EUROPEAN COMMISSION

Community Research

SEVENTH FRAMEWORK PROGRAMME

CARBOWASTE

Treatment and Disposal of Irradiated Graphite and Other Carbonaceous Waste

Grant Agreement Number: FP7-211333

Technical Report T-4.3.3.a

Chemical decontamination by organic solvents treatments ultrasound assisted on LT-NPP i-graphite

Authors: Mauro Capone, Alfonso Compagno, Nadia Cherubini,
Alessandro Dodaro, Tiziana Guarcini

Reporting period: 01/04/2012– 31/03/2013

Date of issue of this report: 31/01/2013

Start date of project : **01/04/2008** Duration : **60 Months**

Project co-funded by the European Commission under the Seventh Framework Programme (2007 to 2011) of the European Atomic Energy Community (EURATOM) for nuclear research and training activities		
Dissemination Level		
PU	Public	
RE	Restricted to the partners of the CARBOWASTE project	**X**
CO	Confidential, only for specific distribution list defined on this document	

Title	**ENEA Technical Report T-4.3.3.a**

Classification: ***L***

Distribution list:

Internal:
Director UTFISST
Secretary UTFISST CATNUC

External:
CARBOWASTE Project Coordinator
CARBOWASTE Work Package 3 Leader
CARBOWASTE Work Package 4 Leader

Contributors: Mauro Capone, Nadia Cherubini, Alfonso Compagno, Alessandro Dodaro, Tiziana Guarcini

Rev.	DESCRIPTION	**Date**	*Author*	*Review*	*Emission*
0	Emission 1	31-01-13	Mauro Capone	Nadia Cherubini	Alessandro Dodaro
			UTFISST-CATNUC	UTFISST-CATNUC	UTFISST-CATNUC

CARBOWASTE		
Work package: 4 **Task: :** 4.3	**CARBOWASTE document no:** CARBOWASTE- -T-4.3.3.a	**Document type:** T=Technical Report
Issued by: ENEA (IT) **Internal no.:**		**Document status:** Draft

Document title

Chemical decontamination by organic solvents treatments Ultrasound assisted on LT-NPP Graphite

Executive summary

A new decontamination approach is studied for irradiated nuclear graphite with non-oxidizing organic solvents extraction combined with prolonged ultrasound bath. Three different organic solvents with good solvency properties and water-miscible (N-Methyl-2-pyrrolidone, N,N-Dimethylacetamide, N,N-Dimethylformamide) are tested on 15 samples of nuclear i-graphite from Latina NPP moderator. Removal efficiencies based on ^{14}C and ^{60}Co extraction were studied by means of LSC and γ-Spectrometry. Good results are shown by Dimethylacetamide (DMA) and Methylpyrrolidone (NMP) for Radiocarbon, with Dimethylformamide for ^{60}Co.

INDEX

1. Objectives of the Work.

The main aim of this Task is the Graphite Decontamination by Chemical Treatment to separate the long-lived radionuclides (^{14}C, ^{36}Cl, ^{60}Co, …) from carbonaceous waste by chemical treatment, important to reduce the long term risk.

The i-GF from Latina NPP, like as all the graphite coming from moderators exposed to a neutron flux (for Latina NPP is up to $5x10^{22}$ n/cm^2), presents a wide range and amounts of activation products.

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

The main idea is to apply an exfoliation process on the graphite by organic solvents (liquid-phase *exfoliation-like* process) to produce unfunctionalized and non-oxidized graphene layers in a stable homogeneous dispersion. 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 interplanar interactions, thanks to the dipole-induced/dipole interactions between graphenes 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.

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

After separating graphenes dispersion from the organic solution containing contaminants, the non-oxidized graphene/exfoliate powdered graphite would be useful in a host of applications in both research and industry.

2. Samples description.

2.1 Original Sample

As part of an agreement between ENEA and So.G.I.N., we received 15 cylindrical samples from Latina NPP. They are taken from the drilling of the core in two different radial positions (channel 7 and 8): from each sample were removed both the surface layer exposed to the fuel channel and the innermost layer; the approximate mean weight is 5 g.

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

In table 2.1 the masses of the samples, after the outer layer removal, are reported; the mean diameter is 1.7 cm and the mean height is about 1.0 cm (see Figure 2.1).

Table 2.1 - Irradiated-Graphite Samples weights in grams (g)

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

As mentioned, 7 samples come from the Channel 8 (08F08), while the other 8 from Channel 7 (07S07); the position of the samples is shown in fig. 2.2. For each of these 2 groups, the samples come from different level (*S*, Superior – *C*, Central – *I*, Inferior), as shown in fig. 2.3.

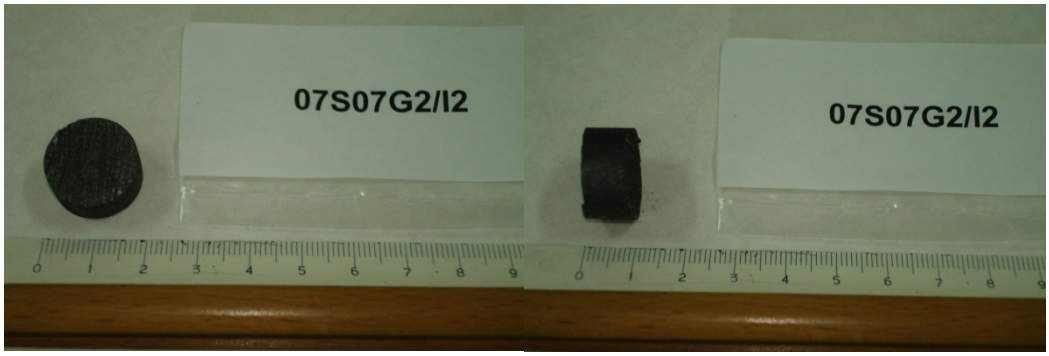


Figure 2.1 – One of the i-Graphite samples from Latina NPP

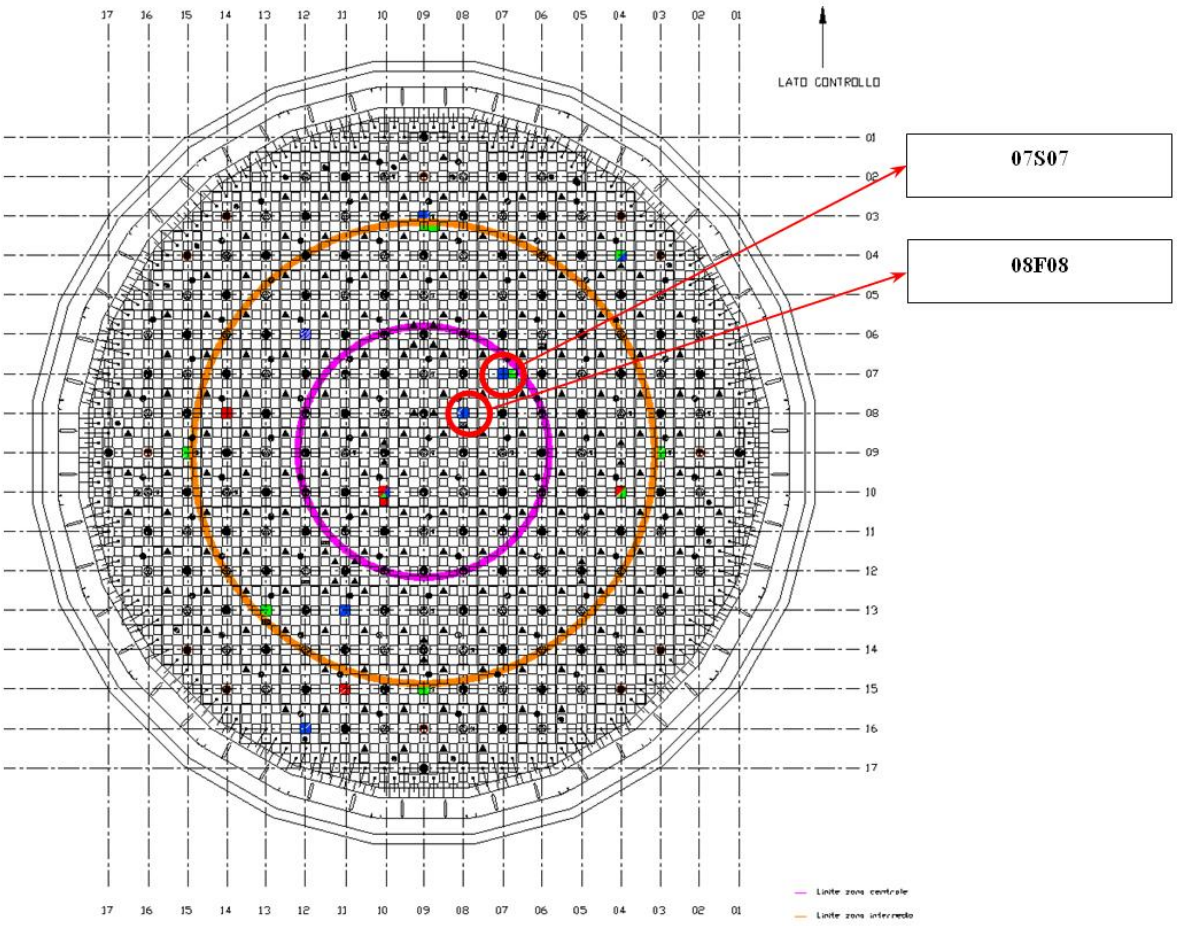


Figure 2.2 – Horizontal section of the core

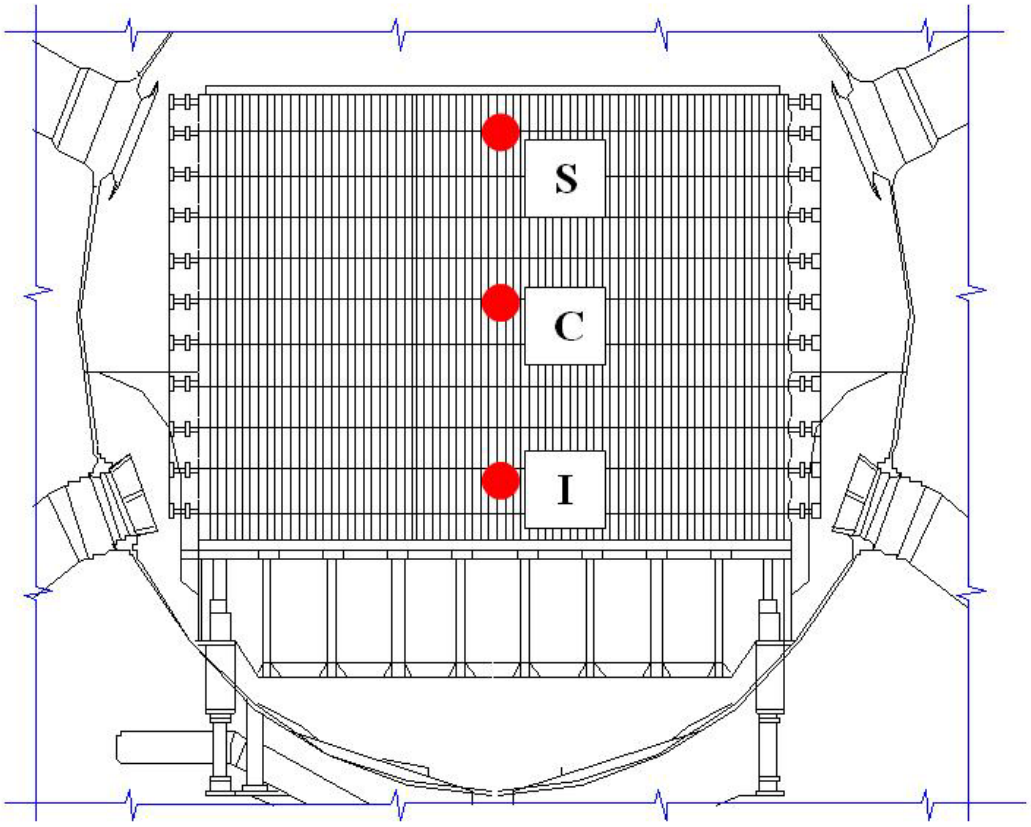


Figure 2.3 – Axial section of the core

2.2 Sample for chemical treatments

All the samples used in this work were firstly crushed by a miller with Titanium knives and then finely grinded by a miller with ceramic knives.
From each of them an representative homogenous aliquot were taken and weighted.

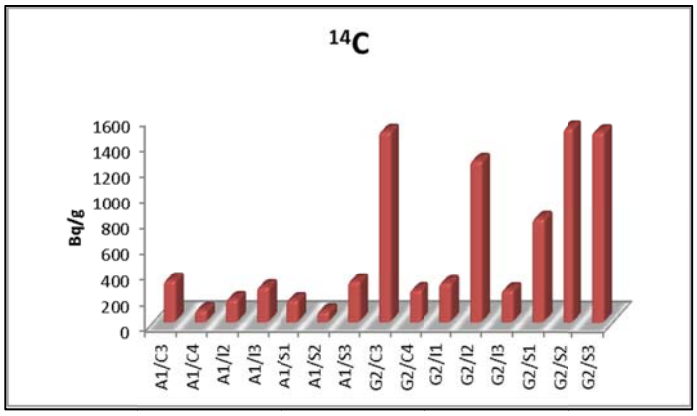
3. Localization of Impurities and Isotopes before Treatment

3.1 Radiocarbon Determination

Radiocarbon has been measured by Liquid Scintillation Counting after pre-treatment of an aliquot of each samples (about 0.12 g/sample) by acid digestion with H_2SO_4-HNO_3-$HClO_4$ mixture at 200°C in closed equipment under inert gas-flow (N_2). The ^{14}C (as CO_2) were trapped with washing bottles (Drechsel) with NaOH 0.1M. The solutions obtained are completely clear and colourless. An aliquot of each solution is taken has been added with Scintillation Cocktail and measured by Liquid Scintillation Analyser TDCR HIDEX 300SL in Dual-Label Mode with $^{3}H/^{14}C$ Reference Standards.
Technical data for Liquid Scintillation Counter HIDEX 330SL TDCR System:

- Multichannel Analysis

- Logarithmic MCA with 1024 channels
- Energy range beta's 0 - 2000 keV
- Efficiency: >95% for ^{14}C unquenched samples
- Background <10 cpm
- LLD (Bq/g) ^{14}C 0.0025



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

Figure 3.1 e Table 3.1 – Radiocarbon characterisation of the Latina NPP i-graphite sample made by Liquid Scintillation Counting

3.2 Gamma-Spectrometry

In order to identify gamma radioactive isotopes and to determine the amount of radioactive material, the samples has been characterized by means of a gamma spectrometry system.
The system operates with an high resolution HPGe coaxial detector, 50% relative efficiency, liquid nitrogen cooled, shielded by means of a lead cylinder (10 cm thick) with two collimation windows allowed: cylindrical (1 cm diameter and 20 cm length) or rectangular (2.5 cm X 10 cm X 20 cm). The internal side of the shield is Cu-lined, to reduce the effect of X-rays from lead. As regards signal analysis, the detector is connected to a Canberra Digital electronic chain and spectra are analysed by Canberra Genie-PC 2000.

The efficiency computation, made by the user, allows accurate efficiency calibrations to be performed rapidly for a wide variety of sample shapes, sizes, densities and distances between the sample and the detector.
To minimize the Minimum Detectable Activity and to reduce the external noises for the measurement, the samples has been inserted in a ultra-low background lead housing.
The Genie-PC software provides peak identification, data and error analysis, and sample quality assurance.

4. Graphite Decontamination by Chemical Treatment with Organic Solvents

The i-GF from Latina NPP, like as all the graphite coming from moderators exposed to a neutron flux (for Latina NPP is up to $5x10^{22}$ n/cm^2), presents a wide range and amounts of activation products.
This distribution of activated elements concerns the bulk of the samples, mainly in the closed porosity or between the typical graphite layers. Anyway, there are not usually involved chemical bonds. So that, in order to achieve an exhaustive and valid extraction for activation products, it is important to increase the surface area of the sample. This should allow to the solvent to reach the inner layers/areas (i.e. closed pores, crystallites, etc.) and extract contaminants in solution.

The main idea is to apply an *exfoliation-like* process on the graphite by organic solvents (liquid-phase exfoliation) to produce unfunctionalized and non-oxidized graphene layers in a stable homogeneous dispersion. 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 interplanar interactions, thanks to the dipole-induced/dipole interactions between graphenes 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 4.1).

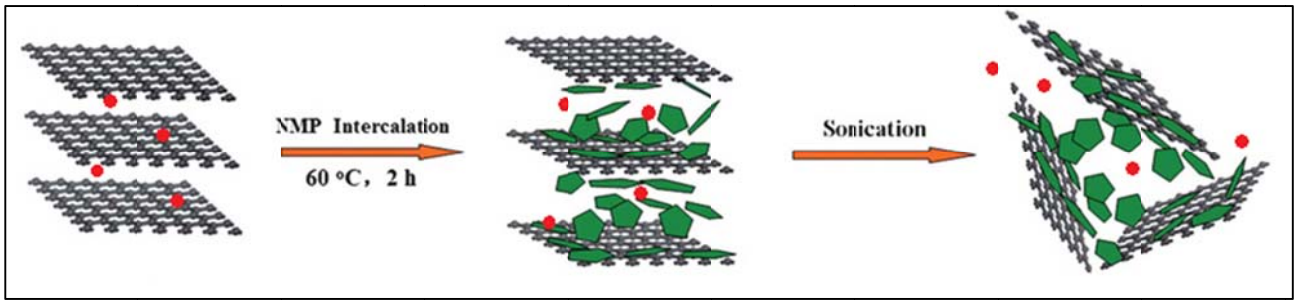


Figure 4.1- Representation of the main steps for the graphite exfoliation process promoted by organic solvents and ultrasound assisted

Moreover, no oxidation process is performed nor super-strong acid actions. This would lead to non-oxidized products so the graphite would be completely recovered as it is.
After separating graphenes dispersion from the organic solution containing contaminants, the non-oxidized graphene/exfoliate powdered graphite would be useful in a host of applications in both research and industry.

The main steps in this process are:

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

4.1. Organic Solvents

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

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

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

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

4.2. Sonication time

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

A. sonic energy input to the sample is sensitive to the water level;
B. exact position of the sample in the bath;
C. volume of the dispersion undergoing to sonication;
D. vessel/vials shapes.

Due to this equipment-related variability the results could differ and be critically depending on the sonication time.
In this work, we have chosen 10 hours with a 35 W Power Sonication Bath.

4.3. Centrifugation/Filtration

Although the right centrifugation rate should be widely tested in order to remove all large aggregates to be reprocessed by following exfoliation step, in this work we chose a high centrifugation rate (12000 rpm) followed by a filtration step. The supernatant liquid phases coming from the centrifugation are filtered on RC (Regenerated Cellulose) Filter Disk of 0.2 μ and the solutions are clear or greyish.

4.4. Experiments and results

We started to test the process considering the three common and widely used dipolar solvents, as mentioned in the section 4.1 of this report, for their good solvency abilities:

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

In this work, we performed a sonication bath for 10 hour in a 35W power device on sample of about 0.1 g of irradiated graphite samples described in sections 2.1 and 2.2 with 10 ml of each solvents. The volume of the solvents used has been chosen for the aim described in the section 4.1.
After sonication, the solution appear grey to dark in colour without a distinguishable sedimentation. They are left standing for a day with no changes in colour. After that, they are centrifuged for 1hour at 12000 rpm. Only the NMP/dispersion still presents dark coloration, the others were clear. All the samples/solutions were filtered on RC (Regenerated Cellulose) Filter Disk 0.2µ and undergone LSC/γ-Spectrometry.

^{14}C							
	Before	After					
		in DMA		in DMF		in NMP	
Sample	Bq/g	Bq/g	Rem. Eff (%)	Bq/g	Rem. Eff (%)	Bq/g	Rem. Eff (%)
08F08A1/C3	312,87	3,38	**1,08**	3,70	**1,18**	46,22	**14,77**
08F08A1/S3	306,18	11,44	**3,74**	1,61	**0,52**	71,89	**23,48**
07S07G2/S3	1467,70	20,01	**1,36**	0,77	**0,05**	80,58	**5,49**
07S07G2/S1	793,90	13,73	**1,73**	1,44	**0,18**	43,39	**5,47**
08F08A1/I3	260,92	72,99	**27,98**	20,54	**7,87**	15,47	**5,93**
07S07G2/C3	1471,64	21,44	**1,46**	2,17	**0,15**	29,19	**1,98**
08F08A1/S1	160,39	11,92	**7,43**	1,54	**0,96**	24,18	**15,08**
07S07G2/S2	1497,72	15,79	**1,05**	3,69	**0,25**	22,40	**1,50**
08F08A1/C4	82,22	22,48	**27,35**	3,15	**3,83**	9,82	**11,94**
07S07G2/I3	237,11	23,35	**9,85**	6,71	**2,83**	4,92	**2,07**
07S07G2/C4	238,92	7,17	**3,00**	6,45	**2,70**	23,96	**10,03**
08F08A1/I2	167,77	25,59	**15,25**	3,93	**2,34**	9,48	**5,65**
08F08A1/S2	72,12	12,03	**16,68**	0,88	**1,21**	8,10	**11,23**
07S07G2/I1	292,73	29,94	**10,23**	4,61	**1,58**	9,76	**3,33**
07S07G2/I2	1241,34	23,59	**1,90**	5,72	**0,46**	56,40	**4,54**

^{60}Co			
	Removal Efficiencies (%)		
	in DMA	in DMF	in NMP
Variation range on all samples	0.1 – 8.9	0.1 – 7.0	0.4 - 2.4

Tables 4.1 and 4.2 – Overviews of Removal Efficiencies for Radiocarbon and ^{60}Co

5. Discussions and Conclusions

Although the overall results seem to be relatively low, these are the first results obtained with this new kind of decontamination process **aimed to preserve the graphite as it is** and avoiding both oxidation of the same and completely dissolution as acidic leaching or extraction perform.
These first and earliest results show that the removal efficiencies in the experimental conditions we used are best for N,N-Dimethylacetamide (DMA) and N-Methyl-2-pyrrolidone (NMP) for ^{14}C removal, and N,N-Dimethylformamide (DMF) in the case of ^{60}Co. The logical answer could lie in the different chemical behaviour and bonding of the two radionuclides in the graphite matrix. Anyway, further investigations would prove the possibilities to reach an overall process able to extract a wide range of radionuclides despite of the differences in chemical properties of the elements.
Another point worth to be assessed is the sonication time plus the sonication power. The energy distributed for mass unit and time in a ultrasound bath is an important point to be investigated in order to reach an exhaustive desegregation (exfoliation-like) of the graphene layers making the intercalated compounds free from the matrix and dissolved in the solvent.

Moreover, a complete ICP-MS/γ-Spectrometry characterisation of the i-GF samples will be performed to validate the destructive and non-destructive measurements carried out. This should be the starting point for the subsequent definitions of the degree of decontamination, comparing these values to those coming from the decontaminations trial and works.
Further investigation will be performed to confirm the results achieved and to improve the organic solvent process. Thanks to the encouraging preliminary results obtained in this new exfoliation/decontamination in organic solvent route, it will planned a complete set of experiments to better define and set up the right process parameters. At this purpose, it will well defined:

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

6. Future activities

In addition to the procedures described at the end of the previous section and in collaboration with Nucleco SpA, it has been studied classic strong acid mixtures decontamination approaches for testing for future works the possibility of “combined” organic solvent/acid mixtures processes to obtain satisfying results and complete the overall decontamination steps.

At this purpose, 3 i-graphite samples coming from Latina NPP and similar to the ones used in this work as describe in sections 2.1, have been divided in 3 sections named S1, S2 and S3.
On the first section S1 of each sample a characterisation of ^{60}Co and ^{137}Cs were performed in order to know the exact quantity of each radionuclide before the different treatments. On the latter two sections acid mixtures leaching tests were tested according to 2 different approaches:

1. Leaching at 200°C (S2).
2. Leaching at room temperature (S3)

The instruments used for the measurements and their characteristics are described as follow:

γ-Spectrometer (for ^{60}Co and ^{137}Cs):

- GEM detector
- Energy Range 50-2000 keV
- 37% Relative Efficiency (1.33 MeV ^{60}Co)
- 1.33 MeV ^{60}Co Resolution 1.90 keV
- Liquid nitrogen cooled

6.1. Leaching Test at 200°C with acid mixtures

The sections S2 of each sample were first grinded to powder and then put in a reflux system composed by a glass Pyrex flask and a water circulation refrigerator together with the different acid mixtures for 20 min. The acid mixtures were as follow:

- Sample **04F10A1/I1**: H_2SO_4/H_2O_2 1:1 v/v
- Sample **10F10A1/I4**: HNO_3/ H_2SO_4 1:1 v/v
- Sample **11F13A1/C4**: HNO_3/HCl 1:1 v/v

After cooling, the solutions were filtered on vacuum Millipore filtration system and then measured by γ-spectrometry.

6.2. Leaching Test at room temperature with acid mixtures

For this test only 2 sections were used instead of the 3 as in the previous test.
Each sections (S3) of the former sample has been leached with different acid mixtures as follow:

- Sample **10F10A1/I4**: HNO_3/ H_2SO_4 1:1 v/v
- Sample **11F13A1/C4**: HNO_3/HCl 1:1 v/v

The samples were kept dipped into the solutions for three days and after were measured.

6.3. Results and discussions on the Leaching Tests

The results obtained from the leaching tests previously mentioned are shown in the Tables 6.1 and 6.2.

Leaching at 200°C	*Removal Efficiency (%)*	
Sample	**^{60}Co**	**^{137}Cs**
04F04A1/I1 H_2SO_4/H_2O_2	78	72
10F10A1/I4 HNO_3/H_2SO_4	94	78
11F13A1/C4 HNO_3/HCl	79	3

Tables 6.1- Results of the tests on S2 sections at 200°C with acid mixtures

Leaching at room temperature	*Removal Efficiency (%)*	
Sample	**^{60}Co**	**^{137}Cs**
10F10A1/I4 HNO_3/H_2SO_4	6	10
11F13A1/C4 HNO_3/HCl	8	19

Tables 6.2- Results of the tests on S3 sections at room temperature with acid mixtures

We can states that in the leaching test at 200°C the best results are reached with mixtures containing H_2SO_4. On the other count the mixture HNO_3/HCl seems to not act as best regarding to the ^{137}Cs. Meanwhile, the leaching at room temperature shows low removal efficiency values in all the cases. It would be interesting to perform, in this last case, a long term leaching test although the results obtained with the warm acid mixtures seem to be more preferable than at room temperature.

In a perspective glance on the next works, it would be interesting to combine the two main procedures illustrated in this work (organic solvents plus acid mixtures) in order to gain a synergic action for an exhaustive removal treatment on i-graphite.

7. References

1. Michael F. L'Annunziata. Handbook of Radioactivity Analysis, Second Edition, 2003, Elsevier Science (USA)

2. Jukka Lehto, Xiaolin Hou. Chemistry and Analysis of Radionuclides, 2011, Wiley-VCH Verlag GmbH & Co KGaA, Weinheim (DE)

3. Umar Khan, Arlene O'Neill, Mustafa Lotya, Sukanta De, and Jonathan N. Coleman, High-Concentration Solvent Exfoliation of Graphene, *Small* 2010, 6, No.7, 864-871

4. Eun-Young Choi, Won San Choi, Young Boo Lee and Yong-Young Noh, Production of graphene by exfoliation of graphite in a volatile organic solvent, *Nanotechnology*, 22 (2011), 365601 (6pp)

5. Yenny Hernandez et al., High-yield production of graphene by liquid-phase exfoliation of graphite, *Nature Nanotechnology*, Vol. 3, September 2008, 563-568

6. Athanasios B. Bourlinos et al., Liquid-phase Exfoliation of Graphite towards Solubilized Graphenes, *Small* 2009, 5, No. 16, 1841-1845