to the behaviour of ^{14}C shows that ^{14}C, displaced from its original structural site through recoil, tends to stabilize into new carbon structures with increasing temperature. In case of prior purification, ^{14}C stabilized into the “hot” parts of the graphite should be more difficult to extract in comparison to ^{14}C present in “cold” and disordered graphite. 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.

2.2 Lithuanian Energy Institute (LEI) summary

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

During the first and the second year of the CAST Project, LEI concentrated on the performance of the Task 5.1 – "Review of CARBOWASTE and other relevant R&D activities to establish the current understanding of inventory and release of ^{14}C from i-graphites" and Task 5.2 – "Characterisation of the ^{14}C inventory in i-graphites". For the Task 5.1, LEI reviewed the outcome of CARBOWASTE 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 will model the ^{14}C inventory in a RBMK-1500 reactor core using new data and to publish the final deliverable D5.17 "Report on modelling of ^{14}C inventory in RBMK reactor core" which is scheduled for the month 42 of the Project.

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 year. Some comments regarding LEI input were received during the second 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 CRP, etc., new models for numerical estimation of RBMK-1500 graphite activation are under development. 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 publicly available soon, including data on ^{14}C. 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 and well supported. For this, new models for numerical estimation of induced activity (direct activation calculation as well as reverse activation calculation) and are under development.

Gathering of new information relevant to the RBMK graphite activation issues is also ongoing. Some recent results of ^{14}C activity in Ignalina NPP graphite were published in the beginning of 2015 [Mazeika et al. 2015]. This paper presents some experimental studies of GRP-2-125 grade graphite rings on the content of ^{14}C radionuclide, which revealed the following results: for the inner part of rings ^{14}C activity concentrations was 2.6×10^5 Bq/g, while for the outer part of rings it was 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 one sample of the reference bushing segment of the temperature channel made of GR-280 were investigated for the content of ^{14}C. Based on the statistical analysis of the sub-samples activity, the average value of the total ^{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.

2.3 Regia Autonoma pentru Activitati Nucleare (INR) summary

Preliminary tests for nitrogen impurities measurement in graphite used in TRIGA thermal column

The chemical decomposition in the presence of a mixture of acids is applied to bring the graphite samples in liquid state. To establish the determination method of nitrogen impurities in virgin graphite, efforts have been made in term of finding the optimal mixture of acids that contribute primarily to the overall release of nitrogen into the solution, but also to a complete decomposition of the graphite samples.

Several experiments in which the graphite mineralization samples were achieved using various mixtures of acids and also different acid/sample ratio were performed so far. The first mixture of acids used to digest different masses of graphite samples (powder type) it has a composition of sulfuric acid (98%) and nitric acid (67%). Eight parallel samples, having a maximum mass of 200 mg, were tested using this mixture, in a microwave digestion system, in TFM™-PTFE pressure vessels. For all samples, a clear solution was obtained, indicating a complete digestion of the graphite samples. The digestion performance of the graphite samples is also a very useful result for the measurement procedure of ^{14}C initial content in irradiated graphite.

For the determination of nitrogen content present at level of impurities in graphite, the use of nitric acid must be avoided since a supplementary nitrogen contribution is added, with an order of magnitude higher than the ppm level, assumed to be found in the nuclear grade graphite. A three step digestion procedure was tested, using an acid mixture composed of HF-HCl, saturated H_3BO_3 and 1.9 M H_2O_2. The liquid samples obtained were filtered and resulted solutions were analysed by ICP-OES method, but the measured nitrogen concentrations were below the detection limits of the spectrometer, that are known to reach the ppb level. This result can mean that during the digestion step, the nitrogen release into solution was not achieved, or it might be lost in gaseous phase.

In order to quantify losses and to determine the nitrogen recovery yield, in the process cycle mentioned above, carried out to bring the samples from solid to liquid phase (compatible with ICP-OES analysis method and Kjeldahl method for total nitrogen measurement) a set of experiments were performed on spectral graphite with known nitrogen content. A number of five identical samples were tested and the reagent used for the digestion step is an acid mixture of HF (48%) and HCl (37%). The pressure vessels were kept closed over the week-end, the solution obtained were filtered and analysed using Kjeldahl analysis method. This step involved the addition of a volume of sodium hydroxide (to facilitate ammonium formation). No nitrogen concentration above the detection limits was measured, bringing evidence that at level of impurity, the nitrogen content might be lost in gas phase.

^{14}C measurement in irradiated graphite to be used in the leaching tests

To measure the ^{14}C activity in the samples selected to be used in the leaching tests, activities performed so far were focused on testing the ^{14}C measurement procedure. The first method is the combustion of the irradiated graphite samples in an oxygen-enriched atmosphere with a continuous flow of oxygen using Sample Oxidizer, Model 307 PerkinElmer®. By this method any hydrogen present is oxidized to water while any carbon is oxidized to carbon dioxide.

If tritium is present then the combustion product will be ^3H_2O and if ^{14}C is present then the combustion product will be $^{14}CO_2$. The water is condensed in a cooled coil and then washed into a vial where it is mixed with an appropriate LSC cocktail while the CO_2 is trapped by vapour-phase reaction with an amine and the resulting product is mixed with an appropriate LSC cocktail. At the end of the combustion cycle, two separate samples (a ^{3}H sample and a ^{14}C sample) are trapped at ambient temperature, thus minimizing cross contamination. Carbo-Sorb® E is used to trap the released $^{14}CO_2$ in form of carbamate that is furthermore flushed into the ^{14}C counting vial using the Perma-fluor® E+ scintillator as a rinsing media.

The ^{14}C activity is measured by liquid scintillation method using a Tri-Carb®3110TR. This analyzer allows for ultra-low level counting mode with typical count rate in the range of 1 – 20 CPM above background.

Preliminary tests were performed on virgin graphite labelled with tritium and ^{14}C to measure the recovery and memory of this method; an average combustion recovery of 100.08% and a memory of 0.04% were obtained.

The acid digestion procedure of the graphite samples, suitable with liquid scintillation counting method is also tested. Optimal acid mixture that contributes to complete digestion of irradiated graphite samples in the microwave field was selected and also the maximum graphite mass that may be used in the digestion experiments. The ^{14}C content measurement is achieved by LSC method using UltimaGold AB as scintillator with a sample/scintillator ratio of 1/19. The ^{14}C recovery obtained by this method was less than 80% and furthermore for ^{14}C measurement in the samples selected for the leaching tests will be achieved by using Sample Oxidizer, Model 307 PerkinElmer®.

Experimental conditions for the leaching tests on TRIGA irradiated graphite

Regarding the release rate determination of ^{14}C from irradiated graphite, a review of the international standards on leaching methodology was conducted. These standardized methods impose more or less different leaching conditions. Thus, different types of test, different leachate replacement intervals, different test temperatures, different geometries and dimensions of the samples and other interdependent factor/conditions were in detail analysed.

The leaching test is intended to be carried out on a long-term basis (> 90 days) until equilibrium is reached and the leachate will be represented by a sodium hydroxide solution (NaOH, pH ~ 12.5), to simulate the pore water of the cement used in a geologic repository. It should be mentioned that the test is to be done at room temperature, the irradiated graphite samples from TRIGA reactor are to be cut into cylindrical shape test specimens. As soon as the Deliverable 5.4 becomes available and a harmonized leaching approach is agreed, the tests will be performed under the condition stated by the procedure.

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 behavior 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 this second year, the data on the speciation of released ^{14}C in French i-graphites were reviewed. Work on the associated CAST deliverable 5.8 is in progress. This deliverable will be focused on two French reactors, SLA2 (Saint Laurent A2, EDF) and G2 (CEA). The studied leaching tests are the same as for D5.1 deliverable. 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 will be presented in the document D5.8.

The experimental procedure gives the possibility to identify the mineral fraction and the organic fraction in the liquid. As a consequence, the deliverable D5.8 will show 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.

The deliverable D5.8 will also give 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 there were not studied yet.

The document will be available by the end of 2015.

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, like as all the graphite coming from moderators exposed to a neutron flux (for Latina NPP is up to 5×10^{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. Anyway, there are not usually involved chemical bonds. So that, in order to achieve an exhaustive and valid extraction for activation products, it is important to increase the surface area of the sample. This should allow to the solvent to reach the inner layers/areas (i.e. closed pores, crystallites, etc.) and extract contaminants in solution.

The main idea is to apply an exfoliation-like process on the graphite by organic solvents (liquid-phase exfoliation) to produce un-functionalized and non-oxidized graphene layers in a stable homogeneous dispersion (Khan et al. 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, being sufficient to remove all the inter-planar interactions, thanks to the dipole-induced/dipole interactions between graphene layers and organic solvents, results in a dispersion of the graphite in a workable media. This facilitates processing, treatment and easy characterization for the contaminants recoveries (Figure 2.5.1).

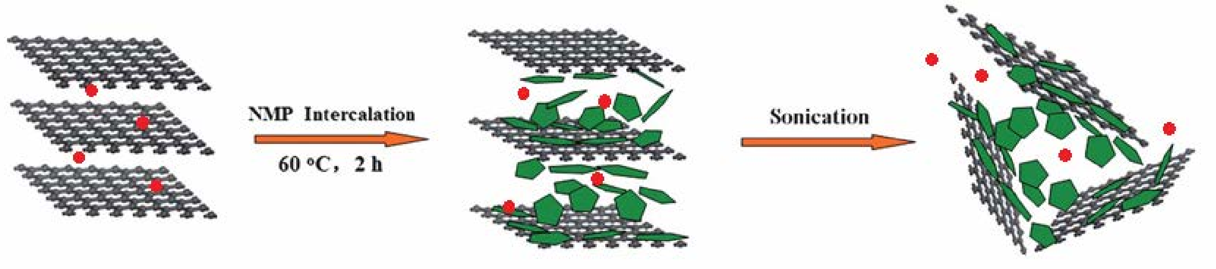


Figure 2.5.1: Representation of the main steps for the graphite exfoliation process promoted by organic solvents and ultrasound assisted

Moreover, neither oxidation process is performed for super-strong acid actions. This would lead to non-oxidized products so the graphite would be completely recovered as it is.

The main steps in this process are:

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

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

- N,N-Dimethylacetamide (DMA)
- N,N-Dimethylformamide (DMF)
- N-Methyl-2-pyrrolidone (NMP)

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

In order to obtain the best removal efficiencies and state this process as a good way to treat and decontaminate the i-graphite, some of the process parameters have to be defined and well assessed. Encouraged by the promising results described in previous reports, at this point some tests have been performed and then described, so to tune the processes in the right direction.

In particular, three groups of experiments have been proved:

1. Comparison of the Nuclear Grade Graphite with the Highly Oriented Pyro Graphite;
2. Optimal ratio graphite/solvent;
3. Best sonication time.

Optimisation of the process parameters: preliminary considerations

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 we have chosen a low centrifugation rate (500rpm) followed by a filtration step. The supernatant liquid phases coming from the centrifugation are filtered on polyvinylidene fluoride (PVDF) filter membranes of 0.10 µm of pore size. Possible investigations about this parameter will be eventually considered further.

Most of the results obtained are expressed in terms of “yield”. The yield hence considered is the yield by weight, defined as the ratio between the weight of dispersed graphitic material and that of the starting material (flakes of HOPG or Nuclear Grade Graphite powder).

This yield in weight does not give information on the amount of single layer graphene, but only the total amount of graphitic material.

In order to determine exfoliation yields it is necessary to characterize exfoliated graphitic material providing both qualitative and quantitative information. At this purpose combined estimation of the concentration and of the quality have been performed with UV-Vis and Raman Spectroscopies.

In order to find the concentration after centrifugation, the graphite dispersions have been passed through the above-mentioned filters. Careful measurements of the filtered mass after removal of the residual solvents by vacuum oven at 60 °C, gave the concentration of dispersed phase after centrifugation. These dispersions were characterized by UV-Vis absorption Spectroscopy. Actually, each of these dispersions was diluted 1:10 and then the absorption spectra were recorded at 660 nm as suggested from literature works (Jorio et al. 2013).

The estimation of the concentration C [mg L^{-1}] of the dispersed graphitic material has been determined *via* optical absorption spectroscopy by exploiting the Beer-Lambert Law: $A = \alpha C I$, where A is the absorbance, I [m] is the length of the optical path, and α [L mg^{-1} m^{-1}] is the absorption coefficient.

Every absorbance value, divided by cell length (I), has been then plotted versus concentration.

When a perfect Lambert-Beer behaviour is observed, then the set of solution can be considered a set of Standards Solution as Calibration Curve for the next measurements.

The number of graphene layers, that gives the qualitative information, although is usually determined *via* Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM), can be easily performed by Raman Spectroscopy. This technique can be applied to all graphene samples and is able to identify also unwanted by-products, structural damage, functional groups, chemical modifications and electronic perturbations introduced during the preparation, processing and others steps. As a result, a Raman spectrum is an invaluable tool for quality control and comparing samples used in different situations and preparations.

Experimental Procedures

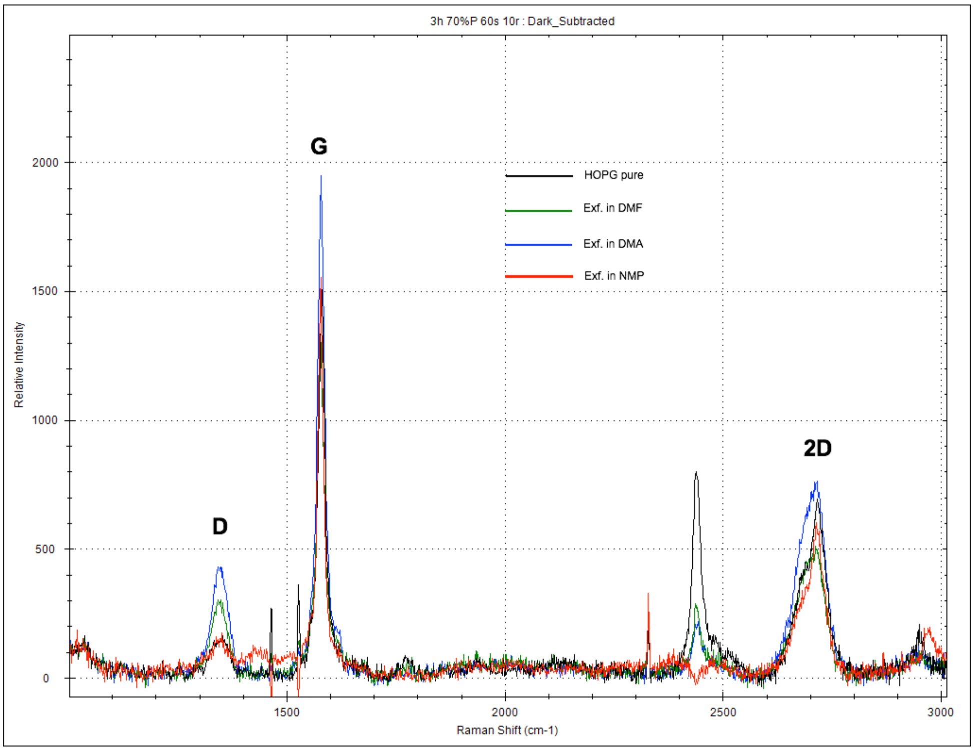
Highly Oriented Pyro-Graphite HOPG Vs. Nuclear Graphite NG

Since all the works on graphite-exfoliation in worldwide literature have been performed only on Highly Oriented Pyro Graphite (HOPG), in order to test the validity also on Nuclear Graphite, similar to HOPG in many ways, a comparison with the commercial HOPG has been performed. The results obtained have been compared *via* Raman Spectroscopy.

At this purpose samples of 25 mg of each of the both kind of graphite (HOPG, NG) have been mixed with 5 mL of respectively DMF, DMA, and NMP.

The time of sonication is set on 3 hours in a sonication bath at the power of 30W – 37 kHz.

The solutions obtained have then centrifuged at 500 rpm for 90 min followed by filtration on PVDF 0.1 μm filters. These filters were then dried in vacuum oven and weighed, and then have been characterized by Laser Raman Characterization (Fig. 2.5.2 and 2.5.3) and on the exfoliated by different organic solvents.



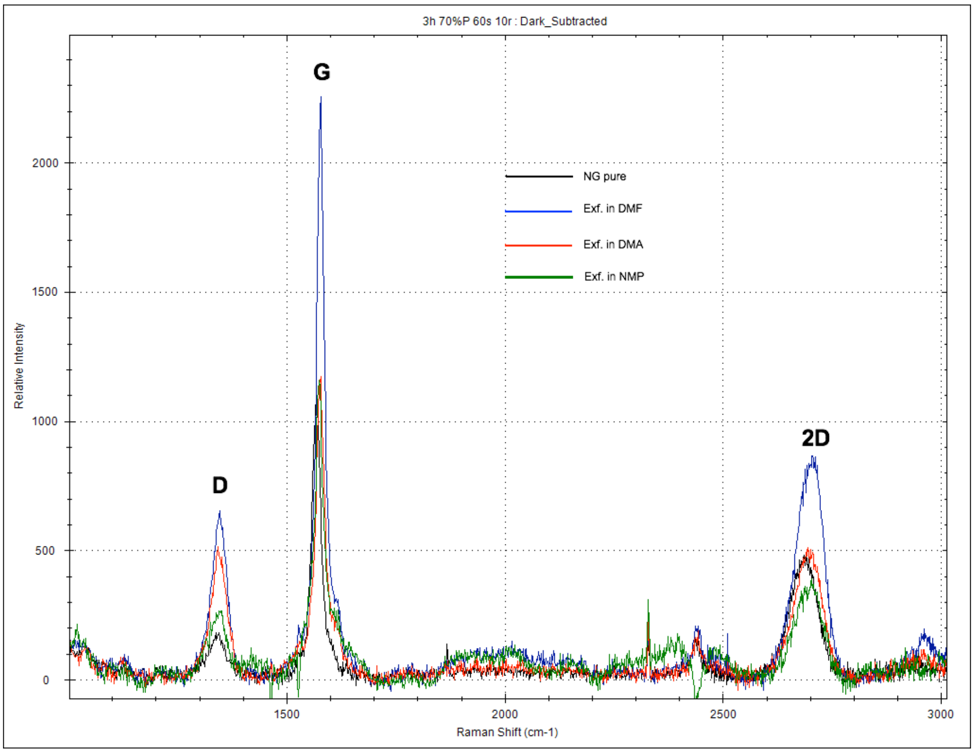


Figure 2.5.2 (*top*) and 2.5.3 (*bottom*) – Raman Spectra on HOPG (top) and NG (bottom) made on pure materials. Note that only peaks D, G and 2D are of interest for the current study, other peaks e.g. in Figure 2.5.2, are not of interest.

Working concentration graphite-solvent

As suggested from literature works on graphite exfoliation processes, the ratio powder/solvent is one among the most important decisions. So, in order to decide which would be the best ratio, different amounts of graphite powder have been tested with the same volume of each of the three solvents. In particular, five different value of graphite: 5-10-25-50-75 mg with 5 mL of solvent.

For this test the time of sonication has been chosen as 3h in a sonication bath at 30W of power and 37 kHz.

Then, the solutions have been centrifuged at 500 rpm for 90 min, followed by a separation of the upper dispersion by filtration on PVDF 0.1 µm. The filters have been dried by solvent residuals on vacuum oven at 60 °C for 2 hours and weighed so to have the amount of graphitic material suspended. These values plotted versus the experimental absorbance value divided-cell length ratio are shown in Figure 2.5.4.

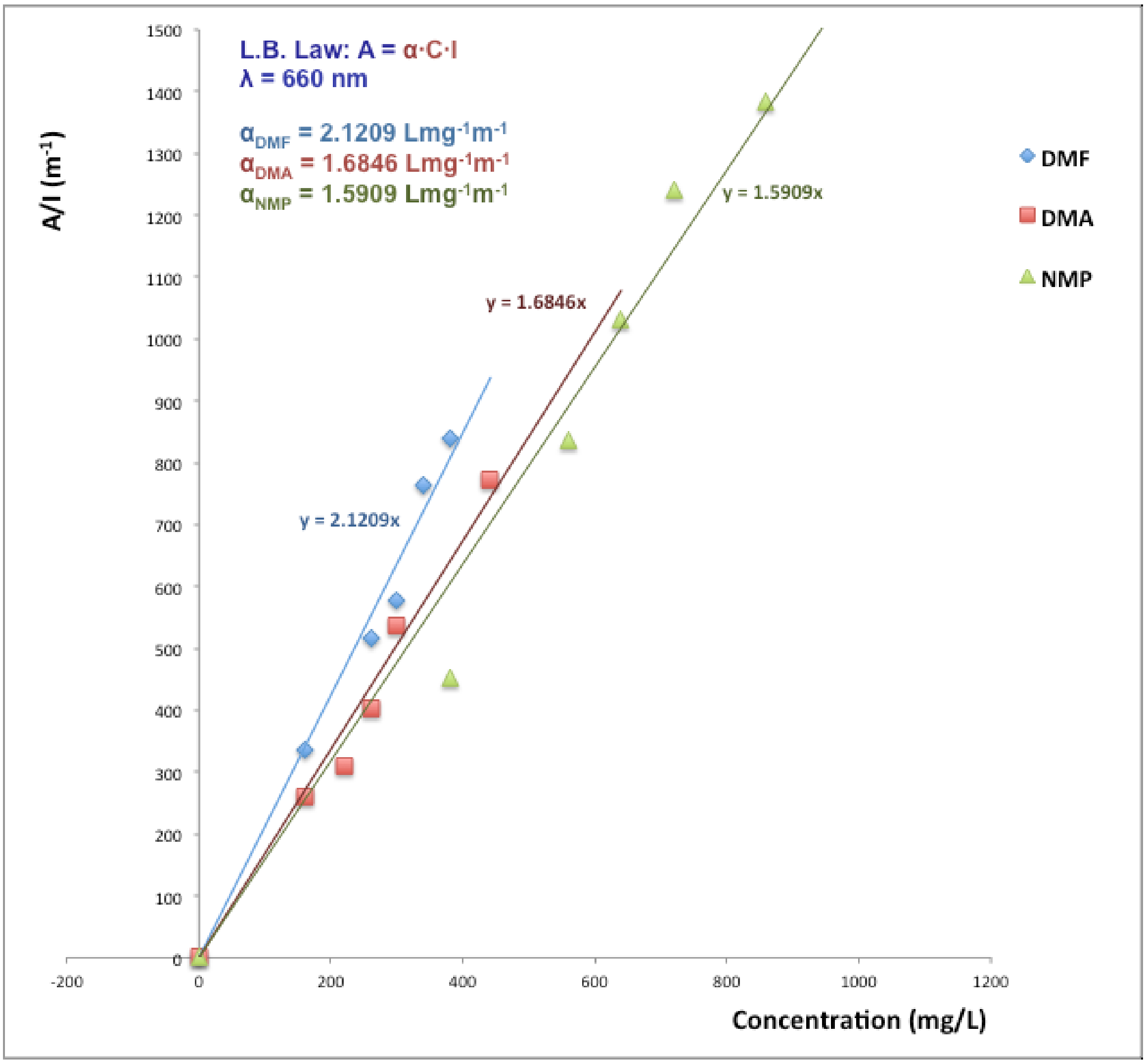


Figure 2.5.4 Optical Absorbance divided by cell length as function of the concentration for suspended graphitic material in three different tested solvents.

Sonication time assessment

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

As it mentioned in literature works (Khan et al. 2011, Choi et al. 2011, Hernandez et al. 2008 and Bourlinos et al. 2009), the sonication times ranged from 30 min to many hours. The common thing is the bath sonication power should be the lowest possible but there is no reference value. This wide range of sonication time and lack in mention of power is a great problem in reproducibility. The sonication process is sensitive to many factors, as example:

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

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

In this test, we have chosen from 0.5 up to10 hours (0.5-1-2-3-5-7-10 h) with a Sonication Bath at 30W of power and 37 kHz frequency.

The Graphite/Solvent (DMF, DMA and NMP) ratio has been set to 10mg/5mL.

Exactly as in the previous test, the solutions have been centrifuged at 500 rpm for 90 min, followed by a separation of the upper dispersion by filtration on PVDF 0.1 µm. The filters have been dried by solvent residuals on vacuum oven at 60 °C for 2 hours and weighed.

By subtraction with respect to starting amounts, the exfoliation yields have been calculated. Both the yields and the suspended graphitic-materials (exfoliated) have been plotted versus the respective time of sonication as shown in respectively in Figures 2.5.5 and 2.5.6.

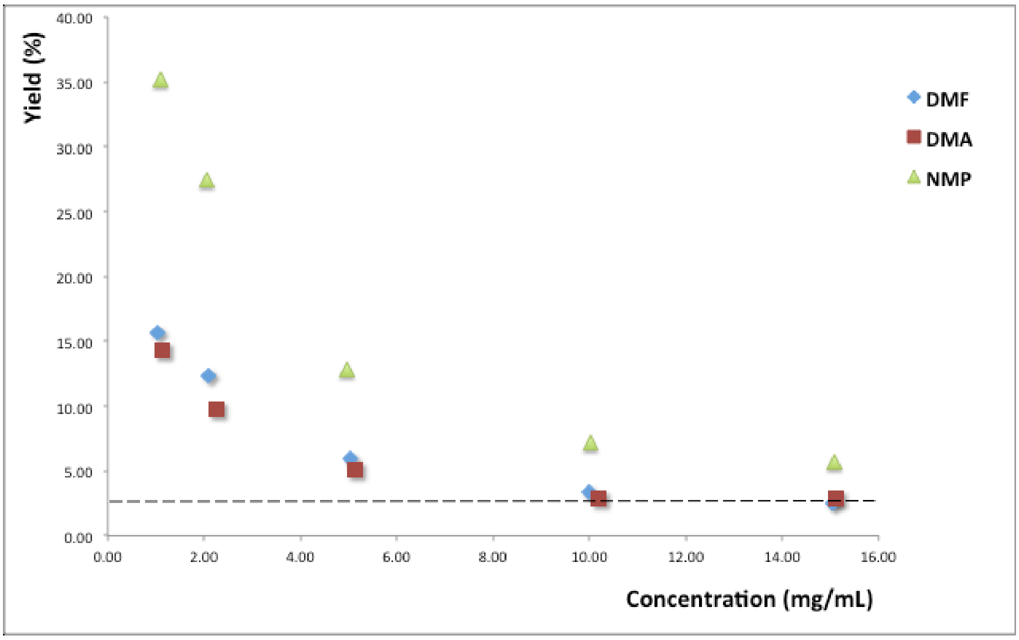


Figure 2.5.5 Yields in weight of the exfoliation process as function of the starting concentration graphite/solvent.

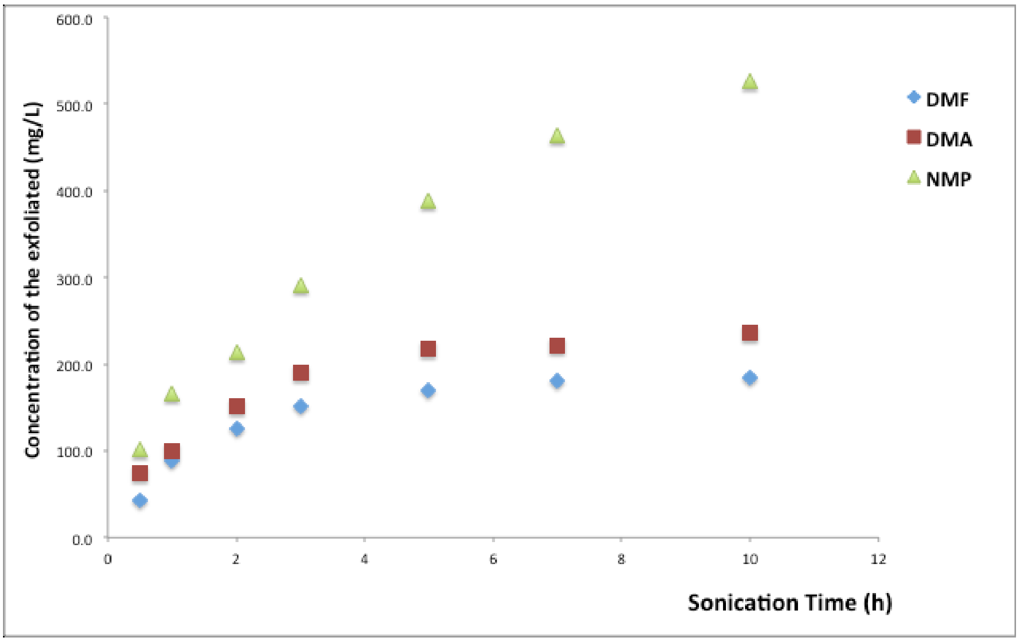


Figure 2.5.6 Concentration of the exfoliated graphite as function of the sonication time.

Results and Discussion

From the comparison of the Raman spectra of the HOPG vs. Nuclear Graphite, it is well clear that the NG matches perfectly the HOPG ones. This is well supported by the presence of the three typical bands related to the graphite to graphene exfoliation processes. These three bands, named D, G and 2D, have the same shapes and the same Raman shift in both cases and are exactly the same as reported in the literature (Jorio et al. 2013). These results confirm that the process chosen and the parameters lead to the exfoliation of both HOPG and Nuclear Graphite. This could be applied also in terms of solvent choice. In fact, all the three solvents show the same results for the HOPG and for NG.

The absorption values plotted towards the concentration on the suspended graphitic materials as in Figure 2.5.4 show a perfect behaviour with respect to Beer-Lambert law. These means that, in this range of concentrations, as well as graphite/solvent ratio, the graphite can be dispersed in all these three solvents and the exfoliation process is reproducible. The average absorption coefficient obtained for the three solvents can be used for the quantitative determinations of the next experiments and the solutions used as Standards.

Concerning to sonication time experiments, the yields of exfoliation seem to decrease when increasing the time. This could be because the graphite/solvent ratio becomes too low so when the amount of the exfoliated material increases in the solution, the solvent is unable and enough to continue efficiently the process. Increasing this ratio, that is increasing the volume of the solvent, could improve the yields for longer times.

In the same time, the amount of the exfoliated material increases with respect to the sonication time. This, compared to the decrease in yields, suggests a kind of “multi-step” procedure: it could be chosen an average time of 3 hours and after separated the suspended from the un-exfoliated after the centrifugation, this last one could be re-processed for another 3 hours. This could be repeated until an acceptable yield is reached.

Anyway, the yields obtained range from 2 to 16 wt% with respect to the yield reported in literature (1 to 12 wt%).

Future activities

At this point, after having set up the starting parameters for the process, experiments on irradiated graphite are needed. The tests will be performed on irradiated graphite samples just to evaluate the degree of removal for the ^{14}C.

Define the degree of decontamination of the whole process to test the effectiveness and efficiency of this newest way.

Depending on these important results, the overall procedure parameters could be partially modified or totally revised in order to tune the whole process to improve the decontamination coefficients.

Note that this technique is not currently able to distinguish between labile ^{14}C and ^{14}C incorporated into the graphite structure; options for progress here need to be evaluated.

2.6 Forshungzentrum Juelich GmbH (FZJ) summary

Within the last reporting period the review of CARBOWASTE and CarboDisp projects was performed in order to establish the current understanding of inventory and release of ^{14}C from irradiated nuclear graphite. This activity is intended to draw together relevant existing information on the ^{14}C inventory in irradiated graphite and its chemical state in graphite and leachate, enabling development of treatment, immobilization and packaging methodologies for a long-term safe disposal.

The activity of FZJ was focused in particular on the development of harmonized leaching procedure. For that the information on leaching approach available in the literature was extensively reviewed and critically discussed with other partners from CIEMAT and NDA. The crucial parameters that need to be controlled in leaching tests were identified and summarized in D 5.4. It is anticipated that developed leaching approach will be used by other project beneficiaries to enable inter-laboratory comparison of the results and provide systematic progress in ^{14}C leaching behaviour.

Sampling campaign of RFR irradiated graphite for upcoming leaching experiments is accomplished. Systematic pre-leaching characterization of graphite samples is in progress.

It has to be noted that the Work Package 5 work at Juelich is part of ongoing PhD theses, whose submission is scheduled in December 2015. Authorization by the PhD candidates is necessary prior to publication or citing of Juelich results.

Progress in Task 5.1

This task is aiming at actual data on irradiated graphite in Germany, i.e. amount, inventory etc. Over 850 metric tons are stemming from two High-Temperature Reactors (HTRs), which are the AVR in Juelich and the THTR in Hamm-Uentrop (see Table 2.6.1). In addition there are more than 25 MTR and research reactors containing graphite for the moderator, reflectors and/or thermal columns. The mass of irradiated graphite of those reactors was estimated to be over 70 metric tons.

Table 2.6.1: Estimation of total amount of irradiated nuclear graphite in Germany.

Reactor	**Site**	**In operation**	**Total mass, [t]**
Hochtemperaturreaktoren			
AVR	Jülich	1967-1988	238.1
THTR	Hamm-Uentrop	1983-1989	618.4
Forschungsreaktoren			
Argonautreactors (Ringcore)			
SAR	Garching	1959-1968	NS[*]
STARK	Karlsruhe	1963-1976	NS
Rossendorfer Ringzonenreaktor (RRR)	Rossendorf	1962	5.34
TRIGA			
FRF-1 / FRF-2	Frankfurt	1958-1968	7.7
FRH	Hannover	1973-1997	1.0
TRIGA HD I/II	Heidelberg	1966-1999	1.6
FRMZ	Mainz	ab 1965	4.4
FRN	Oberschleißheim	1972-1982	27.7
Weitere Schwimmbadreaktoren			
FMRB	Braunschweig	1967-1995	1.5
FRG-1 / FRG-2	Geesthacht	1958-2010 / 1963-1993	11.1
FRJ-1	Jülich	1962-1985	12.9
RFR	Rossendorf	1957-1991	3.9
Schwerwasserreaktoren			
FRJ-2	Jülich	1962-2006	30
FR-2	Karlsruhe	1961-1981	NS
FRM-1 / FRM-2	München		NS
KKN	Niederaichbach	1973-1974	NS
Total:			>963.6

[*] NS: not specified

The option of irradiated graphite disposal in the German KONRAD repository was assessed within the German CarboDISP project. The outcomes of the project represented the important information about ^{14}C in different graphite types, like inventory, speciation in the graphite, leaching behaviour and release behaviour in case of accidents (fire of the transporting vehicle). Investigated samples comprised the irradiated graphite from Juelich research reactors MERLIN (Forschungsreaktor Jülich-1), DIDO (Forschungsreaktor Jülich-2), AVR (Arbeitsgemeinschaft Versuchsreaktor) as well as from RFR (research reactor Rossendorf, German Rossendorfer Forschungsreaktor). According to the disposal requirements of KONRAD, the total ^{14}C activity allowed to be disposed is $4{\cdot}10^{14}$ Bq. Another criterion is maximal allowed ^{14}C-activity in a container. This depends on release rates of ^{14}C from irradiated graphite: the lower release rate the higher amount of irradiated graphite per container is allowed (for more details see WP5 Annual Report – Year 1, Toulhoat et al., 2014). The calculations performed within the project were based on release rates experimentally measured on different conditions relevant to the final disposal (Kuhne et al., 2015). The results of experiments on dry conditions and ambient temperature demonstrated the ^{14}C-release of below 1 %. This case enables a disposal of the highest estimated amount of graphitic waste. In case of storage in humid conditions increased ^{14}C-release was detected, i.e. significantly higher 1%-limit. Additionally, the release of ^{14}C-bearing organic substances and ^{14}CO was observed, which are considered to have lower retention in the waste-packages (e.g. cemented waste) and respectively are more mobile than $^{14}CO_2$. This may allow bioincorporation of ^{14}C during operation time of repository (estimated for 40 years) unless immobilized or preliminary separated. In this regard a special attention will be paid to linking the storage and leaching conditions to the speciation of ^{14}C in released fraction, both in gas and aqueous.

ASSE test repository was used for disposal of 13 metric tons of irradiated graphite (42 drums). It was assumed that an enhanced release of ^{3}H and ^{14}C from this material may occur. Details on this issue have been discussed in the ‘Entsorgungskommission (ESK)’ and can be found on the website of the ‘Bundesamt fuer Strahlenschutz (BfS)’. Investigation of materials exposed to the real disposal conditions is of high interest for CAST. However, up-to-now it was not possible to get samples or exact information on ^{14}C speciation and release.

Progress in Task 5.2

For the Juelich work in CAST, the material of block 4 of RFR graphite will be used for leaching experiments. Previously reported ^{14}C activity (ca. 10 kBq/g) was considered to be high enough to provide an acquisition of reliable data on ^{14}C release. The tritium content is quite low (0.9 kBq/g) as compared to other graphite types. Partial release of gaseous tritium was suspected due to the damage of the thermal column during operation at about 300°C and a significant corrosion of this block in the area facing the highest neutron flux.

Consequently, the block 4 was cut in 10 plates of the same thickness, and plates 5 and 6 were selected for sampling the graphite for leaching experiments. As shown in Figure 2.6.1, specific activities of ^{14}C and ^{3}H in the plates determined by total incineration method reach $1.15\cdot10^4$ Bq/g and $1.7\cdot10^3$ Bq/g respectively.

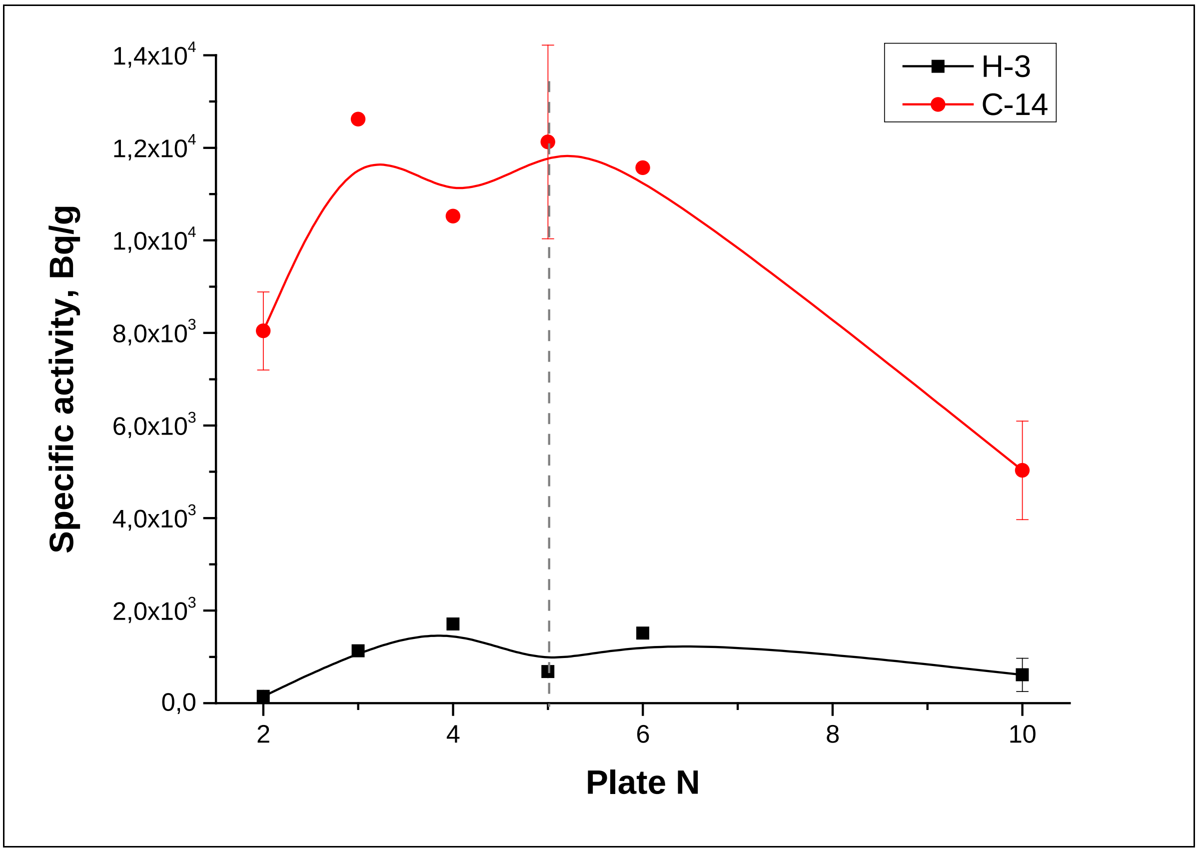


Figure 2.6.1 Specific activity of individual plates of block 4 of RFR graphite.

In order to provide an inter-laboratory comparison, RFR graphite was sampled in a well-defined cylindrical form with (∅20x20 mm), as it was discussed in EC CAST Deliverable D5.4 (Petrova et al., 2015). Sampling map and information on mass for each sample are provided in Table 2.6.2 and Figure 2.6.2.

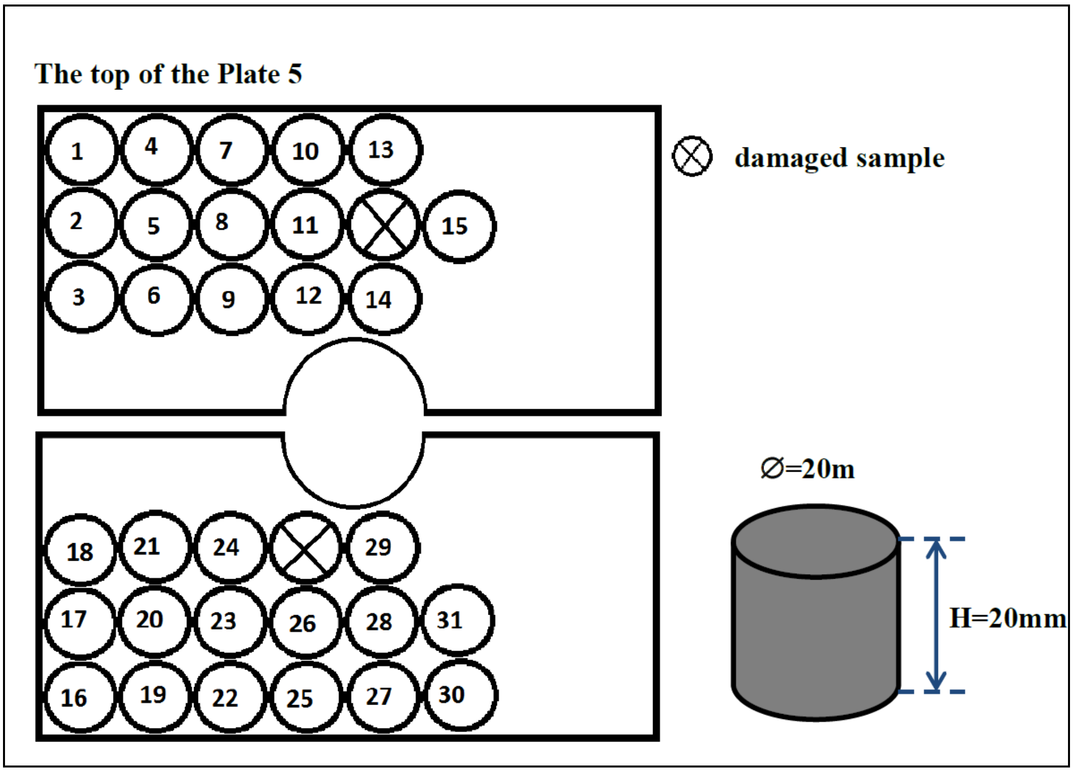


Figure 2.6.2 Scheme of RFR graphite sampling positions in Plate 5 of block 4 and dimensions of a graphite sample to be used in leaching tests.

Table 2.6.2: Masses of RFR graphite samples to be used in the leaching tests.

Sample name	Mass [g]	Sample name	Mass [g]
Pl-5_Nr-01	23.481	Pl-5_Nr-17	23.092
Pl-5_Nr-02	23.288	Pl-5_Nr-18	23.282
Pl-5_Nr-03	23.569	Pl-5_Nr-19	22.735
Pl-5_Nr-04	23.760	Pl-5_Nr-20	22.750
Pl-5_Nr-05	23.630	Pl-5_Nr-21	22.933
Pl-5_Nr-06	23.409	Pl-5_Nr-22	22.670
Pl-5_Nr-07	23.629	Pl-5_Nr-23	22.698
Pl-5_Nr-08	23.249	Pl-5_Nr-24	22.699
Pl-5_Nr-09	23.254	Pl-5_Nr-25	22.548
Pl-5_Nr-10	23.459	Pl-5_Nr-26	22.259
Pl-5_Nr-11	23.257	Pl-5_Nr-27	22.149
Pl-5_Nr-12	23.170	Pl-5_Nr-28	21.949
Pl-5_Nr-13	23.164	Pl-5_Nr-29	22.188
Pl-5_Nr-14	23.076	Pl-5_Nr-30	21.990
Pl-5_Nr-15	22.451	Pl-5_Nr-31	21.926
Pl-5_Nr-16	22.999		

Earlier characterization of specific surface area by BET method of RFR graphite (plate 10) resulted in ≈1 m^2/g. The characterization of specific surface area is intended for all newly sampled graphite from plate 5 in order to provide better understanding of derived leaching rates.

Hot-spots of β and γ activation products (AP) have been observed earlier in the RFR graphite. An inventory as well as distribution of AP is currently under evaluation by means of gamma-spectrometry (Figure 2.6.3 and Table 2.6.3) and SEM/EDX techniques.

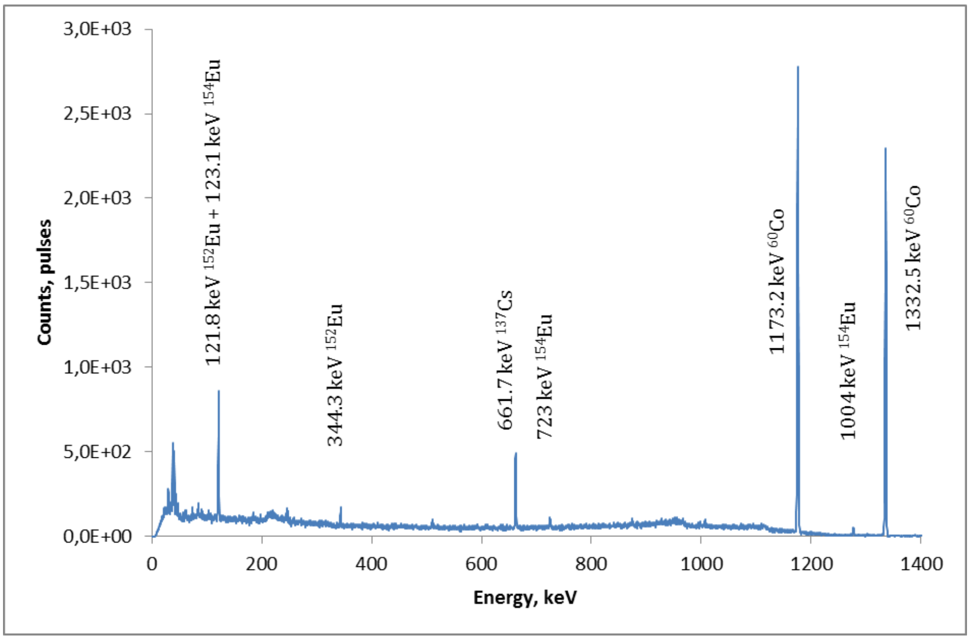


Figure 2.6.3 A typical gamma-spectrum of RFR thermal column graphite.

Table 2.6.3. Isotopic composition and activity of gamma-emitting isotopes in irradiated graphite of RFR (Block 4, Plate 5).

Sample No.	Activity, Bq/g				
	^{152}Eu	^{154}Eu	^{137}Cs	^{60}Co	^{133}Ba
1	0.54	1.44	1.92	27.1	0.34
10	0.21	1.90	2.40	27.6	0.29
14	0.62	2.28	2.19	20.2	0.62
17	2.64	3.34	1.07	50.2	0.23

Progress in Task 5.3

A compilation of information on previous leach tests has been accomplished with contribution of other partners from CIEMAT and NDA in order to establish recommendations on harmonized leaching parameters (see D5.4, Petrova et al., 2015). With that the approach and conditions for up-coming leaching tests were defined (summarized in Table 2.6.4).

Table 2.6.4. Recommended conditions for leaching procedure

Parameter	Recommendation
Vessel	Pyrex glass; Cross-linked PTFE, PEEK.
Specimen geometry	Cylinder block, ∅20x20 mm; Powder $V_{leachate}/S_{solid}$ 0.1 m
T, °C	25±5 – recommended; other – optional, according to specific national regulations.
Leaching solution composition	0.1 M $NaClO_4$ (pH 7), 0.1 M NaOH (pH 13), synthetic ground/pore water (granite-bentonitic water)
Initial gas phase composition	N_2/Ar (anaerobic); air (aerobic)
Sampling, Δt	1, 3, 7, 10, 14 days 2nd week – twice a week 3rd-6th weeks – once a week Thereafter – monthly
Test duration	1 – 1.5 year
Regime	semi-dynamic; stirring; sample is completely immersed
Analyses	**Pre-leaching**: *Solid phase:* ^{14}C inventory (total incineration), surface area (BET), morphology (SEM), AP inventory (γ-spectrometry), particle size distribution; *Leachate:* Background ^{14}C inventory (LSC), pH, conductivity. **Graphite separation:** filtration or centrifugation. **Post-leaching**: *Solid phase:* remained ^{14}C inventory (total incineration), surface area (BET), morphology (SEM), particle size distribution; AP inventory (γ-spectrometry); *Leachate:* ^{14}C inventory (LSC,), ^{14}C speciation

	(HPLC-MS), AP inventory (γ-spectrometry), pH, conductivity; *Gas phase:* ^{14}C inventory (LSC), ^{14}C speciation (GC-MS).
Evaluation of results	$F_n = \frac{\sum a_n}{a_0}$ $R_n = \frac{a_n \cdot V}{a_o \cdot S \cdot t_n} = K \cdot \frac{a_n}{t_n}$ F_n and R_n is reported for every ^{14}C-species separately.

After discussion with project partners within Work Package 5, the gas-tight reactor vessel from Berghof GmbH was concluded to be more suitable for leaching of irradiated graphite (see Figure 2.6.4). The inner part of the reactor is made of radiation stable cross-linked teflon or PEEK, preventing material sorption on the walls. The outer vessel is made of stainless steel. Construction of the reactor allows pressure measurement, gas and liquid sampling [see Berghof website].

Figure 2.6.4. An example of experimental reactor/vessel (Berghof GmbH) for leaching test developed for gas and liquid sampling[2]

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

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

Progress in Task 5.1

CIEMAT has been involved in the Deliverable 5.5 “Review of current understanding of inventory and release of ^{14}C from i-graphite”. In the deliverable has been described several investigations performed to know the nuclide inventory of irradiated graphite, to characterise its physic-chemical behaviour and to determine its structural properties.

CIEMAT has described a summary of the investigations about radiological and physic-chemical characterization and treatment methods in i-graphite from three types of reactors:

- MTR reactors: Samples from JEN-1 (Spain) and samples from Triga (Romania)
- UNGG reactor: Samples from Vandellos-1 (Spain) and from SLA-2 (France)
- Magnox reactor: Samples supplied from Magnox Limited

CIEMAT has also described the way to determine the content and the location of hydrogen in graphite: thermal decomposition and solvent extraction.

Progress in Task 5.3

CIEMAT has been involved in the Deliverable 5.4 “Definition of the scientific scope of leaching experiments and definition of harmonized leaching parameters”. In the deliverable has been summarized experimental conditions used for leaching studies according with the bibliography and based on this a number of parameters, which are important to control in the leaching study, has been recommended.

Besides, in this task has been carried out various tests related to the preparation of the samples IGM (Impermeable Graphite Matrix), the design of both the container and the leaching experiments with the graphite from the Vandellós I NPP, and the set-up of different equipment acquired in the last quarter of 2014: Gas Chromatograph coupled to a Mass Spectrometer (GCMS) and an Ion Chromatography system (IC). This equipment will allow making the determination of the speciation of compounds of carbon released during the leaching process.

a) IGM SAMPLE PREPARATION

The laboratory was prepared to install a pneumatic press during the last quarter of 2014. This press will allow preparing the samples of graphite as it is shown in Figure 2.7.1.

Figure 2.7.1. Sample of graphite with IGM

Throughout the first half of the year 2015 the procedure to prepare the sample has been established. Besides it has been carried out a study of porosity and density, with two types of inorganic binders and with virgin nuclear graphite, in order to establish the conditions of operation of the thermo press machine.

b) LEACHING PROCESS AND SPECIATION

The leaching experiments which permit to analyse gas and liquid phase are being designed. The procedure we would like to follow for developing the leaching tests is based on the standard procedure ISO 6961.

In this case the leaching rate (R_n) will be expressed in cm/day (units given by ENRESA in the acceptance criteria of the surface disposal of radioactive waste located in “El Cabril”)

$$R_n = \frac{a_n}{a_o} \times \frac{V}{S} \times \frac{1}{t_n}$$

where:

a_o: Initial amount of the component in the assay specimen, Bq or mg

a_n: Amount of the component that has passed from the assay specimen to the leachant in the step “n”, Bq or mg

t_n: Duration of the step “n” of the assay, days

V: Specimen volume, cm^3

S: Apparent or geometrical specimen surface, cm^2

The tests will be performed in High Pressure Reactors of Stainless Steel with Teflon (PTFE) Insert at room temperature (Figure 2.7.2).

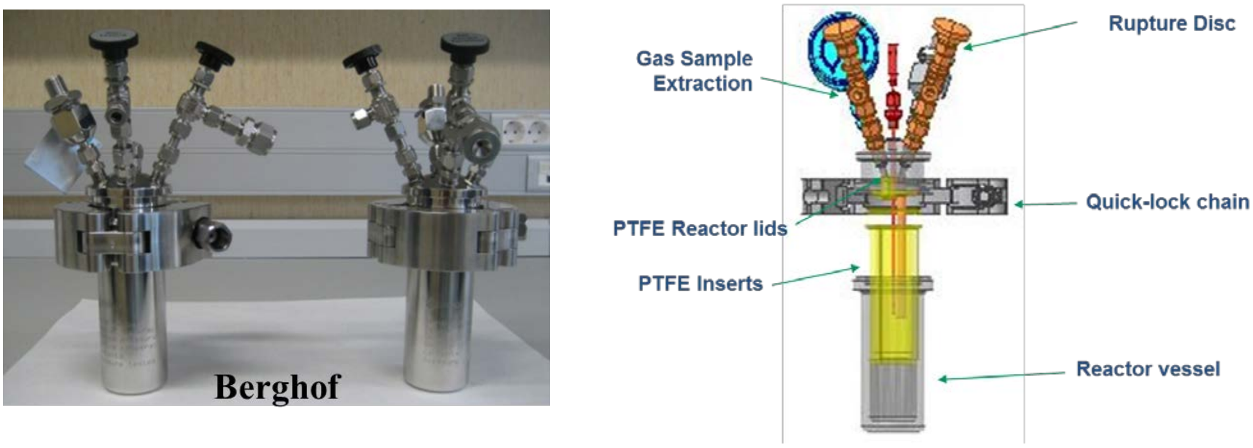

Figure 2.7.2. Leaching graphite reactors

For leachants, the following will be used:

Pure water and

Granite-Bentonitic water (synthetic) at pH = 7

Both the gas and the leachate will be totally renewed after: 14, 28, 56, 90, 180 and 360 days from the start of the test. These periods of time do not have to be inflexible, especially the periods of greater duration, but the calculations have to refer to real time.

First of all the gas will be collected through the gas sample extraction valve (Figure 2.7.2) and analysed by GC/MS.

Once completed the previous step the container will be opened and in the leachate the organic compounds will be analysed by GC/MS and IC, being ^{14}C analysed by Liquid Scintillation Counting using a Quantulus equipment

Both GC/MS and IC are installed in our laboratories from January 2015 and at present it is setting up the conditions of the equipment and carrying out the staff training (Figure 2.7.3).

Figure 2.7.3. Gas Chromatograph coupled to a Mass Spectrometer (left) and Ion Chromatography system (right)

Due to the steel containers for use in the leaching process not arriving at our facilities until the end of June 2015, it has not been possible start the tests yet. It is expected to begin such assays in October 2015.

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

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

- Task 5.1 Review of CARBOWASTE and other relevant R&D activities to establish the current understanding of inventory and release of ^{14}C from i-graphite
- Task 5.3 Measurement of release of ^{14}C inventory from i-graphite
- Task 5.5 Data interpretation and synthesis – final report

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

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

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

Irradiated graphite inventory at IFIN-HH

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

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

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

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

A horizontal cross section of the reactor core is presented in Figure 2.8.1.

Currently, the VVR-S Reactor is undergoing decommissioning. [Decommissioning Plan, 2008]

The i-graphite grades, which are investigated in IFIN-HH have been taken from thermal column of the VVR-S Research Reactors. The mobile thermal column (Figure 2.8.2) is made of 5 graphite discs placed on a mobile truck. Graphite bar-made discs are installed into a 20 mm wall thickness aluminium cylinder. Initially, the thermal column is provided with a cooling system that axially penetrated the graphite plate connected to the water-cooling system. As from the exploitation experience, it was concluded that this system is not necessary; it was given up. The horizontal tubes of the cooling system were filled with nuclear grade graphite rods of the same type as the discs of the thermal column (Figure 2.8.3).

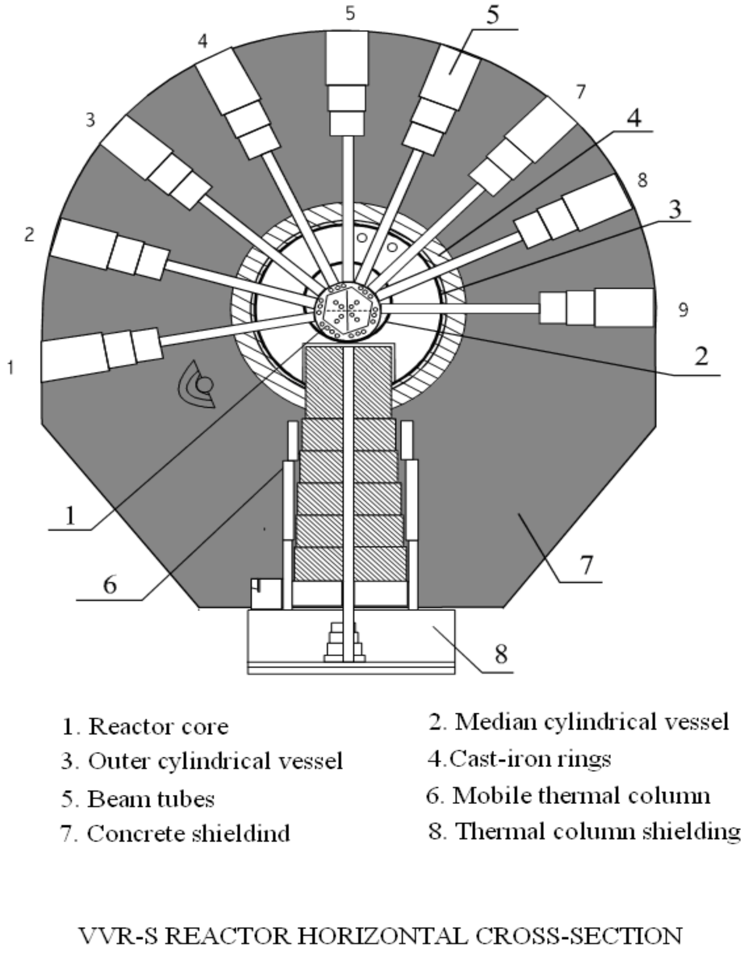

Figure 2.8.1 Horizontal cross section of the reactor core

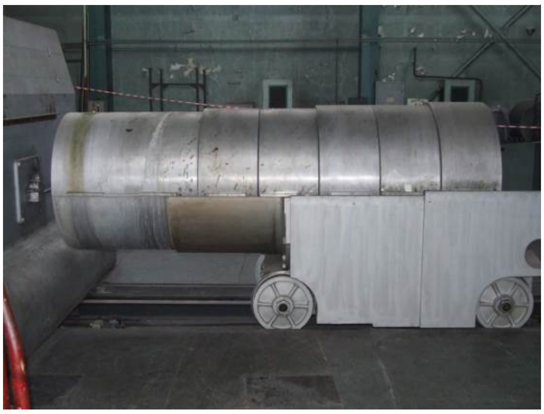

Figure 2.8.2 Thermal column

Figure 2.8.3 Thermal column first disc

Irradiated graphite samples preliminary characterisation

Small samples have been provided from the graphite rods of the first graphite disc located near reactor vessel. Two pieces of i-graphite have been cut from one of the graphite rods to be more easily handled in the radiochemical laboratory. One piece was cut from rod's edge near the reactor vessel (**Sample no 1**) and the other piece from the opposite part of the rod (**Sample no 2**). (Figure 2.8.4)

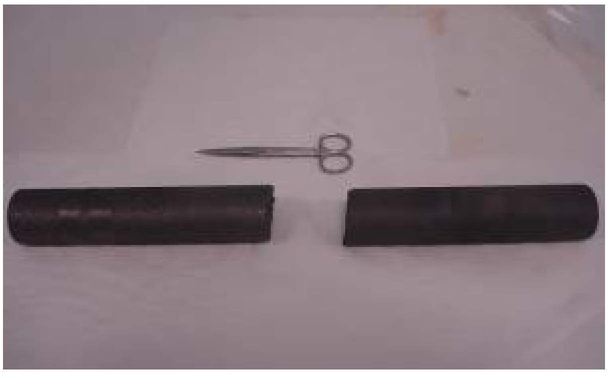

Figure 2.8.4 Irradiated graphite samples

The characteristics of the i-graphite samples no 1 and no 2 (mass, dimensions and dose rate) are presented in Table 2.8.1.

Table 2.8.1 Graphite samples

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

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

The final radionuclide specific activity inventory of the i-graphite from the thermal column of the VVR-S Reactor is presented in Table 2.8.2 (main radionuclides).

Table 2.8.2: Radionuclide specific activity in VVR-S Reactor thermal column

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

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

Our results have demonstrated that the ^{14}C activity decreases along the thermal column due to the thermal neutron flux attenuation) from 3.4x10^{4}Bq/g next to the reactor core to 2.6x10^{2}Bq/g for the first graphite disc.

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

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

Progress in Task 5.1-second year

Additional graphite samples were collected in August 2015 from the second and the fifth disc of the thermal column of VVR-S Reactor. The nearest disc to the reactor vessel is number 6 (see Figure 2.8.5). Two pieces of i-graphite have been cut from each graphite rod. One piece was cut from rod's edge near to the reactor vessel (**Samples 6-1**, **5-1, 2-1**) and the other piece from the opposite part of the rod (including **Sample no 6-2, 5-2**). An additional piece has been cut from the middle of the graphite rod located in the disc no 6.

Table 2.10.3 Graphite samples

Sample (disc no)	Mass (g)	Length (cm)	Rate dose (µSv/h)
6-1	460	21.0	140
6-2	480	21.2	18
5-2	301	25	Background
5-1	241	12	Background
2-1	41	9	Background

The estimation of the radionuclide inventory of the i-graphite has been determined by gamma spectrometry using an Ortec Gamma HPGe detector type GMX. The radionuclide specific activity inventory is presented in **Table 2.8.4** (main radionuclides).

Table 2.8.4 Radionuclide specific activity in VVR-S Reactor thermal column

Graphite sample	^{14}C [Bq/g]	^{60}Co [Bq/g]	^{154}Eu [Bq/g]
6-1	**3.4 E+4**	3.4 E+3	1.3 E+3
6-2	**2.6 E+3**	2.6 E+2	3.3 E+1
5-2	20	2.0	1.6
5-1	4	0.4	0.37
2-1		MDA	MDA

MDA= Minimum Detectable Activity

The specific and the total activity of ^{14}C in the i-graphite of thermal column components have been calculated by means of the scaling factors method using ^{60}Co as the reference radionuclide and the thermal neutron flux distribution in space, according to the data from the literature.

The total weight of each graphite disc was determined (including the aluminium cladding).

Table 2.10.5 Graphite discs weights

Disk	Diameter (cm)	Length (cm)	Weight (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

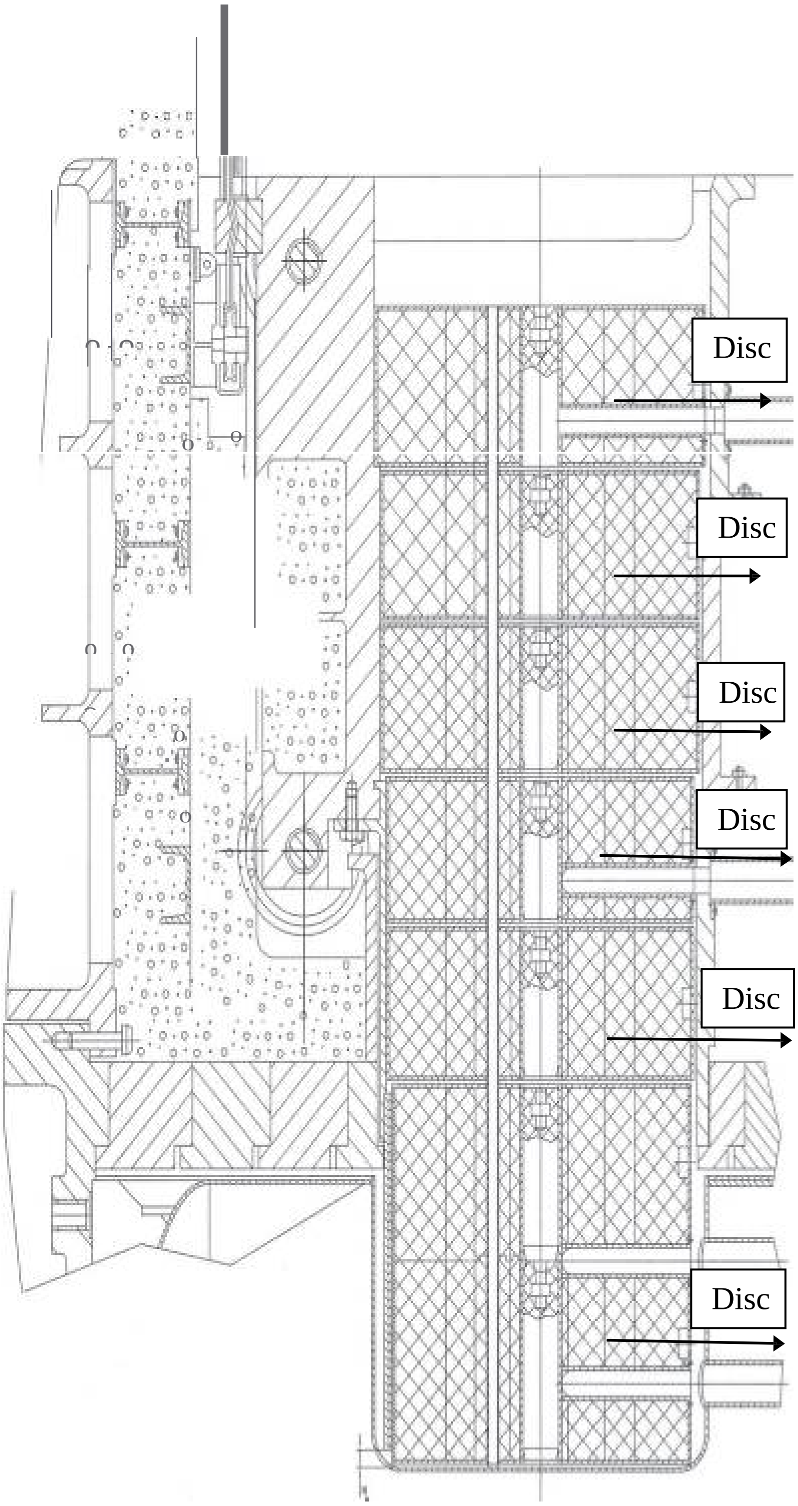

Figure 2.8.5 VVR-S graphite thermal column cross section

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

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

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

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

Progress in Task 5.2 second year

AMS facility based on the 9 MV and 1 MV accelerators of IFIN-HH for measurements of ^{14}C concentration depth profiling in nuclear materials

Introduction

Accelerator Mass Spectrometry (AMS) is a very unique and special method of selecting and counting atoms of a certain kind individually. It has the highest analysis sensitivity known today: 10^{-16} (ratio: isotope/element). By use of reference samples it provides quantitative results expressed in suitable units (Bq/g, atoms/cm^3, atoms/l etc.), which is a certain advantage compared to other employed methods.

The history of invention of this method goes back at the end of the 60's when the new atomic analyzing method was borne from the desire of separating a new light isotope, ^{3}He. The basic idea of which was to try to separate two isobars (^{3}H and ^{3}He) by taking advantage of the differences between charge states, if the ions will completely lose their electrons (1$^+$ and 2$^+$). (In precedent work (Alvarez and Conrog, 1939), it had been recognized that such a charge separation, but also the separation of ion masses in general, will be stronger if the ions have a higher energy that can be gained by using a particle accelerator. In this way, the Accelerator Mass Spectrometry (AMS) had been invented, and L.W. Alvarez and R. Conrog were awarded a Nobel Prize for the discovery of tritium).

The long-lived radio nuclides are analysed by AMS, free of molecular interference, and with the detector background at isotopic ratio as low as 10^{-16}. This is the equivalent with the possibility to select and register one single type of atom from a million of billions of other types of atoms. Today, after about 50 years of development, the applications of AMS nanotechnology are leading researches in many areas of our science and of everyday life.

AMS General Description

AMS measures the rare isotopes concentration in a sample material if this is in solid state. The sample material has to be transformed into a confined ion beam, with good emittance, so that it can be transported on a long path through a particle accelerator and through many analyzers.

A typical AMS facility, as presented in Figure 2.8.6, consists of four major parts: the ion injector (containing the ion source), the tandem accelerator; the high energy analyzing systems and the particle discrimination and detection system.

The sample should be of solid substance with good thermal and electrical conductivity. In the ion source, an accelerated beam of positive ions of ^{133}Cs is accelerated and focused to bombard the sample. By this sputtering process all kinds of atoms will be scattered out. However, only the negative ions will be extracted from the ion source since they are only ions accepted at the entrance of the linear tandem accelerator. The ion source avoiding neutrals and positive ions and molecules represents a first filter for the analyzer (F1).

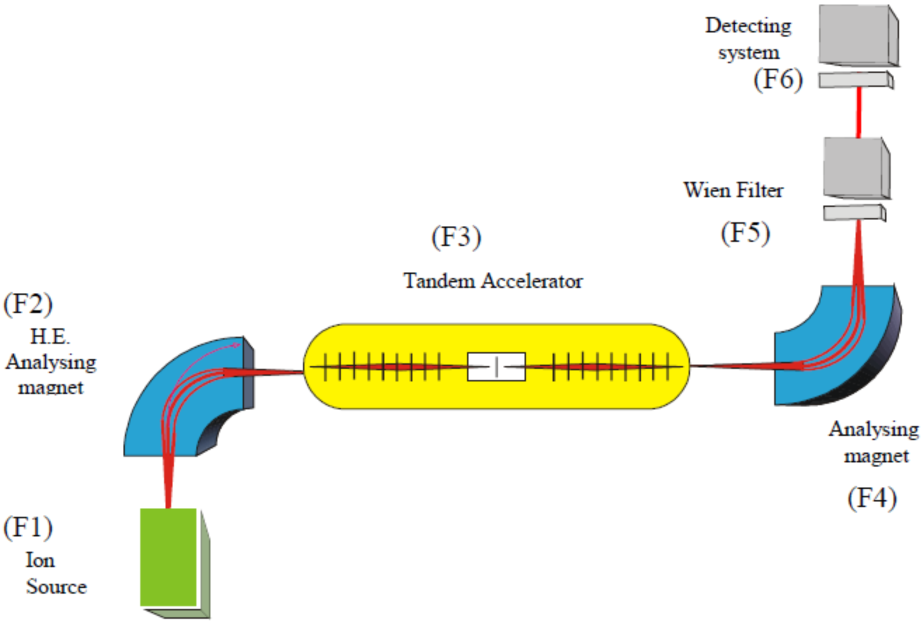

Figure 2.8.6: Schematic diagram of an AMS- facility

A second filter is the 90^0 double focusing analyzing magnet (F2). The negative ions with charge state 1^- will pass through this magnet and will be selected according to their mass value with a resolution of $\Delta m/m=1/250$. Then, before entering into the tandem accelerator, the selected ions species will be further accelerated up to about 70 keV. This energy increase is necessary to reduce the source emittance and in order to match the entrance acceptance of the tandem accelerator. At the central terminal position, the accelerated ions have to pass through the stripper foil (carbon foil or gaseous medium) and loose part of their exterior electrons by a stripping process in the foil. In this way, the negative ions will change to positive charge, with different values according to their energy (q = 2+,3+,4+,5+,6+,7+,..). Molecules passing through the terminal stripping foil are broken and removed from the ion beam. That is the reason why the stripper foil is considered to be a third filter (F3). The now positively charged ions will be repelled by the positive high voltage terminal. They will be accelerated in the second half of the tandem accelerator system, down to the ground potential at the exit of the tandem accelerator. A powerful magnetic analyzer is than performing a mass separation of high resolution. This is the fourth filter (F4). Since the magnetic field cannot separate particles with the same p/q ratio, a Wien velocity filter or an Electric Filter (Electrostatic Analyzer = ESA) can be used to separate ions according to their velocity and in this way remove the magnetic degeneracy. The filter is located in between the HE analyzing magnet and the detection system. This is the fifth filter (F5).

Finally, the AMS facility ends with the particle detection system. This is the last filter (F6) and performs mass and isobar separation. AMS is usually a relative analyzing method and requires standard samples. In this way it delivers the absolute values of the measured concentrations.

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 time 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. The radiocarbon concentrations vary on large scale values in the thermal column of a Nuclear Reactor. Also, the concentration of C-14 in depth of graphite may be different from the surface concentration. Therefore, in this project depending on the expected concentrations of carbon 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 AMS facility at 9 MV tandem accelerator is shown schematically in Figure 2.8.6 and photos of the injector and the accelerator are presented in Figure 2.8.7, below.

Figure 2.8.6 and Figure 2.8.7. Left: the Injector deck of the 9 MV tandem AMS facility in Bucharest: 1) Injector platform polarized at -100 kV; 2) second platform polarized at -30kV in respect to the first platform; 3) the ion source (40 NC-SNICS); 4) 90^0 analyzing magnet; 5) slits and retractable Faraday cup; 6) pre-acceleration NEC tubes. Right: the tandem 9 MV FN accelerator.

The second AMS facility, devoted to hyper-sensitive analyses is presented in Figure 2.8.8

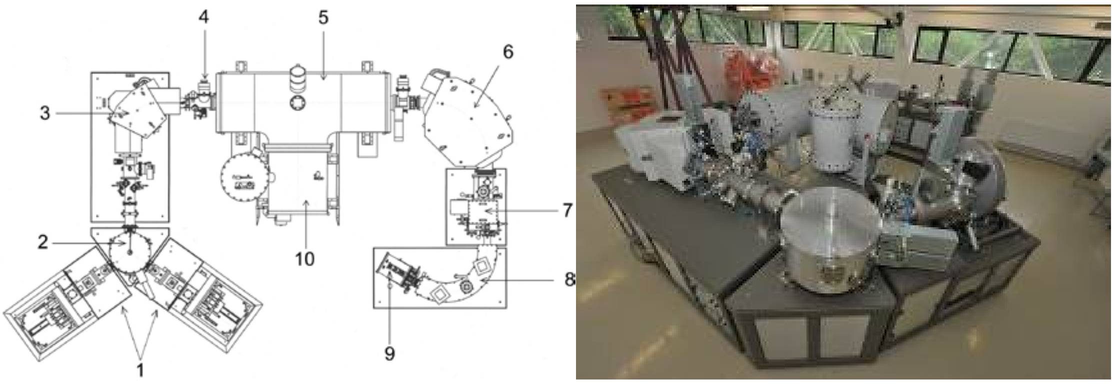

Figure.2.8.8. Left: the general layout of 1 MV HVEE AMS facility in Bucharest, Romania. (1) Two ion beam injectors equipped with SNICS ion sources of type SO110 – 50 sample carousel HVEE and focusing ion lenses; (2) electrostatic switching system; (3) injection Magnet with multi beam switcher (bouncer); (4) faraday cup and Q-Snout device; (5) 1 MV Tandetron accelerator, with gas stripper channel; (6) analyzing Magnet; (7) three offset Faraday cups; (8) electrostatic analyzer; (9) particle detector; (10) Cockcroft–Walton type HV power supply. Right: photograph of the facility.

Experimental Results

Determination of ^{14}C in nuclear samples with low concentration.

As presented in the previous section such measurements are performed with the 1 MV AMS facility in IFIN-HH. The machinery was purchased from the HVEE company and is completely computer controlled (Stan-Sion et al. (2014) and Stan-Sion et al. (2015)).

The samples of ^{14}C were cut from virgin nuclear grade graphite provided by the subcritical assembly Helen and by the Russian nuclear reactor of VVR-S type that was installed in Bucharest, in 1956. It was shut down in December 1997 and it is now under decommissioning. About 20 mg of material of virgin graphite transformed to powder was loaded and pressed into 8 sample holders of the ion source, together with reference and blank carbon samples. Each sample was counted 3 times for 5 min in a process divided into 10 blocks of 30 seconds counting. The total number of ^{14}C for 15 min. was approximately 25000 counts, thus the statistical error was 0.6%. However, due to the amorphous structure of the graphite, the ion current from the ion source was very stable and the relative standard deviation between the measured samples was 0.8%. For reference samples and background samples this error was 0.3% and 0.8%, respectively. All results were corrected for the background value and calibrated according to the reference samples. Figure 2.8.9 presents a bi-parametric spectrum of the reactor graphite sample measured during one of the runs performed.

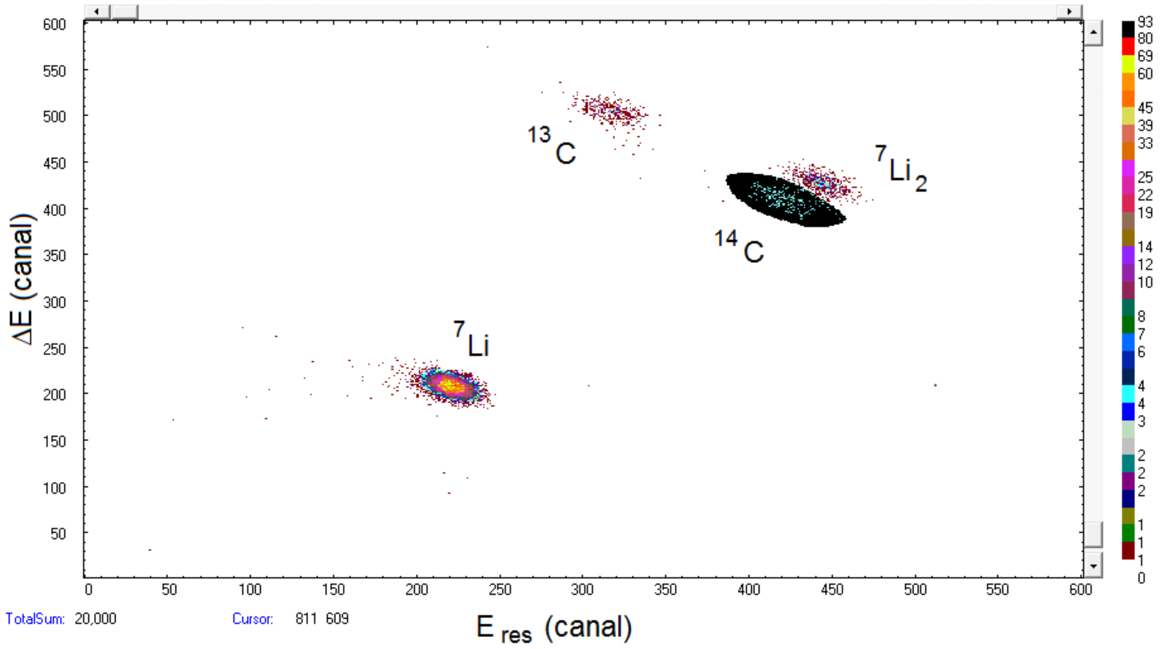

Figure 2.8.9: Two Bi-parametric spectrum showing the ^{14}C concentration.

The upper spectra represent the standard sample. The lower spectra is the measurement of the reactor sample and is containing $^{7}Li_2$ which, is a interfering molecule of mass 14 that partially broken in the two fragments when it enters into the gas field detector. However, the unbroken part of the molecule contributes with its energy release to the upper part of the ^{14}C counting region and affects the recorded data of the true concentration. It will be removed by choosing a gate (black spot), free of Li content.

Figure 2.8.10 and Table 2.8.6 present the results of measurements of ^{14}C in two samples from the subcritical assembly Helen and the VRS reactor. Samples were collected from the surface (surf.) and from the interior (int.) of the associated virgin (unirradiated) graphite rods.

Although all measured samples are cut from virgin graphite of non-exposed rods, the ^{14}C concentrations are 2 orders higher on the surface compared the bulk value (see Table 2.8.6).

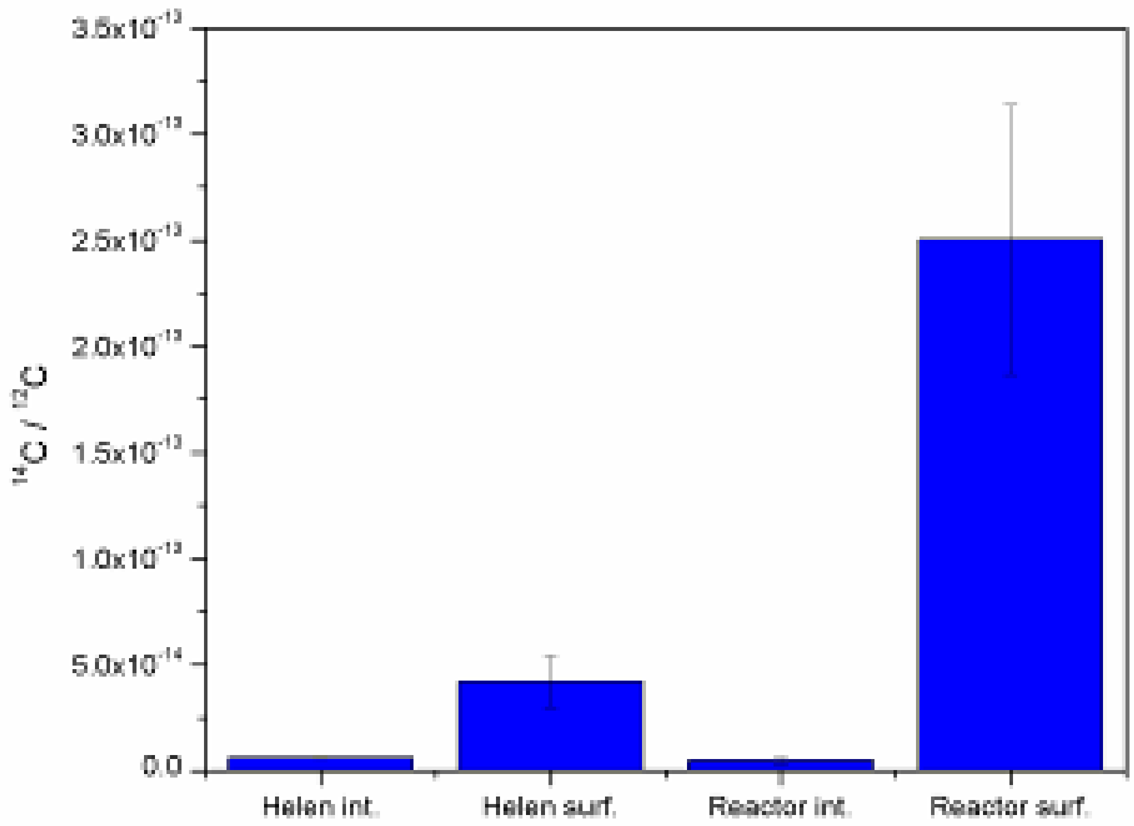

Figure 2.8.10: The ^{14}C concentrations measured from samples of the reactor Helen and the VRS reactor

Table 2.8.6: AMS measured ^{14}C measured values.

Sample	**^{14}C/^{12}C ratio**	
	Average value	**Standard deviation**
Helen int.	6.08E-15	5.01E-16
Helen surf.	4.22E-14	1.21E-14
Reactor int.	5.02E-15	1.5E-15
Reactor surf.	2.5E-13	6.35E-14

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

The samples of ^{14}C were cut from disc no 2 of the graphite column – 3 samples were collected from rod's edge near to the reactor vessel (**Samples 2-1**) and the other 3 samples from the opposite part of the rod (**Sample 2-2**).About 20 mg of material of the samples (from both face of the samples) transformed to powder was loaded and pressed into 8 sample holders of the ion source, together with reference and blank carbon samples (reference sample HOxII: 18.40 dpm/g (0.31Bq/g).

Each sample was counted 3 times for 5 minutes.

The results of the 3 set of measurements are presented in Figure 2.8.11.

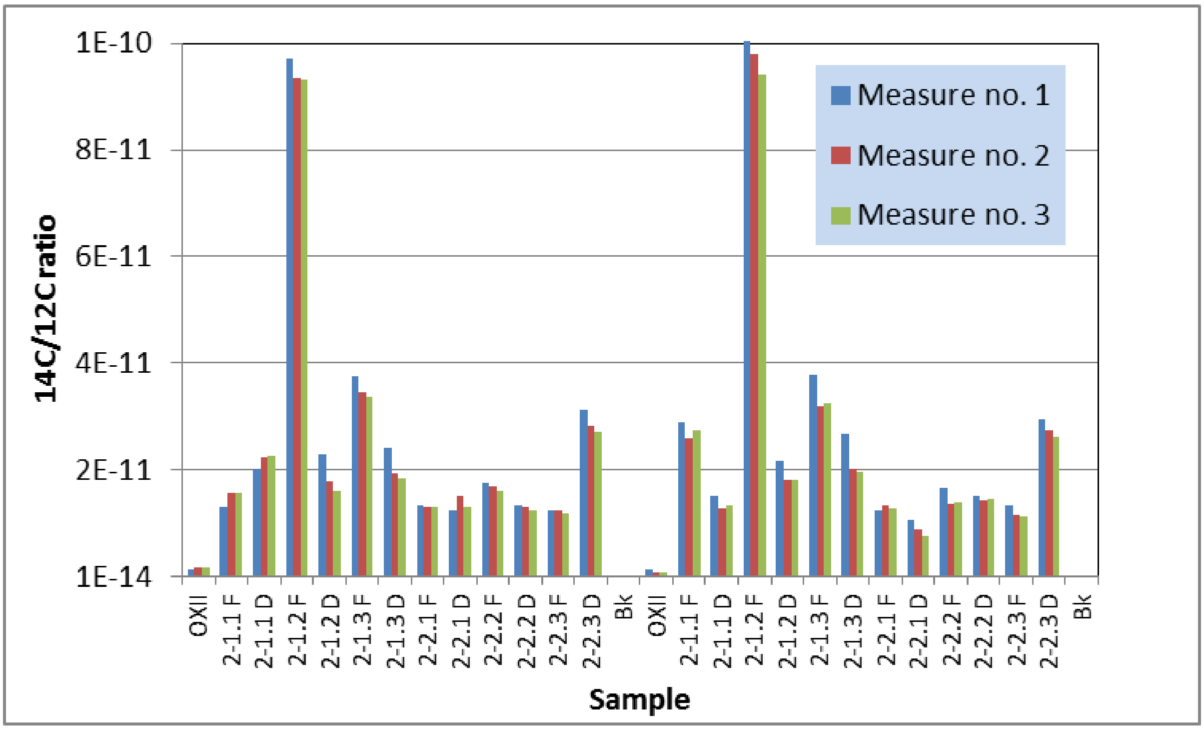

Figure 2.8.11: The $^{14}C/^{12}C$ ratio measured from samples collected from graphite disc no 2; Bk=Blank; OXII=Standard 18.40 dpm/g (0.31Bq/g;), 2-1, 2-2=Samples; F,D=Sample's face; 1,2,3=No of the samples

The ^{14}C concentration (Bq/g), calculated as the average of the 3 measurements, in the sampmes 2-1 and 2-2 from the graphite disc are presented in Figure 2.8.12

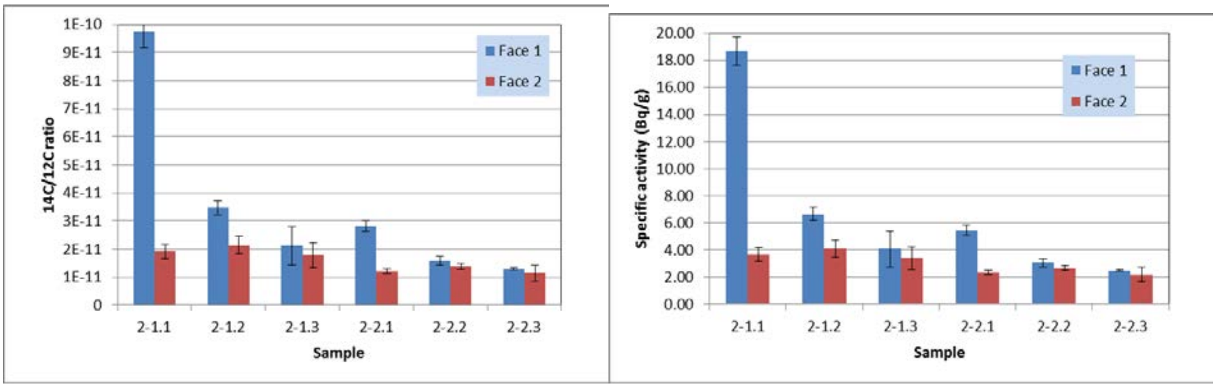

Figure 2.8.12 The $^{14}C/^{12}C$ ratio and specific activity measured from samples collected from graphite disc no 2.

As can be observed, the result from one of the samples (sample 2-1-1, face 1) is about 3 times higher than the other face of the same sample, probably due to a cross contamination. This value was excluded from the final calculation of the ^{14}C specific activity.

- Sample 2-1 (disc no 2-graphite column) = 3.73±0.36 Bq/g
- Sample 2-2 (disc no 2-graphite column) = 2.39 ±0.24 Bq/g

The results are in agreement with the fact that sample 2-1 was collected from the end of the rod nearer the reactor core.

The measurements at ANM 1 MV facility of the graphite samples collected from disc no 1 are in progress.

AMS determination of ^{14}C in nuclear samples of high radiocarbon concentrations.

For measurement of high concentrations of radiocarbon samples and to provide the depth profile of the evolution of these concentrations towards the bulk we use the AMS Depth profiling facility at the 9 MV tandem accelerator.

Since depth profiling is requiring a specialized ion source and special prepared acquisition we took advantage of the upgraded work performed at this machinery. A detailed description is given in [C. Stan-Sion et al., 2015].

Regarding the AMS measurement, since ^{14}C measurement implies the elimination of molecular interferences on the high energy side of the accelerator a velocity filter (Wien Filter) is a good solution. Many interferences occur during ^{14}C measurements like $^{12}CH_2$, ^{13}CH, $^{7}Li_2$, ^{14}N etc. The elimination or reduction of these interferences was the maxim task of these measurements at this stage of the project, since the AMS facility at the 9 MV accelerator is not designed for such special analyses as are the dedicated ^{14}C machines today.

In our test experiments we have been using the ^{13}C ion beam for tuning, that is about 100 times less intense than the ^{12}C ion beam and therefore more suitable for the adjustment of the beam transport and adjusting the values on the Wien Filter. Higher currents will produce the break-down of the high voltage on the deviation plates of the filter.

The optimum value of the magnetic field of the WF has been determined by tuning it accordingly to a maximum current in a Faraday cup, by keeping the value of the electric field set to a constant value of 14 kV. Then, the magnetic field values for ^{14}C were calculated and set blindly. To optimize the WF setting a scanning of different magnetic field values was done according to the obtained data drawn in Figure 2.8.13.

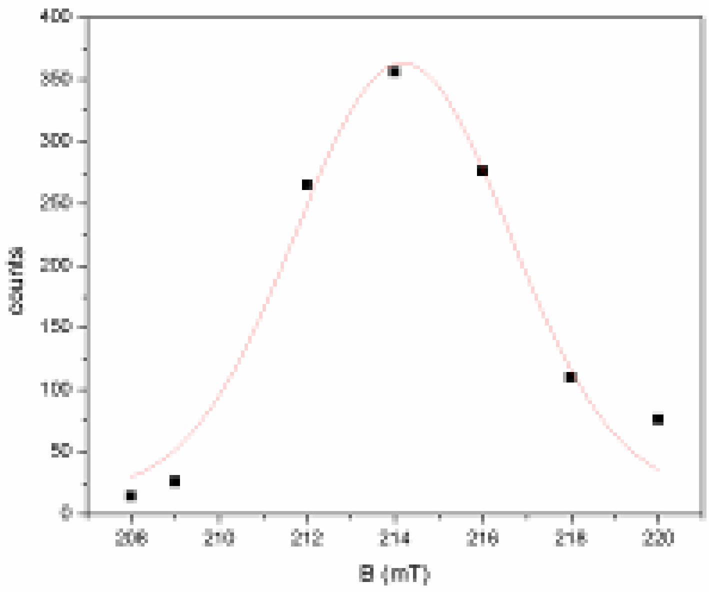

Figure 2.8.13: Determination of the optimum magnetic field setting for the Wien Filter

The obtained results are shown in Figure 2.8.14. The upper spectrum represents the measured ^{14}C concentration without a Wien Filter. Molecular interferences are hiding the ^{14}C peak. The lower spectrum is showing how the Wien Filter is eliminating many of the interfaces and ^{14}C can be distinguished.

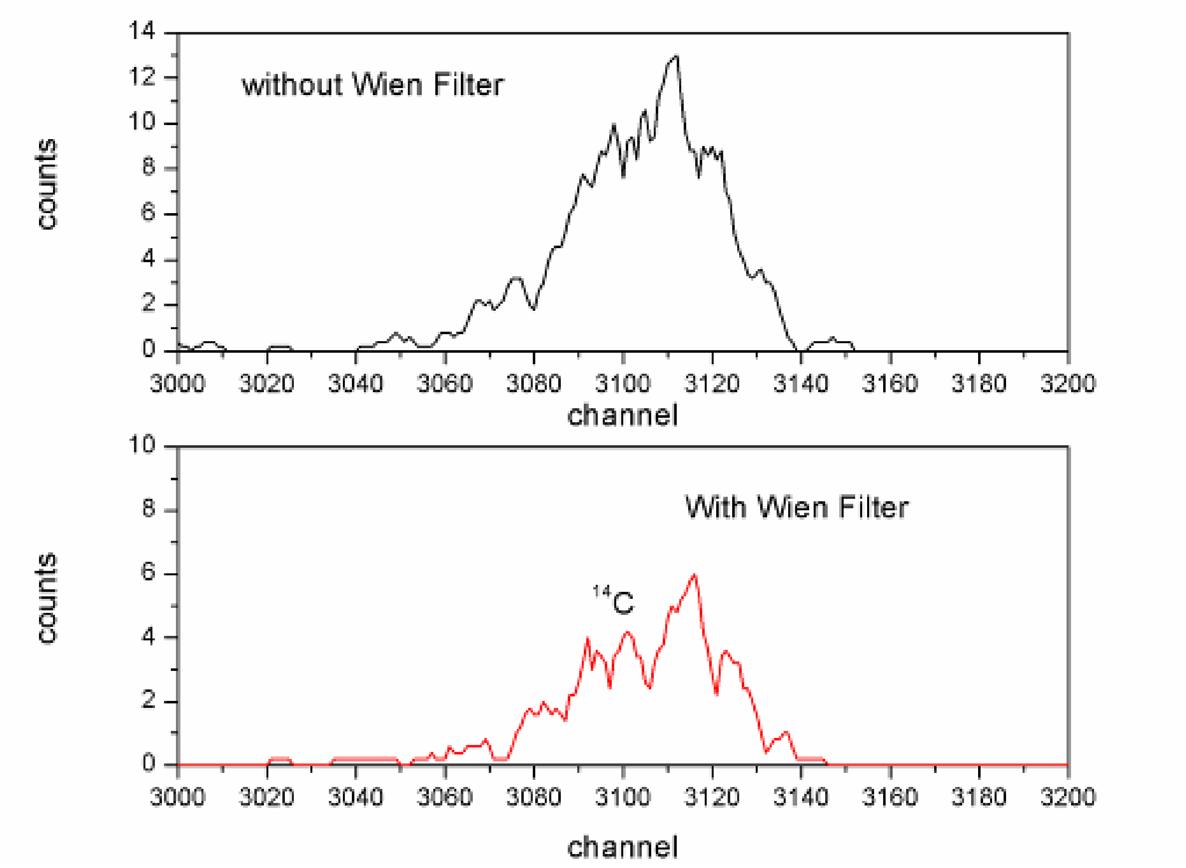

Figure 2.8.14: ^{14}C spectra at the 9 MV tandem accelerator.

Figure 2.8.14 shows how the interference ions and molecules are contributing to the ^{14}C peak since energies are very close. A better separation of the ions of different energies can be obtained if the produced signal in the detector is well adapted as input signal to the Spectroscopic Amplifier by a high resolution and time-rapid Preamplifier with low background contribution. This matches the impedances between the two electronic devices and preserves the energetic separation of the detector.

In this respect the performed experiments have shown that the replacing of the actual Preamplifier is compulsory. Therefore, we purchased form ORTEC Company a 142A PA – ORTEC that provides a maximum noise level of 3.4 keV at 100 pF and a resolution of 50 keV at 5 MeV.

The relative intensity of the ^{14}C signal to the signals of the other participating ions or molecule also contributes to a better separation of the envisaged ion element. Unfortunately, the ^{14}C current intensity was weak due to the malfunctioning of the pre-accelerating tube (NEC) in the existing conditions.

The reason was as follows: the distance, from the exit of low energy 90^0 magnetic analyzer to the entrance into the pre-acceleration stage, was to short and the ^{12}C beam was permanently spread out into the acceleration tube producing its electric brake down. This problem was recently solved by introducing an ion beam aperture defining the ion beam and avoiding lateral out-spreading. This change of the low energy beam line will make it definitely possible to perform measurements without interferences from neighbouring ions improving the overall ^{14}C bean intensity and contributing to a better resolution for the analysis of ^{14}C in conditions of depth profiling measurements.

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

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

Experimental methodology:

- Oxidation of the irradiated graphite samples in oxygen atmosphere;
- Oxidation of the resulted gases at high temperature over a CuO / Pt/Al_2O_3 catalyst bed;
- HTO and ^{14}CO trapping at liquid nitrogen temperature;
- Conversion of CO_2 at Na_2CO_3 using NaOH water solution;
- determination of ^3H and ^{14}C activities using a LSC device**. (** TRICARB 2800 TR).

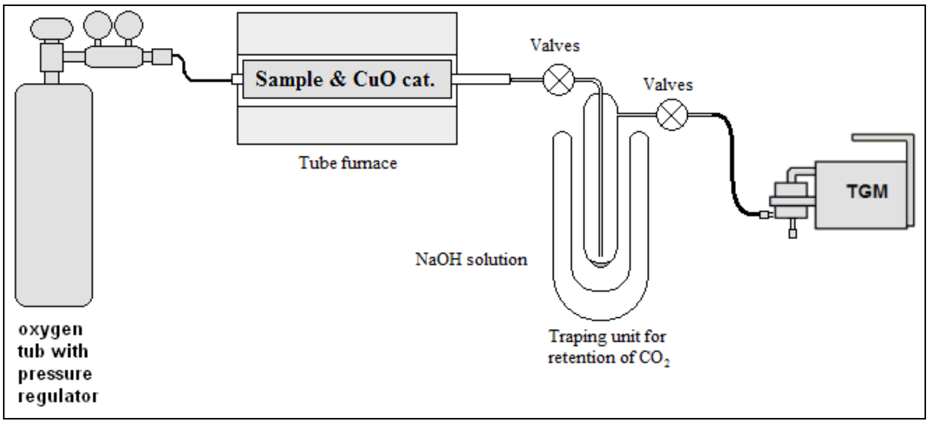

Figure 2.8.15 Apparatus designed for the total ^{14}C and ^{3}H activity measurements

The activities performed up to now consisted in the design of the experimental details and manufactured of the apparatus needed to measure the total ^{14}C activity of the i-graphite samples. (Figure 2.8.15)

Progress in Task 5.3 second year

Introduction

In connection with the decommissioning of nuclear reactors, other than the reactor core, the main radioactivity in the reactor comes from the graphite and construction materials. Due to their large volumes, graphite thermal column and concrete shielding comprise considerable amounts of low-medium radioactive waste. Calculations have shown graphite to be the main source of radioactivity at the time of dismantling of a nuclear reactor.

Several radionuclides are produced through the transmutation of carbon and graphite impurities during neutron irradiation, such as ^{3}H, ^{14}C, and ^{60}Co etc. [Fujii and Matsuo, 2002].

^{14}C is produced the graphite due to three neutron reactions: ^{13}C (n,γ) ^{14}C, ^{14}N(n, p) ^{14}C (the main contributor to ^{14}C due to the high neutron reaction cross section and isotopic abundance of ^{14}N) and ^{17}O(n,α) ^{14}C.

Due to the very high neutron activation cross section of ^{6}Li and the high neutron flux in the graphite the reaction ^{6}Li (n,α) ^{3}H is the main contribution to accumulation of ^{3}H in the graphite.

The present work performed in the second year of the CAST project concerns development of a method for the determination of ^{14}C total activity in the graphite column of the VVR-S reactor. Because ^{14}C and ^{3}H are pure beta emitters, and the energies of their beta particles are relatively low (Emax (^{3}H), 18.6 keV; Emax (^{14}C), 156.5 keV), the samples need to be decomposed in order to separate ^{14}C and ^{3}H from that of the graphite matrix before measurement of their radioactivity by liquid scintillation counting (LSC).

We selected as a rapid decomposition method of the graphite matrix: the combustion in oxygen atmosphere at high temperature.

Experimental methodology:

- combustion of the graphite sample in oxygen atmosphere at temperature 750-800 ^{0}C
- cooling the combustion gases
- trapping CO_2 in a vial containing CARBOSORB (cooled in liquid nitrogen)
- measuring the collected radioactivity at a Liquid Scintillation Counter (LSC) TRICARB TR 2800 Perkin Elmer

A photograph of the apparatus in Figure 2.8.16 and a schematic diagram of the experimental set-up are showing Figure 2.8.17.

The apparatus was installed in a ventilated chamber as can be seen in Figure 2.8.16.

- tubular furnace type RT 50-250/11 available from Nabertherm
- quartz tube equipped with air-cooling mantle
- flow meter,
- valves, pressure gauge
- CO_2 retention system -CARBOSORB E+
- residual CO_2 trapping cartridge.

Figure 2.8.16 The apparatus for the graphite combustion

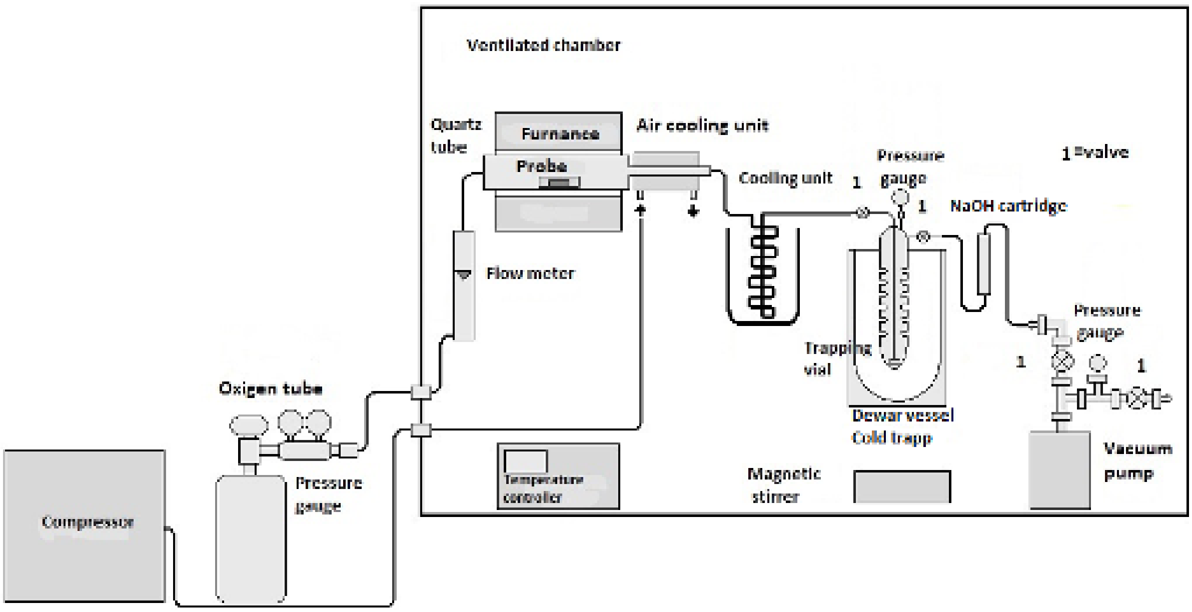

Figure 2.8.17 Schematic diagram of the graphite activity measurements apparatus

Sample preparation

Graphite samples were collected from the thermal column of the VVR-S reactor (disc no 2-2samples, no 5-2 samples and no 6-3 samples).

The irradiated graphite samples were ground to a fine powder and the sample material was weighed on a microgram balance Precisa 120 AT Laborota type.

An inactive graphite (virgin graphite) sample was also prepared from the same type graphite as that used in the VVR-S reactor. The weight of the samples was: 100.3-104.1 mg.

Measurements of ^{14}C by liquid scintillation counter

The ^{14}C (as CO_2) was trapped in vial with Carbo-Sorb E+ (Perkin Elmer). The solutions obtained are completely clear and colourless. An aliquot of each solution (two millilitre 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.(90% counting efficiency) The sample and the blank were measured for 20 min. and 3 cycles, and the averages of three cyclic measurements was calculated.

Results

The retention yield of CO_2 was determined by the following procedure:

In the first step the Carbo-Sorb E+ inside the trapping vial was replaced with NaOH and after the complete combustion of the graphite sample the vial was removed from Dewar vessel and allowed to reach the room temperature. The pressure inside the vial was measured and CO_2 mass was calculated, based on vial volume and temperature.

In the second step: NaOH cartridge was dissolved in 100 mL of water, an aliquot of solution was mixed with 10 ml of Permafluor and ^{14}C residual activity was measured.

The residual ^{14}C residual activity in the NaOH cartridge was measured and the results were compared for both type of trapping compounds (NaOH and Carbo-Sorb E).

The retention yield was calculated and the value obtained was 92-94% (NaOH and Carbo-Sorb E).

Based on activity value, sample weight and yield the specific activity of ^{14}C in each i-graphite sample was calculated. The results of the specific activity variation of ^{14}C along the length of the graphite rod collected from the thermal column disc near the reactor core (disc no 6) is presented in Figure 2.8.18.

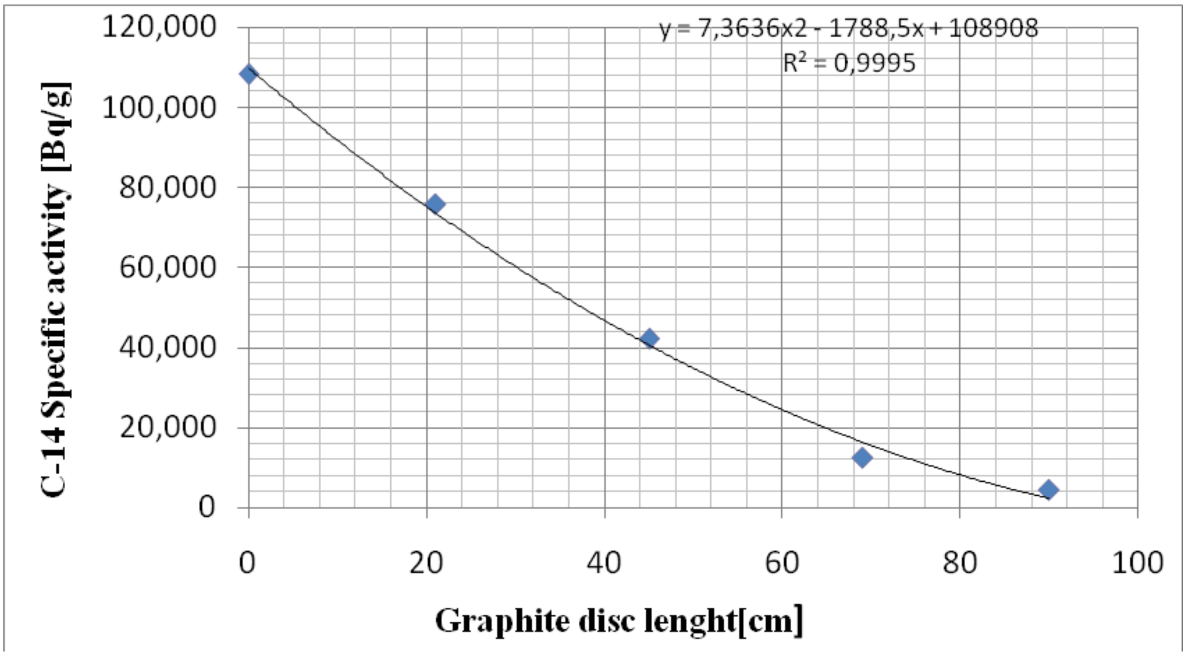

Figure 2.8.18 ^{14}C specific activity variation in graphite disc no 6

Conclusions

- the first estimation of the inventory of the i-graphite arising from the VVR-S thermal column has been determined.
- experimental methodologies and apparatus for the total ^{14}C activity measurements have been developed.
- The inventory of the i-graphite from the VVR-S thermal column has been determined.
- ^{14}C concentrations in two graphite samples from the subcritical assembly Helen and the VRS reactor have been measured using the AMS facility at 1 MV Tandetron. Samples were collected from the surface and from the interior of the virgin (unirradiated) graphite rods.

- Experimental conditions and methodology for AMS determination of ^{14}C in nuclear samples of high radiocarbon concentrations have been established.
- An apparatus for graphite combustion and ^{14}C total activity measurements has been developed.
- ^{14}C total concentrations and specific activity variations in the thermal column discs of VVR-S reactor have been determined.

2.9 Radioactive Waste Management Limited (RWM) summary

Over Year 2 of Work Package 5 of the CAST project, RWM undertook its role as Work Package 5 leader.

RWM also contributed to Deliverables D5.4 (Petrova et al., 2015) and Deliverable D5.5 (Toulhoat et al., 2015a) during the year.

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 second 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. 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". For the Task 5.1, the outcomes from the CARBOWASTE Project were reviewed, summarised and reported for the RBMK-1500 reactor, and for Task 5.2 new models for the numerical estimation of RBMK-1500 graphite activation are under development. 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 in i-graphite of the whole core of Ignalina NPP Unit 1 reactor.

3. The main objective of the INR 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. INR will perform leaching tests on irradiated graphite samples from this thermal column in order to determine the leaching rate and to measure the inorganic and organic fractions of ^{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 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 this second year, the data on the speciation of released ^{14}C

in French i-graphites were reviewed, and associated work towards deliverable D5.8 is in progress.

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

6. Within the last reporting period the work of FZJ was involved in the development of harmonized leaching procedure. For that the information on leaching approach was extensively reviewed, critically discussed (with an input of CIEMAT and NDA[3]) and summarized. Previous experience of leaching tests with RFR graphite performed in the frame of CarboDisp project at FZJ is considered. It is anticipated that developed leaching approach will be used by other project participants to enable inter-laboratory comparison of the results and provide systematic progress in the studies of ^{14}C leaching behaviour.

7. CIEMAT's Work Package 5 input to date considers different preliminary studies that have been performed to prepare the leaching experiments on irradiated powder graphite from Vandellós I NPP, samples of which are available in CIEMAT's laboratories, and on a graphite glass coating waste form - IGM (Impermeable Graphite Matrix) – material that has been developed by ADL-France and that will be prepared in the CIEMAT facilities. CIEMAT's laboratory is being conditioned to

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[3] From April 2014 onwards, work previously undertaken by the UK Nuclear Decommissioning Authority (NDA) Radioactive Waste Management Directorate (RWMD) has been undertaken by Radioactive Waste Management Limited (RWM), a wholly-owned subsidiary of the NDA.

work with the equipment needed to prepare samples of i-graphite for use in experiments to be reported as part of CAST WP5.

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