# CArbon-14 Source Term

# CAST

# Exfoliation of irradiated nuclear graphite by treatment with organic solvent assisted by ultrasound

# (D5.11)

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## CAST – Project Overview

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

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

The objectives of the CAST project are to gain new scientific understanding of the rate of re-lease 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

# Executive Summary

For the past 50 years, graphite has been widely used as a moderator, reflector, and fuel matrix in a variety of gas-cooled reactors. The result is approximately 250,000 metric tons of irradiated graphite waste. Characterization of existing irradiated graphite indicates that a most significant long-lived radioisotope from graphite reactors similar to the HTGR is carbon-14 ($^{14}$C). With a half-life of 5730 years, this species is of concern for deep geologic disposal of irradiated graphite because when present in the environment it is readily mobile in groundwater and atmospheric systems. Dependent on national strategy, removal of $^{14}$C from large irradiated graphite reactor components may reduce the disposal cost, while also allowing the possibility of recycling this very pure nuclear grade material. Moreover, the graphite source (moderator, fuel compartments details-sleeves) could give rise to various radionuclides. Over the last twenty years, numerous proposals have been made for the long-term treatment of radioactive graphite waste.

In this deliverable, the behaviour of nuclear graphite (NG) through the exfoliation process has been studied, carried out with different organic solvents to remove primarily radiocarbon and estimate the "Removal Efficiency" (as percentage of the recovered activities after treatment in comparison to the original values) of the used solvents in order to propose a reliable approach to produce graphite for recycling or/and safety disposed as L&ILW.

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# 1      Introduction

Graphite has been used as a moderator and reflector of neutrons in more than 100 nuclear power plants as well as many experimental reactors and plutonium production reactors in various countries. Graphite is also used for fuel sleeves and other components, which are disposed of during operation and in some cases the volume of the graphite involved is of the same order as the core itself. Considering that the core of a typical graphite moderated reactor may contain 2000 tons of graphite, the volumes involved are considerable. Most of the older graphite moderated reactors are already shut down and therefore decommissioning planning and preparation represents a very serious matter. Radioactive graphite dismantling, handling, conditioning and disposal are a common part of the decommissioning activities. The radioactive graphite coming from nuclear installations has different characteristics than other radioactive waste due to its physical and chemical properties and also because of the presence of tritium and carbon-14. Even after many years of irradiation, graphite retains most of the good mechanical properties and is relatively insoluble and not otherwise particularly chemically reactive. It appears therefore to fulfil most of the general requirements for a solid radioactive waste form suitable for disposal. However, the evaluation of the radioactivity inventory of graphite moderators and other details of graphite used in nuclear reactors, as reported in Technical Committee meeting IAEA (1999), shows that depending on the National Waste Management strategy and associated regulatory criteria, this graphite may not be accepted by existing disposal sites without particular conditioning. Depending on the graphite source (moderator, fuel compartments details-sleeves), various radionuclides are present, mainly tritium and $^{14}C$, but also corrosion/activation products and small amounts of uranium and transuranic elements.

With a half-life of 5730 years, $^{14}C$ is of concern for deep geologic disposal of irradiated graphite. Removal of $^{14}C$ from large irradiated graphite reactor components may reduce disposal cost, while also allowing the possibility of recycling this very pure nuclear grade material. It has been widely reported in IAEA TECDOC 1790 (2016) the effect of fast and slow neutrons: the first ones cause damages to the graphitic crystal structures (Figure 1)

leading components to shrink and distort, to crack, while the others create new radioactive isotopes both from the graphite (i.e. $^{14}C$) and from impurities.
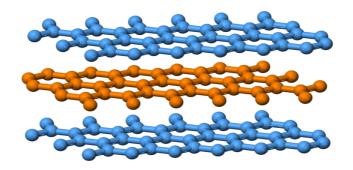


**Figure 1: Graphite structure with graphene layers**

Over the last twenty years, numerous proposals have been made for the long-term treatment of radioactive graphite wastes. These plans have ranged from sea dumping through incineration to land-based disposal, sometimes preceded by a variable period of "safe-storage" within the original reactor containment, to allow for the decay of shorter-lived isotopes ahead of dismantling. The burning of nuclear graphite would be an efficient method for volume reduction, but would not be accepted by the public if all the $^{14}C$ was emitted into the atmosphere in the form of $CO_2$. The required separation of the $^{14}C$ from the off-gases is difficult and not economic because this carbon isotope has the same chemical properties as the $^{12}C$ from the graphite matrix. The solidification of the whole amount of $CO_2$ would cancel out the volume reduction advantage of burning, has been reported by Fachinger et al (2008). A number of novel chemical or physical pre-treatments of the graphite, with the objective of facilitating its subsequent disposal or improving the environmental consequences of the chosen disposal route, have also been suggested in IAEA document TECDOC-1790. Due to the great interest about the retrieval, characterization, treatment, reuse and disposal of irradiated graphite, the aim of this paper is to propose a process to remove the radiocarbon in such a way that the potential risk associated with this nuclide is reduced, by treating the graphite such that it could be recycled or/and safely disposed as L&ILW.

## 1.1 *Formation of $^{14}C$*

Formation of $^{14}C$ in graphite occurs by bombarding target nuclei with neutrons. $^{14}C$ is then produced through neutron capture by carbon-13 ($^{13}C$), nitrogen ($^{14}N$), and oxygen-17 ($^{17}O$) as seen in Eqs. (1)–(3) [Gougar, M.L. 2014].

$$^{14}N + n \quad \rightarrow \quad ^{14}C + p \quad (Eq. 1)$$

$$^{13}C + n \quad \rightarrow \quad ^{14}C + \gamma \quad (Eq. 2)$$

$$^{17}O + n \quad \rightarrow \quad ^{14}C + \alpha \quad (Eq. 3)$$

The concentration of $^{14}C$ on the surface is dependent on its location within the reactor, core design, flux, manufacturing and environment. Graphite naturally absorbs air; consequently $^{14}N$ and $^{17}O$ are readily found on the graphite surface. Oxygen and nitrogen adsorption occurs during graphite manufacturing component assembly and storage, and as a result of air leaks into the reactor coolant gas. The neutron capture cross sections and isotopic abundances of $^{14}N$ and $^{17}O$ (Table 1) indicate the neutron activation of $^{14}N$ is likely the main source of $^{14}C$ on the surfaces of irradiated graphite [Gougar M.L, 2014; Podruhzina T., 2005].

**Table 1: Properties of $^{14}C$ precursors**

| Species | Capture cross section (Barns) | Isotopic abundance (%) |
|---|---|---|
| $^{14}N$ | 1.8 | 99.63 ($^{14}N$/N) |
| $^{13}C$ | 0.0015 | 1.07 ($^{13}C$/C) |
| $^{17}O$ | 0.235 | 0.04 ($^{17}O$/O) |

The majority of studies on chemistry of graphene involve Highly Oriented Pyrolytic Graphite (HOPG) or Graphene oxide (GO) but only few are related to Nuclear Graphite (NG), even though the irradiated graphite is a concern for deep geologic disposal.

Pyrolysis and oxidation have been suggested as decontamination methods [El-Genk 2011]. Thermal treatment may prove a viable process for removing much of the $^{14}C$ from graphite

surface [Smith T.E. 2012]. It is a complex process in which graphite is heated at constant temperature under forced convection with an inert gas. Graphite is oxidized due to the presence of absorbed air, thus releasing gasified carbon-oxygen compounds [EPRI Technical report 1013091 March 2006].

Under high temperatures (~300 °C) close to reactor conditions, carbon can exist in a greater variety of chemical forms (table 2). The predicted forms include $CO_2$ (plus carbonic acid and bicarbonate), and simple organic carbon compounds of mixed oxidation states. Elemental carbon ('graphite') would not be stable under these high temperature conditions. The other dominant forms include a narrow formaldehyde field at low pH, and a larger stability field for formic acid at high pH (~4–11), both under mildly reducing conditions. The reduced field is dominated by $CH_3OH$, while the $CH_4$ field is present under strongly reducing potential. [Man-Sung Yima, 2006].

**Table 2: Chemical form of C in graphite**

| |
|---|
| $^{13}C(n,\gamma)^{14}C$    $^{14}C \dashrightarrow$ in the same structural lattice |
| $^{17}O(n,\alpha)^{14}C$    $O_2 \dashrightarrow {}^{14}CO, {}^{14}CO_2$ |
| $^{14}N(n,p)^{14}C$    $N_2 \dashrightarrow {}^{14}C\text{-}C$ ⎰ *Inorganic CO, $CO_2$, $HCO_3^-$, $CO_3^{2-}$* <br> ⎱ *Organic $–CH_x$, $–COH$, $–CO–$, $–COOH$, $CH_4$, $-C{\equiv}N$, …* |

## 2     The Organic Solvents Treatment Ultrasound Assisted

Nowadays, graphite can be exfoliated by different chemical methods in liquid phase. One of the simplest approaches to disperse graphene sheets is ultrasonic treatment in organic solvents, which makes graphite's atomic planes chemically loosened and intercalated. It is a

simple process that leads to stable dispersions of submicrometer graphene crystallites and allows mass production for industry applications.

Some dipolar aprotic solvents such as N,N-Dimethylacetamide (DMF) or N-Methyl-2-pyrrolidone (NMP) have been shown to be effective in the stabilisation of graphene in solution without re-aggregation [Xia 2013]. These dispersions unfortunately have some drawbacks: it has been pointed out that the best organic solvents tend to be toxic so it would be preferable to achieve concentrated graphene dispersion in "green" (environmentally friendly) and low- boiling –point solvents. Ricardo [2014] reported the effect of basic aqueous mixtures of salts as lithium, potassium and sodium chloride (pH 11) on the exfoliation process and the capability of mixture water/acetone to produce highly stable graphite dispersion [Nonomura Y., 2010].

Since the graphene has, in recent years, attracted tremendous attention due to its peculiar properties, graphite exfoliation can be carried out by some other effective but disruptive approaches such as the covalent modification, a strong oxidation which produces graphene oxide (GO), and the electrochemical exfoliation process, which is also characterized by cyclic voltammetry (CV). One of the commonly accepted rationals about graphene exfoliation is that the more defects are introduced in the lattice, the more soluble are the sheets and the more efficient is the exfoliation. Sheet solubility is for sure fundamental to stabilize graphene in solution; however, the exfoliation process itself is a complex phenomenon that, in analogy to other solubilisation processes, will depend on a complex competition between chemical, electrostatic and Van der Waals interactions [Xia, 2013].

It is a fact that the scientific production is focused on studying the behaviour of graphite toward the exfoliation process, but there is a lack of information about the capability of these methods to remove radionuclides: the intention of this current work is to fill this gap investigating the behaviour of NG towards the solvents exfoliation method and measuring the radioactivity removed. In this report, taking into account the results obtained by the exfoliation of 27 aliquots of three activated NG samples (iGF1; iGF3; iGF4) coming from Latina NPP, which have been treated with 5 ml of N,N-Dimethylacetamide (DMF), N-Methyl-2-pyrrolidone (NMP) and N,N-Dimethylformamide (DMF), a new approach has been accomplished. 12 portions of iGF4 have been exfoliated in a mixture of the same

solvents with NaOH pellet (50mg/ml) (9 samples) and  in a mixture water/acetone (85/15 %
v/v)  (3 samples), with the final purpose being to estimate if this improvement is more
reliable for the removal of $^{14}$C.

Since the literature data are mainly focused on the production of graphene from pristine
graphite but not on the removal of $^{14}$C from NG, the optimization of experimental
parameters and the assessment of the reproducibility of the procedure were necessary. For
this aim, preliminary comparison experiments comparison have been carried out on a batch
of brand new NG, coming from Latina NPP warehouses, and commercial Highly Oriented
pyro–graphite (HOPG).

## 2.1  *The Exfoliation Process*

The exfoliation process (Figure 2) of the graphite surface through organic solvents drives
towards the production of no-functionalized and non-oxidized graphene layers in a stable
homogeneous dispersion. The process is helped by mild sonication and it consists in
separating the individual layers in a more or less regular manner. Such a separation, being
sufficient to remove all the interplanar interactions, results in a dispersion of the graphite in
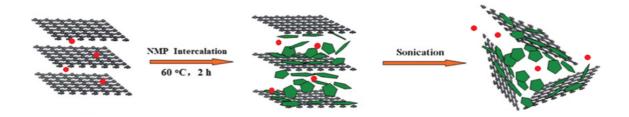a workable media. This should provide an easier characterization for the contaminants
recoveries**.**



**Figure 2: Exfoliation process scheme**

The most suitable solvents required to contribute to this process should have the following
characteristics:

- to be a dipolar solvent;

- to be miscible with water, aqueous acid solution and the majority of the solvents;

- to have a good solvency properties, able to dissolve a wide range of chemicals and exfoliate graphite to graphene layers.

With the aim of demonstrating the applicability of the exfoliation process on nuclear graphite, a comparison test between 25 mg of Highly Oriented Pyrographite (HOPG) (Aldrich product 332461, batch number 06106DE) and 25 mg of NG has been performed. The samples were suspended respectively in 5 ml of NMP, DMA and DMF. All the solvents, purchased by Sigma Aldrich, are Analytical grade (spectrophotometric grade >99.0%). The solutions were sonicated for 3 hours in a sonication bath at 30 Watt of power and 37 kHz; then centrifuged at 500 rpm for 90 min and characterised by Laser Raman Spectroscopy (experimental parameters are summarized in Table 3) and scanning electron microscopy (SEM).

**Table 3: Experimental parameters**

| Graphite (NG) | 5-10-25-50-75 mg |
|---|---|
| Solvent (each) | 5 mL of DMF, DMA, NMP |
| Sonication time | 3h |
| Sonication Power | 30W – 37kHz |
| Centrifugation | 500 rpm for 90 min |
| Separation | Filtration on PVDF 0.1 μm |
| UV-wavelength | 660 nm |

## 2.2 *Raman Spectra and Scanning Electron Microscopy Analysis*

Raman spectroscopy is a fast and non-destructive technique for the characterization of carbons, offers high resolution, gives structural and electronic information, and is applicable at both laboratory and mass-production scales. It is particularly useful for graphene because

the spectrum contains information about both atomic structure and electronic properties [Ferrari A., 2013]. It is also capable of differentiating multilayer graphenes and also the atomic layer resolution for the thickness up to four layers. The spectra exhibit simple structures characterized by three principal peaks G, D and 2D. In Figures 3 and 4 are shown the Raman spectra of HOPG and NG before and after the treatment.
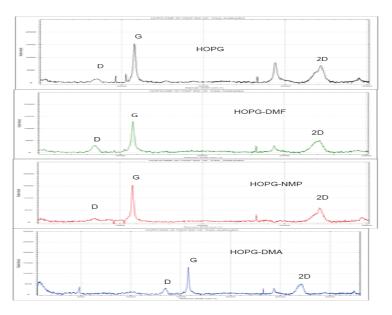


**Figure 3: Spectra of HOPG (before and after exfoliation process)**
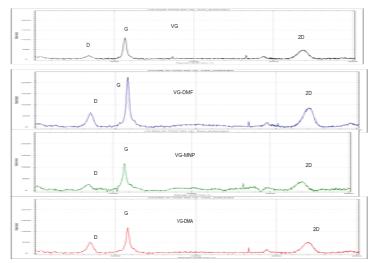


**Figure 4: Spectra of NG (before and after exfoliation process)**

Scanning Electron microscopy (SEM) is routinely used to generates high-resolution images of the shapes of objects and to show spatial variations in solid materials and it is the more suitable completion of the Raman results, since the spatial resolution of SEM images can be

much higher than in the case of Raman maps. Three of all exfoliated samples have been examined by scanning electron microscopy (SEM) with a SEM Benchtop PhenomPro (produced by PhenomWord). In Figures 5-8 the SEM spectra of graphite powder before and after treatment are compared: the effect of exfoliation is clearly visible.
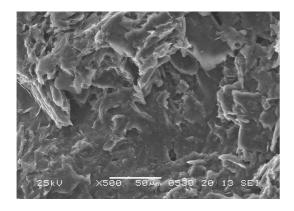


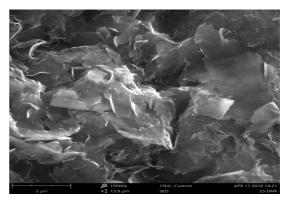**Figure 5: SEM of Virgin nuclear graphite**



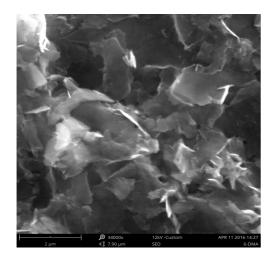**Figure 6: SEM after treatment with NMP**



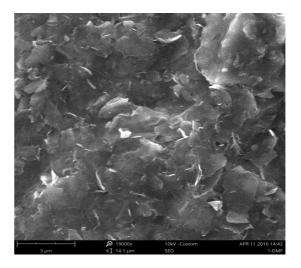**Figure 7: SEM after treatment with DMA**



**Figure 8: SEM after treatment with DMF**

## 2.3  *Optimisation of the process parameters*

It has been demonstrated by literature data that the experimental parameters of the exfoliation of power graphite by solvent assistance needs to be optimised in order to

improve the concentration of dispersion [Xia Z.Y., 2013] and, theoretically speaking the amount of radionuclides removed. Since this method hasn't been applied before on NG, some of the variables (as ratio powder/solvent; sonication time; linearity of the process) have been monitored in the current study.

### 2.3.1   Graphite powder/Solvent ratio

In accordance with the international literature on graphite exfoliation processes, the ratio powder/solvent is one of the critical points. Taking into account that one of the most effective methods to reduce the strength between the adjacent layers is liquid immersion, several tests with five different NG graphite amounts (5-10-25-50-75 mg) were performed. The samples were treated with 5 mL of N-Methyl-2-pyrrolidone (NMP), N,N-Dimethylacetamide (DMA), N,N-Dimethylformamide (DMF) and filtrated on Polyvinylidene Fluoride (PVDF) 0.1 µm filters (the experimental parameters are showed in Table 3). The PVDF filters with the upper dispersed material have been dried in a vacuum oven at 60 °C for 2 hours at 1 mbar and weighed to obtain the amount of graphitic material suspended. In Figure 9 is showed the trend as a function of the ratio of graphite powder (mg) versus solvent (ml).
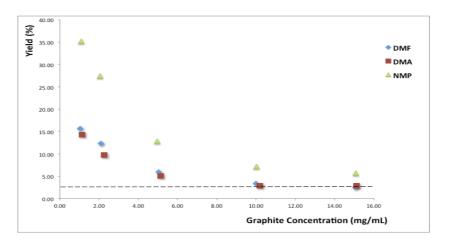


**Figure 9: Optimization of ratio graphite (mg)/solvent (mL)**

## 2.3.2    Optical characterization of graphite dispersions

The absorption coefficient α, related to the absorbance per unit path length $A/l = \alpha C$, is an important parameter in characterizing any dispersion.  This parameter has to be determined experimentally to accurately determine the graphene concentration. In Figure 10 the optical absorbance (660 nm), divided by cell length, is plotted versus concentration of graphene (mg/L) in the solvents. The process has shown Lambert-Beer behaviour. It should be noted that the value α remains almost constant for DMA and NMP solutions.
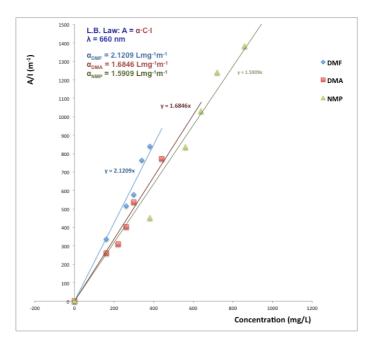


**Figure 10: Absorption coefficient at 660 nm for graphene in NMP, DMA and DMF**

## 2.3.3    Sonication Time

Sonication time is another crucial point that should be optimised. During sonication over 3 hours the bath tended to heat up to ~ 60°C and evaporation occurred. Since it was demonstrated that this situation leads to the degradation of the solvents and consequently to poorer results, the experiments were carried out taking into account this scientific evidence. Another problem when using sonic baths is reproducibility, because the sonic energy input to the sample is sensitive to the water level, volume of dispersion, vessel shape [U.Khan; 2010]. To keep as much as possible under control the process parameters all the sonication steps were performed using the same bath and the type of vessel. All the volumes (water

11

level and solvent) have been accurately measured.

## 2.4   *Exfoliation process with a organic/aqueous mixtures solvents*

Water and acetone have been previously considered poor solvents or non-solvents for graphene [Yi M., 2013]. Mixing water with organic solvents sometimes led to a mixture whose properties are significantly different from those water and solvent alone. A highly stable dispersion was obtained in aqueous mixture containing up to 40%wt of acetone [Nonomura 2010]. Authors have demonstrated [Yi M., 2013] that the maximum graphene concentration occurs at an acetone mass fraction of ~ 75%, which can be taken as the optimum mixing ratio, showing an high level of stability. In order to investigate the $^{14}C$ removal efficiency of organic and inorganic mixtures 2 different experiments have been performed:

A – 9 aliquots of iG4 were treated with a mixture of 5 ml of solvent/NaOH (50 mg/mL)

B – 3 aliquots of iG4 were treated with 5 ml of a mixture $H_2O$-Acetone (15%) /NaOH.

All the samples were exfoliated for 3, 5 and 10 hours. In order to avoid collateral effects of overheating, the sonication bath was equipped with a refrigeration system.

## 2.5   *Solvent removal efficiency*

As previously reported, one of the goals of this paper is the evaluation of the recovered activities after treatment in comparison to the original values to produce graphite for recycling or/and safe disposal as L&ILW. To do this, as first step, three different NG samples (labelled as iGF1, iGF3, iGF4) had been fully processed. About 0.1 g of powder has been taken and added to 100mL of a mixture of $H_2SO_4$-$HNO_3$-$HClO_4$ 8:3:1 v/v/v for the determination of $^{14}C$ by Wet Oxidation-Acid Digestion. The hot acid digestion was performed through a closed system under $N_2$ flow connected with a series of Drechsel bottles for trapping the $^{14}C$ as $CO_2$ in 3-methoxypropylamine (3-MPA). About 0.01 g of each sample has been treated with DMF, DMA and NMP. As noted in Figure 5, different sonication times have been used. Since one of the purposes is to investigate the possibility of obtaining a good removal efficiency with less toxic and high boiling point mixture as a

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sonication solvent, the effect of the mixture water/acetone has been studied. It has produced a complete stable exfoliation, slightly coloured (Figure 11). Those samples have been decolorized with $H_2O_2$, a very effective bleaching agent, before being analysed by LSC.
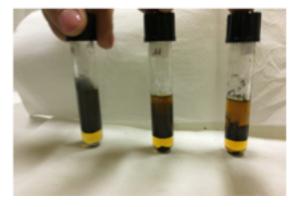


**Figure 11: Samples after sonication with water/acetone**

# 3     Results and discussion

In this paper has been proposed that the exfoliation method is a reliable method to remove $^{14}C$ from the nuclear graphite, paving the way for the production of graphite for recycling and/or safe disposal. To support this method, a lot of evidence has been collected. It is very clear that the sonication allows the solvent to easily reach the target radiocarbon in the closed porosity and extract it (see Figure 2): successful exfoliation requires the overcoming of the Van der Walls attractions between adjacent layers. Solvents with surface tension ($\gamma$) ~ 40 $mJm^{-2}$ are the best solvents for the dispersion of graphene and graphitic flakes, since they minimize the interfacial tension between solvent and graphite. Solvents used in this work show a surface tension between 36,7 $mJm^{-2}$ (DMA) and 40,1 $mJm^{-2}$ (NMP). Unfortunately these solvents have some disadvantages: NMP is an eye irritant and may be toxic to the reproductive organs, while DMF may have toxic effect on multiple organs [Cieselski A., 2013]. Therefore the search of alternative solvents (possibly "green" and with low toxicity) is highly recommended: the mixture water/acetone is a first step to achieve graphene dispersions in a low-boiling point solvent.

It has been demonstrated that the process is applicable to NG: its linearity has been demonstrated through UV-Vis analyses. This is one of the most important parameters to validate an analytical procedure, and is defined as its ability, within a given range, to obtain test results that are directly proportional to the concentration of analyte in the sample. As showed in Figure 6 the absorption coefficient ($\alpha$) at 660 nm of filtrate in NMP, DMA and DMF follows a Lambert and Beer behaviour with no substantial influence by the nature of the solvent: this confirms the robustness of the method. Furthermore, the reproducibility of the sonication process has also been taken into account. It is well known that the sonic energy input to a sample is sensitive to the water level, the exact position in the bath, the volume of dispersion, vessel shape and so on: for this reason nominally identical baths tend to give different results [Khan U., 2010]. In this work, the samples have been sonicated in a fixed position, in one sonic bath. Since the sonication temperature can reach more than 50°C, to avoid the collateral effects of the overheating the sonic bath was connected to a refrigerating system. It has been also demonstrated that the ratio powder/solvent has a crucial position in the optimization of the whole procedure. The recovery of exfoliated graphite increases when the ratio powder/solvent is low (see Figure 9): to maximize the effect of the solvent it could be very useful to operate with a recovery and recycling system, also due to the fact that the solution produced from the exfoliation of nuclear graphite is highly radioactive.

Raman spectra represent the most important evidence of the effect of the exfoliation process. It is also capable of differentiating multilayer graphenes and also the atomic layer resolution for the thickness up to four layers to differentiate.
In this study 27 different portions from nuclear graphite samples have been processed  and the removed activity (RE%) of the process has been evaluated. Then, a new set of 12 samples of nuclear graphite  (iGF4) has been treated modifying the procedure previously applied.
It has been described by Liu (2011) that NaOH can be added to organic solvent to increase the direct exfoliation of graphene. Because it seems plausible to affirm that NaOH increases the interplanar spaces of the adjacent graphitic layers, the new experiments were performed by mixing NaOH pellets to solvents previously used. Furthermore with the purpose to abandon toxic solvents for more " green" mixtures, a set of 3 aliquots of iGF4 has been

sonicated at the same times with water-acetone (15%)/NaOH mixture following the evidences already demonstrated on HPGO by Nonomura (2010). NG showed in this ternary mixing a very stable dispersion and almost complete exfoliation. Raman spectra performed on the no.3 graphite samples exfoliated by aqueous mixture and compared with pristine graphite are showed in Figure 12.
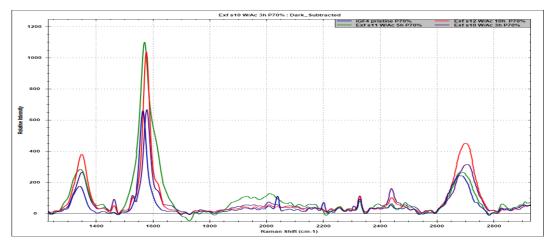


**Figure 12: Raman spectra of exfoliated samples by ternary mixture compared with pristine graphite**

The exfoliated samples show a net increase in the most prominent features in Raman spectra of monolayer graphite. The comparison of the Raman peaks show the following characteristics, confirming that the exfoliation occurred with success:

- increasing of the D band;

- shifting of G band to higher Raman shift values;

- enhancement of 2D band;

- ratio 2D/G enhanced in exfoliated fraction.

For explanatory purposes, the Raman peaks value of one aqueous sample and a pristine graphite are summarized in the Table 4:

**Table 4: Raman peaks values**

| Sample | Band | Raman peak cm-[1] | Intensity | Ratio 2D/G |
|---|---|---|---|---|
| iGF4 pure | D | 1343 | 175.0 | 0.37 |
| | G | 1565 | 660.9 | |
| | 2D | 2700 | 242.3 | |
| *Exfoliated in Water/NaOH/ acetone* | D | 1348.9 | 380.5 | 0.45 |
| | G | 1578.3 | 1036,4 | |
| | 2D | 2700.5 | 451.3 | |

In Table 5 are shown the removed activity values already obtained by exfoliation with DMA, DMF and NMP recalculated taking into account the recovery of the process. In Table 6 are summarized the new results achieved by using NaOH /solvent mixture.

In these last two tables are listed both the Removal Efficiency (RE) in percentages and an Activity Removed partially in percentage too. The first one is calculated by the measurement of the radiocarbon content in the solvent separated by filtration from the exfoliated material (weighed on the filter to calculate the yield of exfoliation) on the original radiocarbon content in the pristine iGF before the treatment. The second one is calculated taking into account the same radiocarbon content in the filtered solution but related to the yield of exfoliation. This would give an idea of the extraction capability of each solvent independently from the exfoliation ability of each solvent used.

**Table 5: Removed activity (%) on NG samples exfoliated by DMF, DMA, NMP**

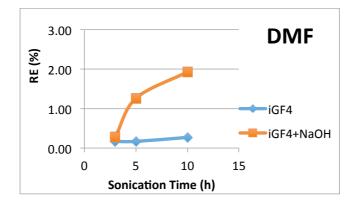| Sample iGF | Solvent (5 mL) | Time (h) | Removal Efficiency (%) | Partially Removed Activity (%) |
|---|---|---|---|---|
| iGF1 | DMF | 3 | 0.12 | 1.88 |
| | | 5 | 0.45 | 3.23 |
| | | 10 | 0.34 | 1.21 |
| | DMA | 3 | 0.02 | 0.84 |
| | | 5 | 0.22 | 2.28 |
| | | 10 | 0.41 | 2.14 |
| | NMP | 3 | 0.09 | 0.72 |
| | | 5 | 0.11 | 0.41 |
| | | 10 | 0.32 | 0.42 |
| iGF3 | DMF | 3 | 0.06 | 0.84 |
| | | 5 | 0.21 | 1.70 |
| | | 10 | 0.29 | 1.82 |
| | DMA | 3 | 0.10 | 0.65 |
| | | 5 | 0.38 | 1.66 |
| | | 10 | 0.48 | 0.93 |
| | NMP | 3 | 0.24 | 1.11 |
| | | 5 | 0.20 | 0.66 |
| | | 10 | 0.33 | 1.01 |
| iGF4 | DMF | 3 | 0.16 | 3.39 |
| | | 5 | 0.17 | 2.72 |
| | | 10 | 0.27 | 1.23 |
| | DMA | 3 | 0.04 | 1.46 |
| | | 5 | 0.06 | 2.14 |
| | | 10 | 0.14 | 2.42 |
| | NMP | 3 | 0.19 | 4.04 |
| | | 5 | 0.19 | 1.48 |
| | | 10 | 0.44 | 1.78 |

**Table 6: Removed activity (%) on NG samples exfoliated by mixture**

| Sample iGF | Solvent (5 mL) | Time (h) | Removal Efficiency (%) | Partially Removed Activity (%) |
|---|---|---|---|---|
| iGF4 | DMF/NaOH | 3 | 0.28 | 5.53 |
| | | 5 | 1.26 | 12.84 |
| | | 10 | 1.93 | 15.04 |
| | DMA/NaOH | 3 | 0.17 | 5.81 |
| | | 5 | 1.16 | 11.09 |
| | | 10 | 2.06 | 17.43 |
| | NMP/NaOH | 3 | 1.05 | 13.97 |
| | | 5 | 2.77 | 17.19 |
| | | 10 | 4.15 | 21.97 |
| iGF4 | Water-Acetone (15%) /NaOH | 3 | 14.00 | 16.61 |
| | | 5 | 15.25 | 17.51 |
| | | 10 | 22.76 | 23.85 |

Reporting these results in graphic form where the removal efficiency for each solvent used is compared to the same with NaOH, as function of the sonication time (Figures 13-14), it is evident how this addition can improve the yields in exfoliation and radiocarbon extraction.

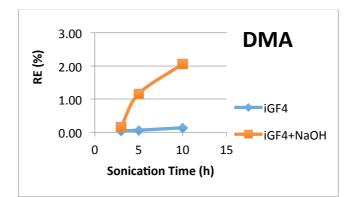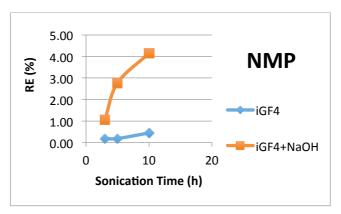**Figure 13: Removal Efficiencies vs. sonication time for DMF**

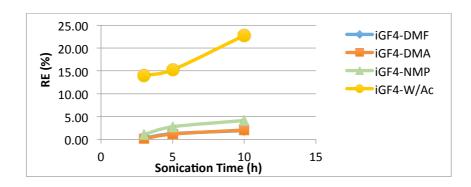**Figure 14: Removal Efficiencies vs. sonication time for DMA**



**Figure 15: Removal Efficiencies vs. sonication time for NMP**



Comparing all these results it seems that the overall efficiencies can be scaled according to an "ability scale" as follow:

NMP > DMA > DMF

But comparing these results to those in water/acetone mixture (figure 16) it arises that the ability of this last solvent mixture is higher than the others:

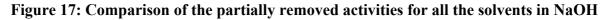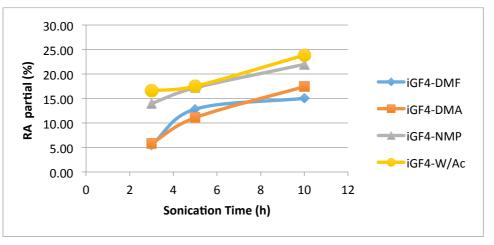**Figure 16: Removal Efficiencies vs. sonication time for all the solvents**

It is then possible to establish that the new "ability scale" is

Water/Acetone ≫ NMP > DMA > DMF (with NaOH)

Figure 17 shows the suite of results obtained.

**Figure 17: Comparison of the partially removed activities for all the solvents in NaOH**



At one glance is possible to figure out that the extracting abilities of each solvent are quite comparable. Since the partially removed activity is independent of the yield degree, these results can be interpreted on the basis that not all the $^{14}C$ species in the irradiated graphite are the same and only the ones not chemically bonded or in those forms that have some chemical or physical-chemical affinity with the extracting media are likely to be removed. These first results are promising enough to promote further investigations in this direction. Furthermore, there is no doubt that the basic aqueous mixture is more efficient in the removal of $^{14}C$ respect to the organic solvents. NaOH increases the production of carbonate (highly soluble in water) confirming that the next experiments have to be designed following this evidence, focusing on efforts to develop a "total green" procedure.

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