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CAST

Vandellós I Graphite Compilation Report: Thermal Decontamination and IGM Waste Form Results WP5 (D5.13)

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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:
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CAST

VANDELLÓS I GRAPHITE COMPILATION REPORT: THERMAL DECONTAMINATION AND IGM WASTEFORM RESULTS from WP5 (D5.13)

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VANDELLÓS I GRAPHITE COMPILATION REPORT: THERMAL DECONTAMINATION AND IGM WASTEFORM RESULTS from WP5 (D5.13)

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1 Introduction

The radiocarbon content of irradiated graphite is the highest obstacle to the management of Spanish irradiated graphite coming from Vandellós I NPP as L&ILW, due to it exceeding the maximum permitted inventory for the near surface repository of EL CABRIL. Therefore the extraction of ^{14}C (and tritium also), with keeping the integrity of the graphite structure or/and the encapsulation of graphite in an appropriate waste form, show up as potential management options to be studied.

The encapsulation of graphite is based on its conversion into an Impermeable Graphite Matrix (IGM) [1] by hot pressing as an alternative waste treatment option, if the thermal treatment fails. Beside the usage of a long term stable inorganic binder material, the resulting material is homogenously filled and therefore mechanical damage would not reopen an unsealed pore system.

It has been demonstrated that irradiation of graphite produces changes in its structure than promote the corrosion of the material [2], leaching behavior from graphite is also directly related to the open pore structure of graphite.

All the described effects on the graphite structure could be neglected, if the pore system could be sealed for disposal-relevant time scales. The repository safety assessment could be modified by the leaching products speciation and, consequently, the leached gaseous and liquid species have to be studied in order to determine the mobility of radiocarbon in the repository environment. Investigations were performed also in relation to the utilization of IGM for the production of an improved waste form out of irradiated graphite for final disposal.

The behavior of IGM was investigated in the contact with different aqueous media, deionized water and granitic- bentonite water. The leaching experiments were being performed with virgin graphite to determine the corrosion progress by mass loss and chemical analysis of the leachates. In particular, the corrosion behavior of glass will be a key parameter for the applicability of IGM as a waste matrix.

The obtained results of the investigations with IGM on virgin graphite show the principal applicability of IGM. A second phase of investigations was performed with i-graphite from Vandellós, to determine the leaching rates of the incorporated radionuclides.

World first IGM [1] samples made with irradiated graphite have been manufactured with this technology in CIEMAT.

Up to now, seven leaching steps on samples of graphite cylinders and IGM have been performed. In this report, is summarised the results available so far but the leaching experiments are going on. The set-up of the equipment for speciation studies (GC-MS and IC) was completed and the analysis methods for both gas and liquid samples were established.

The reactor Vandellós I has been operated with CO_2 as coolant and significant amounts of graphite have already been oxidized.

The thermal treatment of i-graphite will try to separate ^{14}C contents without a significant corrosion of the matrix, in order to maintain the properties and mass of the graphite.

The aim of this investigation was the validation of whether a ^{14}C decontamination can also be achieved with graphite from Vandellós I.

In order to tune-up the experimental system and characterize the material to be treated and its behavior, in the assay the influence of processes that a priori are the most relevant parameters were studied. These parameters are: Furnace Temperature, atmosphere in which the treatment will take place (inert oxidant,..), gas flux, graphite particle size and treatment time.

The parameters were optimized in function of the obtained results and all of them are essential to selective recovery of ^{14}C.

2 Impermeable Graphite Matrix (IGM)

2.1 *Introduction*

Graphite is a geologically stable material proven by its natural occurrence but its porous structure enables the penetration of aqueous phases into the graphite and therefore radionuclides can be leached. However, graphite could be transferred into a long term stable impermeable graphite matrix (IGM) which would inhibit ingress of water and disable the release radionuclides resulting in a safer final disposal.

Therefore crushed graphite mixed with a suitable glass powder has been pressed at high temperature in a moderated vacuum. A Vacuum is required to avoid gas enclosures in the obtained products, which themselves have densities that have to be above 99% of theoretical density of graphite blocks to be disposed.

An optimized protocol to manufacture the IGM specimens in the hot vacuum press was established through performing a set of experiments including characterization of obtained specimens.

The relative amounts of glass and graphite are chosen according to the pore volume of the graphite to be conditioned. A ratio 80-20 graphite-glass is adopted to maximise the graphite conditioned according to the pore volume determined in previous studies [3]. The method allows the production of encapsulated graphite without increasing the disposal volume.

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

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

The leachants used to investigate the long term behavior of IGM waste form are deionized water and granitic-bentonite water. Granitic-bentonite water was selected to simulate the conditions of potential Spanish HLW deep geological disposal, and deionized water was chosen as a reference leachant due to it being the more conservative case. In the absence of ions, this leachant becomes the best media for the ions from the waste form to be leached.

2.2 *Manufacturing IGM samples by hot vacuum press*

ALD- France (FNAG) fabricates a specific hot vacuum press at lab scale to manufacture the IGM specimens in control area. The system used in the experiments is shown in Figure 1.

Figure 1. Hot Press

The procedure to prepare the specimens is:

- ✓ Graphite is grand to obtain graphite powder (particle size ∅ ≤ 250 µm)
- ✓ The obtained graphite powder is mixed with the glass in the appropriated proportion (usually 80% of graphite- 20% of glass), in order to obtain a density ≈ 2,2 g/cm^3 in the final form.
- ✓ The mixture is introduced into the pressing tool (Figure 2). Previously the tool wall has to be covered with graphite foil to prevent the mixture baking together with the wall of the tool.

Figure 2. Pressing Tool of 2 cm diameter

The tool is mounted into the furnace, Figure 3.

Figure 3. Inside view of furnace

- ✓ A specimen automatic fabrication process is applied
- ✓ The cooled specimen is demolded (extracted) from the tool by a hydraulic press and is weighed with graphite foil, afterwards the foil is mechanically (by a cutter and sandpaper) removed from the specimen. The obtained specimens are shown in the following picture.

Figure 4. IGM samples

The procedure for IGM with i-graphite is the same as that described above. The procedure is performed in this case into a flexible glove box which was set up in a hood (Figure 5).

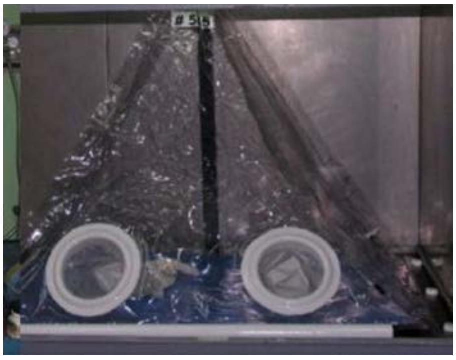

Figure 5. Glove box

With this methodology two IGM samples have been manufactured for this project. The same graphite [4] used for cylindrical blocks; Ref. GC-2 was selected. The density was measured by Archimedes balance.

The leaching process is described in section 2.3. Teflon beakers, under high dose rates contaminate leachant with small amounts of fluoride, which complexes certain nuclides (as was demonstrated at Jülich with Th (IV) in Teflon beakers[1]). The original beakers were therefore changed from Teflon to PEEK (Polyether ether ketone) in order to avoid misleading in the leaching results in this study.

To solve the described problem of Teflon, containers of PEEK have been acquired used with the IGM samples. The volume of these containers is less than the PTFE containers, so only 100 ml of leachant was used.

2.3 *Leaching Procedure*

Leaching experiments were performed with deionized water (Milli-Q® water) as the leachant for sample IGM-4 and granitic-bentonite water (Table 1) as the one for sample IGM-5. The characteristics of leaching IGM specimens (4-I and 5-I) are collected in Table 2 and Table 3 respectively.

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[1] Private Communication: B.G. Brodda, J.Fachinger; Research Centre Jülich

Table 1. Granitic-bentonite water composition

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

The selected reactors were high pressure stainless steel containers with PEEK beaker inside. The leaching process [5], [6] of the IGM specimens was performed as follows:

- ✓ The tests were performed at room temperature (approx. 20-25° C). Negligible amounts of leachant by vaporization have been registered during the leaching time at this temperature range.
- ✓ The specimen is suspended in 100 ml of leachant by means of a PFTE thread and surrounded by at least 1 cm of liquid in all directions (Figure 6). The vessel (total volume is 120 ml) was cleaned up with deionized water at the beginning of the leaching test and after each step.

Figure 6. Leaching containers for deionized water and granitic-bentonite water

The initial gas phase composition consists on synthetic air (21 % oxygen, 79 % nitrogen) supplied from a high-pressure gas bottle.

The leaching steps frequency was selected in consideration of materials, radioactivity concentrations and the sensitivity of methods and equipment to be use for different measurements.

- ✓ Based on that, it was planned to renew both the gas and the leachate after approximately 14, 28, 56, 90, 180 and 360 days from the start of the test.
- ✓ After each step, the gas sample (volatile species) is collected through the gas sample extraction valve by means of a gas tight syringe and immediately injected into the GC-MS system.

Figure 7. The gas sample extraction by a syringe

- ✓ The container is opened; the specimen is withdrawn from the leachant, and finally transferred to a HDPE (High Density Polyethylene) bottle. The liquid is conveniently stored for other analyses.
- ✓ Once stored the leachate is stored, the PEEK bottle is cleaned up with deionized water, refilled with fresh leachant, the specimen immersed in the liquid and the reactor closed with its headspace purged with synthetic air.

2.3.1Characterization

^{14}C Separation and Determination

The ^{14}C in the leachate was separated quantitatively by a catalytic furnace (Harvey OX500) using specific trapped solutions

Activity of ^{14}C in the leachate was analyzed by LSC systems (Packard Tricarb 3110 TR/LL LSC and Quantulus LSC system

Ionic Chromatography.

Determination of organic dissolved species (carboxylic acids) was undertaken with an IC Dionex ICS-900 Ion Chromatography System with Ionic Reagent Free Controller (RFC) with an AS11-HC column.

The results of the deionized water leachates were obtained with the column AS-11, with a gradient of concentrations (1.5 mM KOH (0-8 min); 40 mM KOH (27 min) and 1.5 mM KOH (35-40 min) and a flow of 1 mL/min

Gamma Spectrometry

Gamma emitters were measured in the leachate with a Canberra BEGe 3830 HPGe Detector. In the case of deionized water only in the first step is it possible to find ^{137}Cs, close to MDA (Minimum Detectable activity).

Gas Chromatography.

The gas and leachate volatile species were measured with an Agilent GC-MS 7890B system (Agilent DB624UI 60m column type for liquid samples and Molsieve 5A Porabond Q column for permanent gases and CO_2).

The methodology to analyse leaching gases in the optimal conditions with a Molsieve 5A column and alcohols and aldehydes with DB-624UI (L = 60 m; ID = 0.25 mm and F = 1.40 µm) was developed throughout the project.

2.4 *Leaching results and discussion*

In this section is described the characteristics of waste form specimens, primary waste (i-graphite), and leachant physicochemical properties. Also explanations of experimental evidence are given in the framework of the knowledge acquired in the project.

The main properties studies are:

- ✓ Macroscopic physical characteristics of specimens
- ✓ Activity of ^{14}C of the waste form and leachant
- ✓ pH and electrical conductivity (EC) of leachant
- ✓ Identification of volatile carbon species in leachate gases
- ✓ Identification of solved gaseous carbon species in leachant
- ✓ Identification and concentration of carboxylic acid in the leachant
- ✓ Leaching rate of ^{14}C and the correlation with other gamma emitters (^{60}Co and ^{137}Cs)

Characteristics (size and weight) of the specimens used in the experiments are shown in Table 2:

Table 2. Physical properties

Sample Ref.	**Mass (g)**		**H_{avg} (mm)**	**$Ø_{avg}$ (mm)**	**ρ (g/cm^3)**
IGM-4	Total	7,6945	11,50	20,67	2,04
	i-graphite	6,2478			
IGM-5	Total	7,8097	11,01	20,70	2,01
	i-graphite	6,1556			

The initial activities of the specimens are indicated inTable 3:

Table 3 . Activity (Bq/g)

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

These activities are determined by non-destructive methodologies using numerical calibration (ISOCS). In fact, ^{14}C is separated by a destructive assay system due to the use of an automatic catalytic furnace, but in these experiments, as the amount of sample used is lower than 10 mg, the methodology is considered a non-destructive assay. Radiocarbon activity was calculated by the average of the measures obtain by LSC.

The pH and electrical conductivity of leachant and leachate are determined before and after each leaching step (see Table 4).

Table 4. pH and EC control of leaching solutions

Media	**Leaching Period**	**pH**		**EC (µS/cm)**	
		Initial	**End**	**Initial**	**End**
Deionized Water IGM-4	Period 1 (13 days)	5,72	8,99	3,55	46,5
	Period 2 (28 days)	6,04	8,08	2,68	18,88
	Period 3 (59 days)	5,87	8,03	3,85	19,5
	Period 4 (91 days)	5,73	8,01	1,57	9,59
	Period 5 (184 days)	5,29	6.97	1,89	8,79
	Period 6 (215 days)	5,91	6,86	1,47	3,55
	Period 7 (356 days)	5,82	6,92	1,88	8,77
Granite-Bentonite Water IGM-5	Period 1 (13 days)	7,06	8,13	21400	22000
	Period 2 (28 days)	7,24	7,04	20400	21300
	Period 3 (59 days)	7,31	7,11	21900	21900
	Period 4 (91 days)	7,01	7,14	21900	18960
	Period 5 (184 days)	6,83	6,92	19320	21400
	Period 6 (215 days)	6,34	7,36	21500	21500
	Period 7 (356 days)	7,47	7,00	20400	20000

In the case of granitic bentonite water, the pH and EC are practically the same before and after each step. With deionized water the pH and the EC increase which means the amount of ions increase in the leachant.

To verify this, the concentrations of the ions found in the leachate in the crystal matrix studies, as already mentioned in the introduction, have been represented for two samples. As a comparison, the electrical conductivity is also represented. It is observed that the increase in conductivity coincides effectively with the presence of dissolved ions

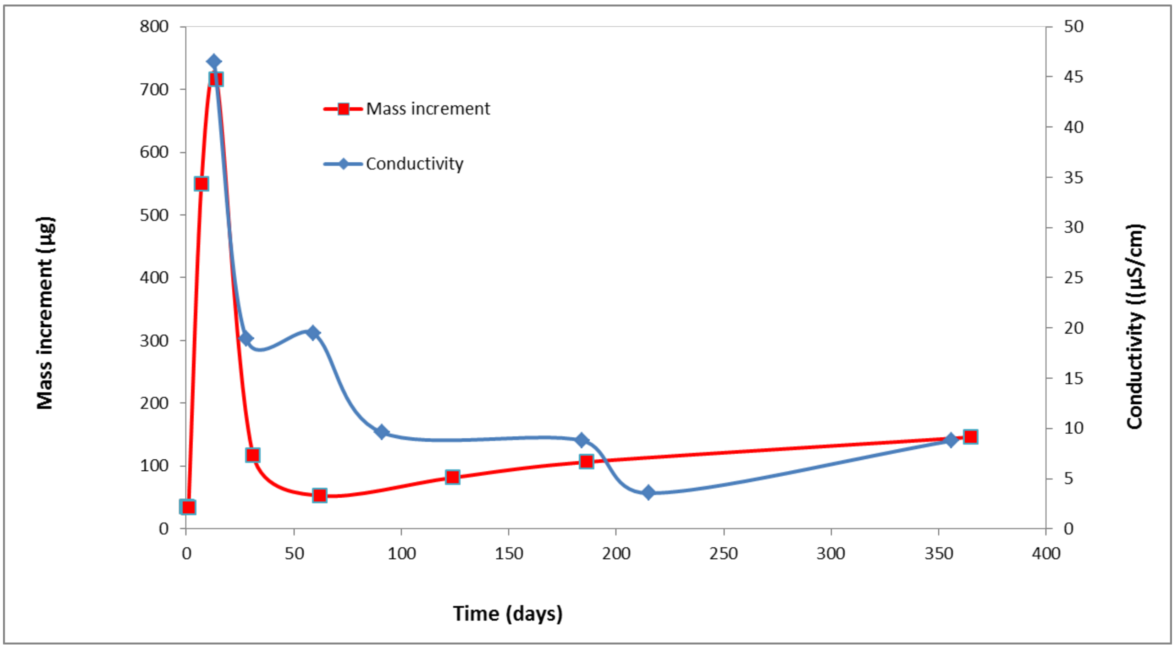

Figure 8. Mass increment versus conductivity of IGM H-037 9-5-1 in deionized water.

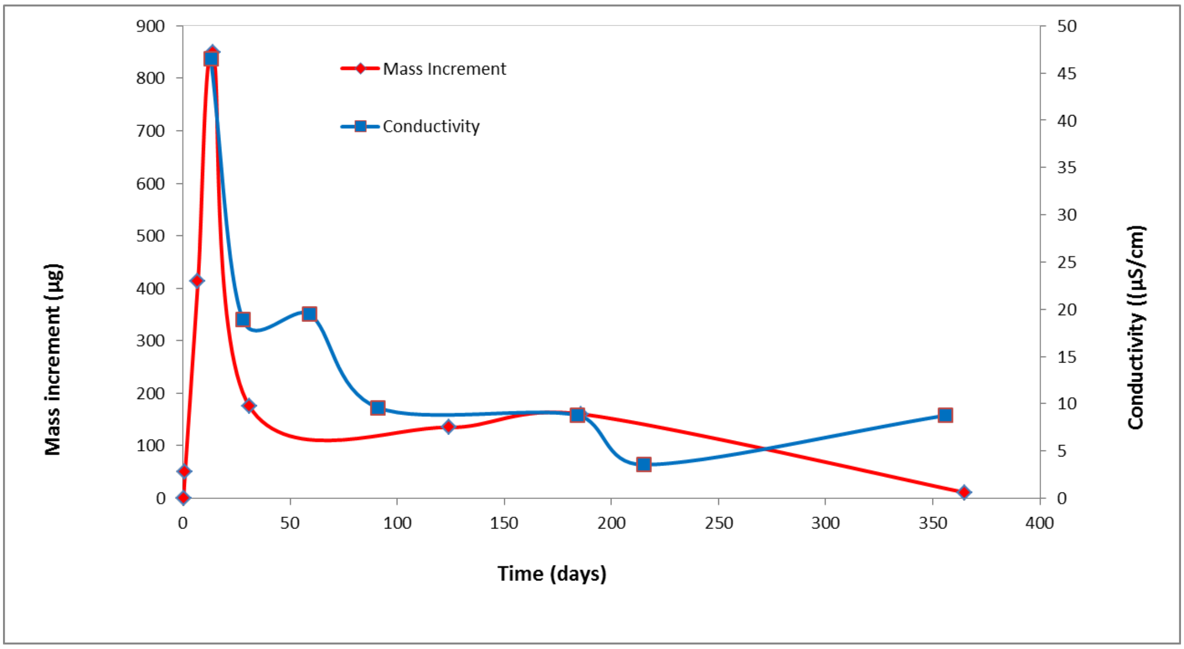

Figure 9. Mass increment versus conductivity of IGM H-037 9-5-1 in deionized water

The additional increase of the ion concentration by dissolution may result in ion concentrations in the leachant leading to the precipitation of secondary phases.

2.4.1Results of Organic Carbon Compound

The results of the deionized water leachates, are shown in Table 5.

Table 5. Organic carbon leached in Deionized water

	Acetate		Formate		Oxalate	
	[] (mg/L)	U (mg/L)	[] (mg/L)	U (mg/L)	[] (mg/L)	U (mg/L)
Day 13	< 0.03	---	<0.05	---	<0.03	---
Day 28	<0.03	---	**0.07**	**0.01**	**0.13**	**0.04**
Day 59	<0.03	---	<0.05	---	<0.03	---
Day 91	<0.03	---	**0.12**	**0.01**	<0.03	---
Day 184	<0.03	---	**0.09**	**0.01**	<0.03	---
Day 215	<0.03	---	**0.03**	**0.01**	<0.03	---
Day 356	<0.03	---	<0.02	---	<0.03	---

*[]: Concentration, U: Uncertainty

The organic carbon present in the leachates are formate ($HCOO^-$) (in samples from day 28, 91, 184 and 215) and oxalate $(COO)_2$ (only sample from day 28).

Organic carbon leached to granitic-bentonite water was not measured due to the presence of high concentrations of other anions that mask the detection of carboxylic anions. Additionally the expected concentrations of carboxylic acids in the leachant are also low, independent of the macro-components that interfere in the determination.

2.4.2 ^{14}C results and gamma emitters

The results are shown in the following tables:

Table 6. ^{14}C leached in Deionized Water

	^{14}C Bq/mL
IGM-AD-13	<4.98E-02
IGM-AD-28	<4.96E-02
IGM-AD-59	<5.34E-02
IGM-AD-91	<5.42E-02
IGM-AD-184	<5.37E-02
IGM-AD-215	<5.33E-02
IGM-AD-356	<2.3E-02

Table 7. ^{14}C in Granitic-Bentonite Water

	^{14}C Bq/mL
IGM-AG-13	<5.11E-02
IGM-AG-28	<5.05E-02
IGM-AG-59	<5.39E-02
IGM-AG-91	<5.38E-02
IGM-AG184	<5.17E-02
IGM-AG-215	<5.38E-02
IGM-AG-356	<2.1E-02

As can be observed, all values obtained are lower than the Minimum Detectable Concentration (MDC), it can be concluded that the leaching rate is below a certain limit, which can be calculated from the detection limit.

The equation is:

$$\mathbf{Rn = (A_n/A_o)*(V/S)*(1/t_n)}$$

Where:

A_o: Initial Activity,(Bq)
A_n:Activity in the leachant in the step n, (Bq)
V: Volume (cm^3)
S: Apparent surface, (cm^2)
T_n: Duration of the step n, (days)

The leaching rate calculated in this way is called "incremental leaching" rate, it is expressed in the units given by ENRESA in the acceptance criteria of the surface disposal of radioactive waste located in El Cabril. This equation is based in the norm ISO 6961-1982(E) with some modifications. References [5] and [6]

This leads to an maximum leaching rate (Rn) for ^{14}C of less than 6,15 E-09 cm/day.

Table 8. Leaching Rates of ^{14}C in deionized and Granitic Bentonite water

Day	t_n	^{14}C R_n (cm/day) Deionized water	^{14}C R_n (cm/day) Granitic Bentonite water
13	13	< 6,00E-09	< 6,15E-09
28	15	< 5,17E-09	< 5,26E-09
59	31	< 2,70E-09	< 2,72E-09
91	32	< 2,65E-09	< 2,63E-09
184	93	< 9,03E-10	< 8,69E-10
215	31	< 2,69E-09	< 2,71E-09
356	141	< 2,55E-10	< 2,33E-10

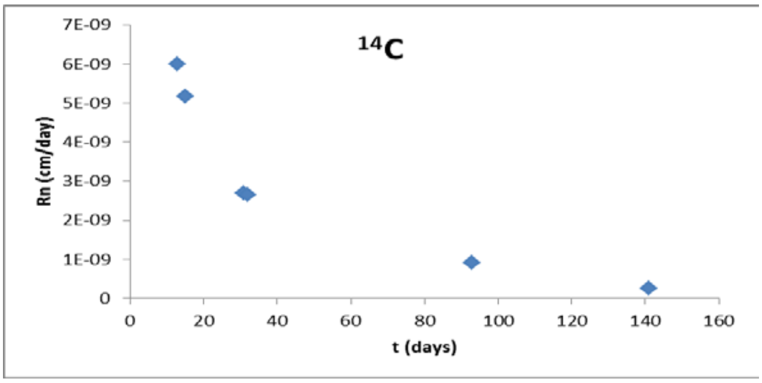

Figure 10. Leaching rates of ^{14}C in Deionized water

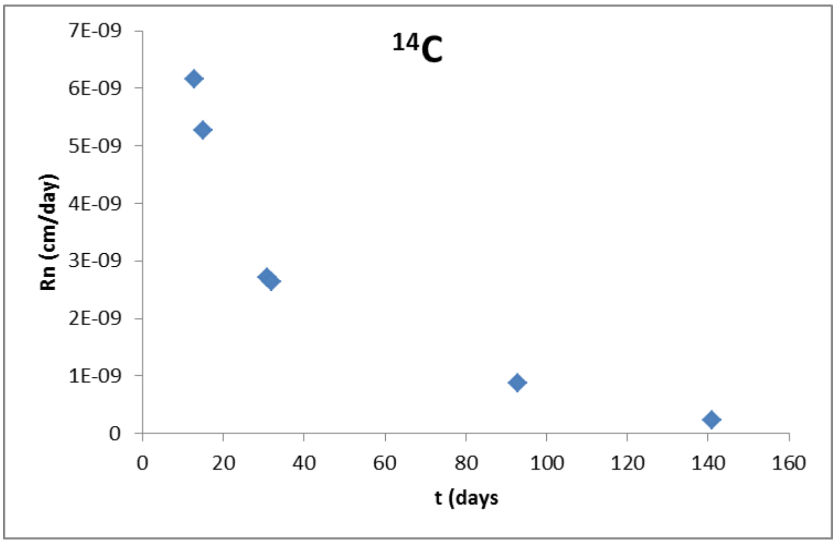

Figure 11. Leaching rates of ^{14}C in Granitic Bentonite water

Table 9. Activity ^{60}Co and ^{137}Cs in deionized Water

Day	^{60}Co (Bq/ml)	U(%)	^{137}Cs (Bq/ml)	U(%)
13	< 2,71E-3	---	5,15E-03	20,39
28	< 2,52 E-3	---	< 3,10E-3	---
59	< 2,67E-3	---	< 3,17E-3	---
91	< 3,48E-3	---	< 3,70E-3	---
184	< 2,23E-3	---	< 2,02E-3	---
215	< 3,67E-3	---	< 3,84E-3	---
356	< 2,74E-3	---	< 2,79E-3	---

The activity concentration is below the detection level except for ^{137}Cs in the first leachate for day 13. This could be a surface contamination. With these data it is impossible to establish a leaching trend for this radionuclide. Assuming the detection limit as a release rate, the following maximum leach rate could be calculated: ^{137}Cs < 1e-3 Bq/day

The principal beta-gamma emitters detected are ^{60}Co and ^{137}Cs in Granitic- bentonite water. The results obtained a long leaching process are indicated in Table 10.

Table 10. Activity of ^{60}Co and ^{137}Cs in Granitic Bentonite water

Day	^{60}Co (Bq/ml)	U(%)	^{137}Cs (Bq/ml)	U(%)
13	3,23E-03	30,96	7,66E-02	3,51
28	< 2,84E-03	---	4,21E-02	4,56
59	3,40E-03	29,41	4,85E-02	4,29
91	< 3,20E-03	---	2,80E-02	6,145
184	4,39E-03	22,78	3,10E-02	4,615
215	---	---	9,65E-03	12,33
356	1,24E-02	6,925	4,26E-02	4,53

The percentage leached of ^{60}Co and ^{137}C of the total contains in the piece (80% graphite, 20% of silicate) are shown in the Table 10:

Table11. Percentage leached of ^{60}Co and ^{137}Cs in Granitic Bentonite water

Day	% leached	
	^{60}Co	^{137}Cs
13	0,06	1,03
28	0,05	0,57
59	0,06	0,65
91	0,05	0,38
184	0,08	0,42
215	---	0,13
356	0,23	0,57

In all steps less than 0.1% of ^{60}Co was leached except at the step of 356 days, which is higher. For ^{137}Cs, less than 1% of ^{137}Cs was leached except in the first step.

Regarding the main beta-gamma emitters detected in the leaching test with Granitic-Bentonite water, in the Table12 are shown the leaching rates (R_n) of ^{137}Cs and ^{60}Co.

Table12. Leaching Rates of ^{60}Co in Granitic Bentonite water

Day	t_n	^{60}Co R_n (cm/day)	^{137}Cs R_n (cm/day)
13	13	1,03E-05	1,73E-04
28	15	3,68E-06	4,43E-05
59	31	2,38E-06	2,42E-05
91	32	1,08E-06	9,06E-06
184	93	9,85E-07	4,96E-06
215	31	-	1,32E-06
356	141	1,44E-06	3,52E-06

The data of the leaching rate of ^{60}Co versus the time are shown in the Figure 12.

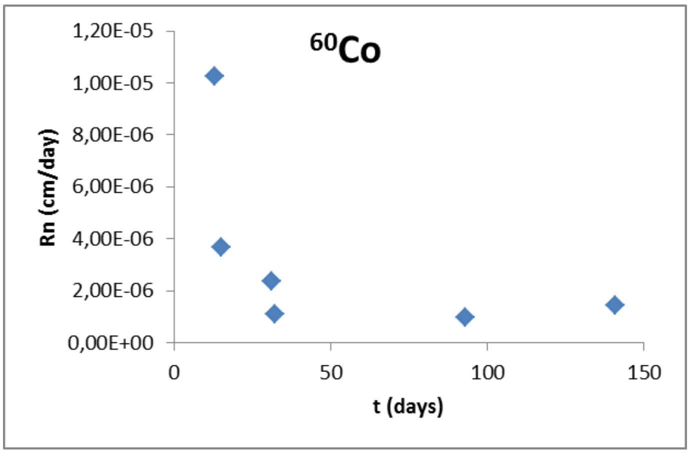

Figure 13. Leaching rates of ^{60}Co in Granitic bentonite water

The data of the leaching rate of ^{137}Cs versus the time are shown in the Figure 14.

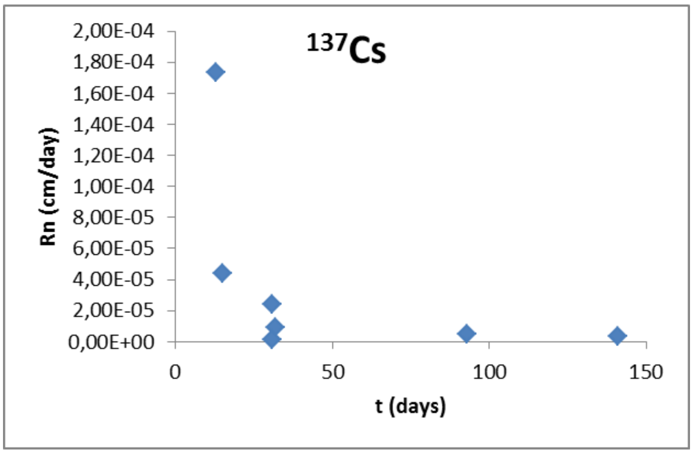

Figure 15. Leaching Rates of ^{137}Cs in Granitic Bentonite water

The obtained results reveal a difference in leaching behaviour in deionized water and granite-bentonite water which requires further more detailed investigations of this effect. However the low leaching rates (except the fast release fraction after 13 days which are related to surface effects) indicate the enclosing potential of IGM.

2.4.3 Gas and Leachate Volatile Species by GC-Mass Spectrometry

The assays to analyse CO was performed in isothermal conditions (70 ºC) and with a split flow of 50 mL/min. The GC-MS calibration curve applied is shown in Figure 16.

The assays to analyse alcohols and aldehydes was carried out with the following gradient of temperature:

- ✓ 40 ºC (2 min);
- ✓1 ºC/min to 45 ºC (5 min.);
- ✓1 ºC/min to 50 ºC (5 min) and
- ✓50 ºC (2 min) with a Split 100:1.

The technique of head space sampling was used with 30 seconds of incubation time at 40ºC.

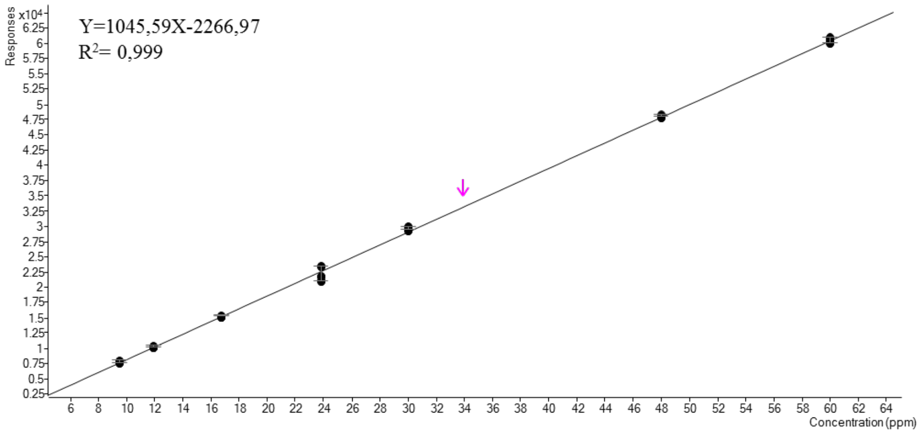

Figure 17. Calibration curve applied for CO determination

As an example, a chromatogram corresponding to 13 days leaching is shown in Figure 18:

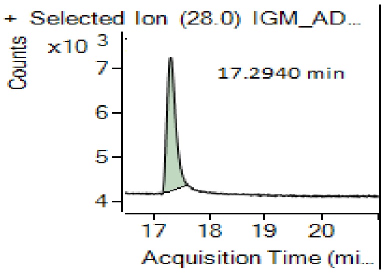

Figure 19. Chromatogram corresponding to 13 days

The results of CO and volatile species produced in the different steps of the process are shown in Table 13.

Table 13. Detected concentration of CO and volatile organics by GC-MS in Granitic Bentonite water

	CO		**Formate**		**Oxalate**	
	[] mg/L	**U mg/L**	**[] mg/L**	**U mg/L**	**[] mg/L**	**U mg/L**
Day 13	30,9	---	Not Detected		Not Detected	
Day 28	10,4	---				
Day 59	< 3,5	---				
Day 91	---	---				
Day 184	---	---				
Day 215	---	---				
Day 356	---	---				

Alcohols and aldehydes have not been detected in any step of the leaching process, the absence of a signal for these organics could be due to there being not enough time to form these molecules from the graphite or there were no thermodynamic and kinetic conditions the formation from the materials of the waste form.

On the other hand, CO has been detected, but it is not possible to determine the presence of ^{14}C in CO due to a technique to trap this gas not being available.

3 THERMAL TREATMENT

3.1 *Introduction*

There is 3680 tons of i-graphite, mainly from Vandellós I, in Spain to be managed as radioactive waste. This i-graphite contains long lived nuclides such as ^{14}C in such amounts that is not allowed to dispose of this waste in the ENRESA-EL CABRIL near surface repository for I&LL active waste. Therefore it is necessary to undertake R&D in decontamination methods that enable the transfer of i-graphite to a waste form which fulfills the Waste Acceptance Criteria (WAC). This is the origin of the necessity of extracting this radionuclide from the graphite.

It is demonstrate in other i-graphite [7] types that thermal treatment is effective in the selective decontamination of radiocarbon. Chemical behavior of ^{14}C is not different of ^{12}C, only different bonds of activated forms or different positions in the structure of i-graphite can be distinguished and for this reason the release of ^{14}C also implies the release of ^{12}C and consequently a corrosion of the treated matrix [8], [9].

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

$$C+O_2 \rightarrow CO_2$$

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

To perform thermal treatment, the system elements are:

- ✓ A rotating furnace from ALD France,
- ✓ A particle filter,
- ✓ A mass flow controller system,

- ✓ A pneumatic sample injector,
- ✓ A single quadrupole mass spectrometer by AMG Coating,
- ✓ A catalytic oxidizer furnace by Nabertherm that contains a nickel dioxide catalyser,
- ✓ Four washing bottles (special design for trapping the gases of interest (with the elements /nuclides to be studied).

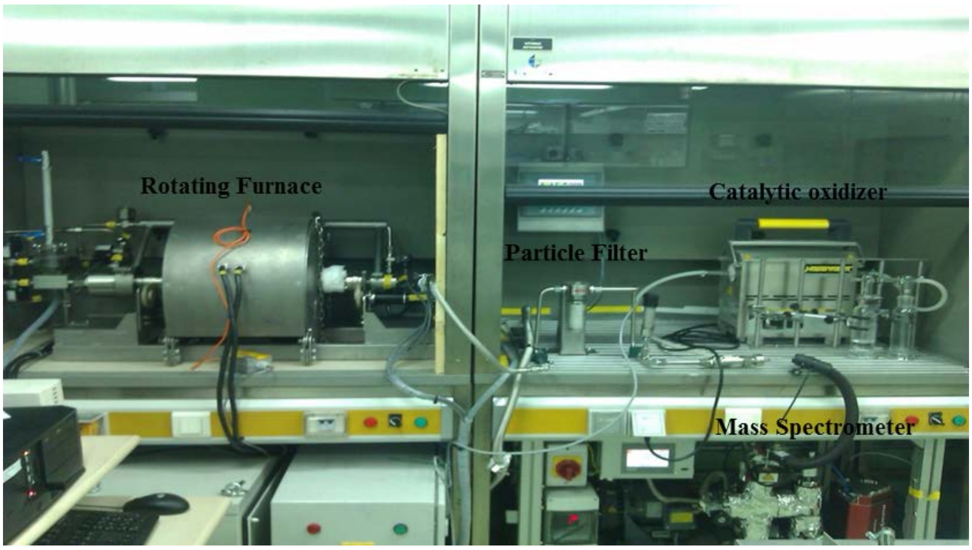

Figure 20. Thermal Treatment Facility

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

- ✓ The gas flow has to be constant in order to has no influence in the mass spectrometer background;
- ✓ The washing bottles have to have the same liquid level in order to have no influence in the total pressure of the system;
- ✓ The lab room temperature has to be constant in order to have no influence in the amplifier signal of the mass spectrometer;
- ✓ The system stabilization time has to be higher if the system is not operative for a long time;
- ✓ The spectrum signal has to be maintained stable after every experiment step.

3.2 *Procedure*

The strategy is based on obtaining the data for control parameters for an effective treatment process for graphite in such a way that ^{14}C is decontaminated whilst also ensuring that the stability of the structure of graphite is not altered. The variables that have a relevant influence on the oxidation of graphite and consequently on the corrosion rate of carbon to be studied are:

- ✓ Study of the influence of treatment temperature;
- ✓ Study of the influence of oxidizing agent;
- ✓ Study of the influence of active gas flow;
- ✓ Study of the influence of grain size.

The studies are undertaken separately in order to parameterize the effect of the variables independently.

The procedure consists on:

- ✓ Introducing in the rotating furnace (using the pneumatic injector or directly into furnace tube) the selected size and weighed amount of graphite to be treated
- ✓ Passing through an inert atmosphere (Ar) until the work temperature is reached, after which is followed an oxidizing atmosphere (O_2).
- ✓ Adjusting the experimental temperature in the furnace corresponding to the experiment to be performed
- ✓ The off- gas passing through a particle filter
- ✓ The mass spectrometer allows a qualitative monitoring of the experiment including relative amounts of different gaseous reaction products produced in the oxidation.
- ✓ After the MS a catalytic furnace, where the CO is oxidized from CO to CO_2(which is the species to be trapped and measured at the end of the experiment, due to ^{14}C treated in an oxidant atmosphere being released as $^{14}CO_2$ or ^{14}CO).
- ✓ CO_2 is trapped in NaOH and the corrosion rate of carbon is calculated by precipitation with barium nitrate as $BaCO_3$. The mass spectrometer allows a qualitative monitoring of the experiment.

The MS is not used to determine the CO and CO_2, due to the variability of the overall system, which is difficult to calibrate.

3.3 *Corrosion Rate*

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

The pneumatic injector was used to introduce the virgin powder graphite into the glass tube. The amounts of carbon processed in the initial experiments were smaller than the injected amounts, which was caused by static charges of graphite powder that form a bridge in the injector, resulting in the complete injection of the sample not be achievable.

Figure 21. Pneumatic Injector

The injector was tapped until the whole graphite sample fell into the box situated at the bottom. The irradiated graphite was therefore introduced directly in the glass tube in order to minimize cross contamination and mass losses in the experiments.

The experiments have been undertaken to obtain information about the behavior of Vandellós I graphite under thermal treatment and to adjust the process parameters to optimize the operational conditions both for the maximum efficiency of the system and for any unexpected operational drawbacks resulting from pressure control of the process.

Table 14 summarises the main data of the inactive experiments for different temperatures and flow rates of oxygen.

Table 14. Experiments with virgin graphite at 700ºC, 900ºC and 1100ºC

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

The volume of NaOH 5M in the washing bottles was increased to ensure an excess of NaOH for complete trapping of the generated CO_2, reducing the uncertainty in the mass balance of the process and furthermore avoiding the release of CO_2 to the atmosphere and especially $^{14}CO_2$ in case of experiments with i-graphite.

An additional washing bottle with CO_2 trapping agent (as Carbosorb® or similar) was connected to the system in order to ensure the retention of all CO_2 generated in the process on the basis of corrosion rates and negative mass balances (carbon consumed vs gasified carbon), which in some cases is found.

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

3.4 Results and discussion

The irradiated graphite used came from sample GC-2 (coarse grain size) from the sleeves of fuel elements. The activity was determined as: $3.50 \cdot 10^4$ Bq/g of tritium and $1.42 \cdot 10^4$ Bq/g for radiocarbon.

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

An increase of CO and CO_2 release, in inert atmosphere, is observed when temperature is reaching 400 ºC. Around this temperature, O_2 and CO_2 chemisorbed on the surface react with graphite.

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

3.4.1 Experiment 1

Procedure

- ✓ Graphite was treated with a flux of 100 L/h of Ar at 700ºC for 4 hours.
- ✓ After that treatment the flux was changed to 97 L/h of Ar and 3 L/h of oxygen for 4 hours in order to oxidise the graphite.
- ✓ To calculate corrosion rates total combustion of graphite was performed increasing the temperature up to 1100ºC.

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

Results

The qualitative releases of CO/CO2 were measure by the MS. The total amounts of ^{12}C for each treatment period and the final amount was obtained by a gravimetric method, getting 94.20% of the initial mass of graphite which was 1.0060 g.

Tritium recovery from the first HCl washing bottle was 13% (relative to initial inventory). This low recovery rate led to increasing the volume of HCl (from 100 mL to 200 mL) and adding a second HCl washing bottle. Results are collected in Table15:

Table15. Release ratios of ^{14}C and ^{12}C at 700ºC.

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

* Time when a sample is taken in each washing bottle

Figure 22 shows the experimental data obtained in Experiment-1. It is observed that there are no releases of ^{14}C in the inert atmosphere nevertheless when oxygen is injected at this temperature the ratio ^{14}C /^{12}C is around 1.5 and after one hour treatment 51% of ^{14}C was release with a corrosion rate of 36%.

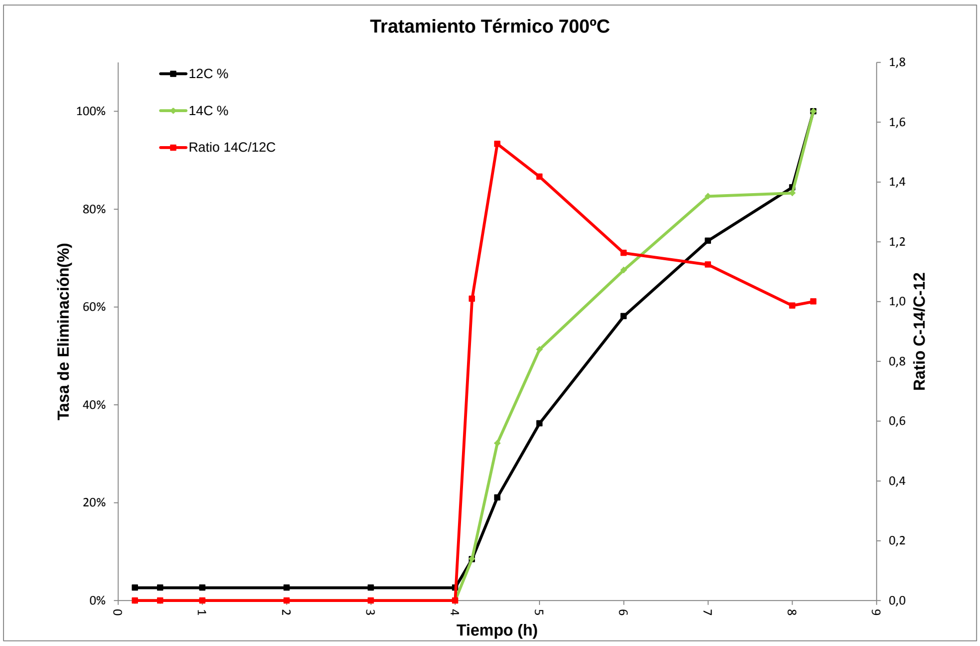

Figure 23. ^{14}C and ^{12}C release rate by thermal treatment at 700ºC

3.4.2 Experiment 2

Procedure

✓ The graphite was treated with a flow of 100 L/h of Ar at 1100 ºC for 1 hour

✓ Holding the gas flux constant, the temperature was reduced to 300 ºC.

✓ The flux was changed to 95 L/h of Ar and 5 L/h of oxygen for half an hour after 300 ºC was reached.

✓ Temperature was raised again until 1100 ºC and the gas flux was changed to 100 L/h of Ar for half an hour.

✓ Finally a gas flux of 95 L/h of Ar and 5 L/h of oxygen was applied until total oxidation of the graphite sample.

Results

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

The results of Experiment-2 are in **Table16** :

Table16. Release ratios of ^{14}C and ^{12}C at 1100ºC

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

The mass of carbon obtained in this experiment was 91.1% of the initial graphite mass (m_0 =1.0139 g). Additionally a 32% of ^3H was recovery in this process.

It is observed that, once oxygen is chemisorbed, in a treatment process at 1100º C in inert atmosphere a depletion of ^{14}C has a ratio of 2.6 compared to ^{12}C depletion (in 30 minutes).

That indicates chemisorption is higher at low temperature and reaction (and consequently corrosion) is produced at higher temperature.

Data obtained are plotted in Figure 19:

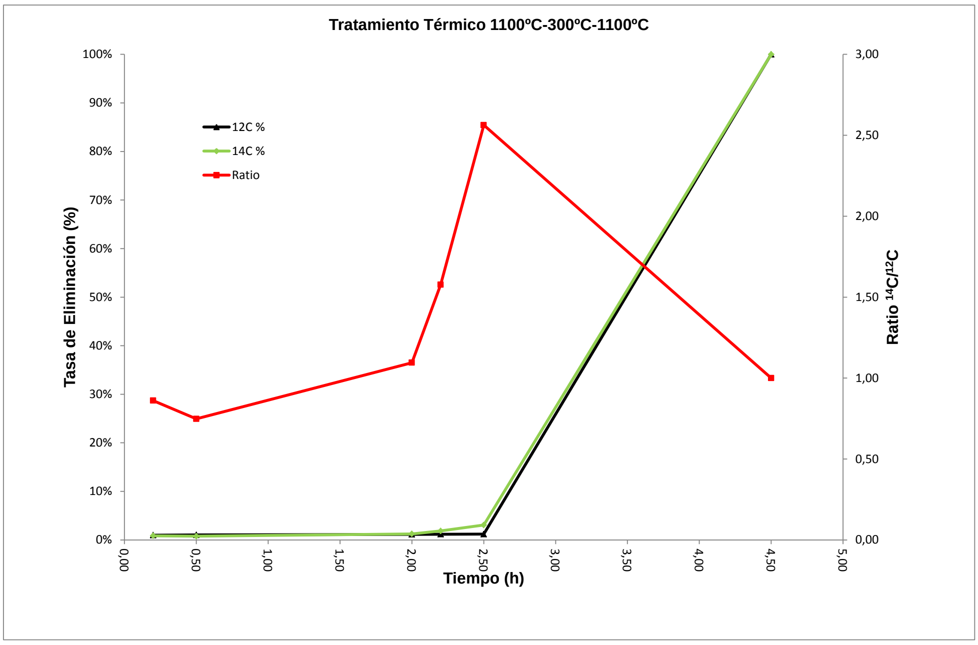

Figure 24. ^{14}C **and** ^{12}C **release rate by thermal treatment at 1100ºC-300ºC-1100ºC**

3.4.3 Experiment 3

Procedure

- ✓ The graphite was treated with a flow of 100 L/h of Ar at 1100 ºC for 4 hours
- ✓ The flux was changed to 97 L/h of Ar and 3 L/h of oxygen till total oxidation of the graphite sample.

Results

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

Table17. Release ratios of ^{14}C and ^{12}C at 1100ºC.

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

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

Obtained data are represented in Figure 20:

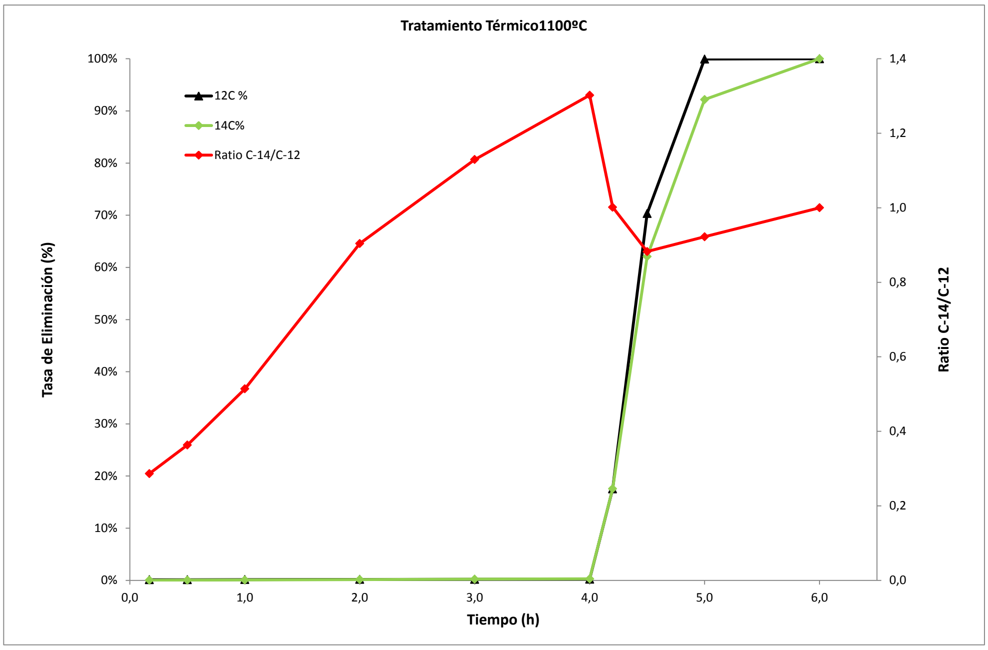

Figure 25. ^{14}C and ^{12}C release rate by thermal treatment at 1100ºC

3.4.4Experiment 4

Procedure

Conditions of Experiment- 4 are the same as for Experiment-1. The graphite was treated with Ar for 4 hours at 100 L/h and 700º C, after that the flux was changed to 97 L/h of Ar and 3 L/h of oxygen for 4 hours in order to oxidise the graphite. For total combustion of graphite the temperature was increased to 1100ºC.

Results

In this case the results are:

Table 18. Release ratios of ^{14}C and ^{12}C at 1100ºC

Sampling time*	**Temp (ºC)**	**O_2 (L/h)**	**Ar (L/h)**	**^{14}C (Bq)**	**^{14}C %**	**^{12}C g**	**^{12}C %**	**^{14}C/^{12}C**
10 min	700	0	100	4.59	0.04	0.0003	0.03	1.2118
30 min	700	0	100	4.14	0.04	0.0004	0.05	0.7830
1h	700	0	100	7.18	0.06	0.0006	0.07	0.9617
2h	700	0	100	6.99	0.06	0.0009	0.10	0.6212
3h	700	0	100	12.61	0.11	0.0012	0.13	0.8515
4h	700	0	100	17.21	0.15	0.0014	0.16	0.9478
10 min	700	3	97	1242.82	11.16	0.0459	5.30	2.1043
30 min	700	3	97	3970.21	35.65	0.1459	16.87	2.1133
1h	700	3	97	6414.03	57.59	0.2694	31.15	1.8491
2h	700	3	97	8426.06	75.66	0.4609	53.29	1.4197
3h	700	3	97	9523.76	85.51	0.6060	70.06	1.2206
4h	700	3	97	10093.23	90.63	0.7102	82.10	1.1038
Final Sample	1100	0	100	11137.27	100.00	0.8650	100.00	1.0000

Release of ^{14}C in an inert atmosphere is very low at this temperature, similar to the results obtained in Experiment-1, on the other hand, in an oxidizing atmosphere, ratios of ^{14}C/^{12}C close to 2 were observed with a ^{14}C release of 11% versus a release of 5% for ^{12}C 10 minutes after oxygen flux started. This percentage became 58% for ^{14}C and 31% for ^{12}C in 1 hour.

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

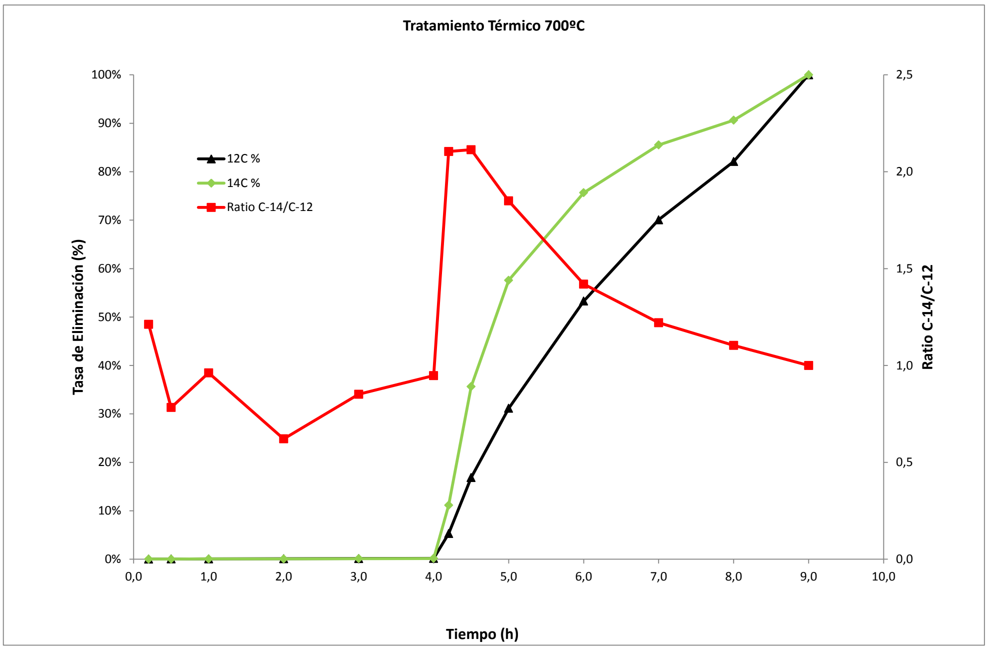

Figure 26. ^{14}**C and** ^{12}**C release rate by thermal treatment at 700ºC**

In order to study the influence of t total flow and the flow of the oxidant agent in the corrosion rate, some experiments were performed. The temperature was established in 700ºC, 600ºC, 500ºC and 400ºC. The flows selected were 20, 50 and 100 l/h.

The results are in the following tables:

Table 19. Corrosion Rates by Precipitation

PRECIPITATION				
Graphite Mass(g)	**Flow(L/hour)**	**700ºC (%)**	**1100ºC (%)**	**Recovery Total(%)**
1,0091	Ar: 82,4 O_2:17,6 Total:100	31	68	78
1,0040		12	75	78
1,0136		21	78	83
1,0119		30	77	84
1,0126	Ar: 41,2O_2 :8.8 Total: 50	41	134	120
1,0233		32	122	115
1,0115		32	86	91
1,0152		24	93	95
1,0903	Ar:17 O_2: 3 Total:20	29	122	116
1,0195		42	140	123
1,0158		24	93	95
1,0018		25	98	99

Table 20. Corrosion Rates by Precipitation 600ºC

PRECIPITATION				
Graphite Mass (g)	**Flow (L/hour)**	**600ºC (%)**	**1100ºC (%)**	**Recovery total (%)**
1,0287	Ar: 82,4 $O_{2:}$ 17,6 Total: 100	3,7	77,7	81,4
1,0210		4,2	93,0	97,1
1,0123	Ar:17 O2: 3 Total:20	4,4	94,3	98,6
1,0272		3,8	87,6	91,4

Table 21. Corrosion Rates by Precipitation 500ºC

PRECIPITATION				
Graphite Mass (g)	**Flow (L/hour)**	**500ºC (%)**	**1100ºC (%)**	**Recovery total (%)**
1,0131	Ar: 82,4 O_2:17,6 Total:100	3,6	96,6	100,2
1,0468		4,8	101,4	106,2
1,0176	Ar: 41,2 O_2 :8.8 Total: 50	6,4	93,3	99,7
1,0103		4,6	105,1	109,7
1,0122	Ar:17 O_2: 3 Total:20	3,1	102,6	105,8
1,0145		8,8	98,3	107,0
1,0166		5,5	99,8	105,3

Table 22. Corrosion Rates by Precipitation 400ºC

PRECIPITATION				
Graphite Mass (g)	**Flow (L/hour)**	**400ºC (%)**	**1100ºC (%)**	**Recovery total (%)**
1,0138	Ar: 82,4 O_2:17,6 Total:100	3,8	78,8	82,6
1,0109		4,2	93,9	98,1
1,0163	Ar:17 O_2:3 Total: 20	2,7	61,8	64,5
1,0136		2,6	81,1	83,7

Figure 22 plots the corrosion rates vs treatment temperatures for three oxygen flows tested and shows the behavior/evolution of oxidation in such a way that is easier to select the treatment conditions (temperature and oxygen flux) to get the minimum of corrosion and maximum of ^{14}C decontamination.

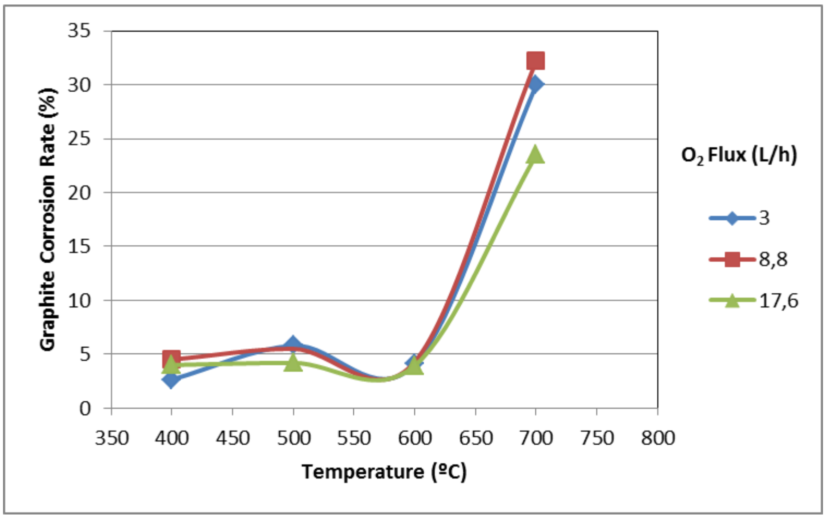

Figure 27. Corrosion rate for different fluxes vs treatment temperature

The slope of corrosion rate vs temperature is practically null for temperatures < 600ºC and the corrosion values in this range is ≈5%. However the slopes for temperatures > 600ºC is in the range 0.20 -0.28, being lower for high flux (17.6 L/h).

In order to achieve the lowest corrosion rate of graphite and the highest decontamination factors of ^{14}C, the working temperature need to be in the range of 400ºC -600ºC and the O_2 flow rate lower than 9 l/h.

Corrosion of the total mass of graphite can be higher than 100%, due to the increase of C coming from the absorption of atmospheric CO_2, depending on the delayed time for sampling and analysis (sometimes higher than 24 hours); the increment in some cases is lower than 10%.

It was observed in all experiments that CO_2 and CO concentrations increased over some minutes in an inert atmosphere, starting from 400ºC, (temperature of reaction for O_2). The explanation that sounds most plausible is that both O_2, chemisorbed in the surface and pore system, and the labile C, which is also in the graphite surface (may be as CN groups, react at elevated temperatures without the addition of an additional oxidant.

4 Conclusion

IGM samples

- In the case of granitic bentonite water the pH and *conductivity* are practically the same before and after each step due to the higher ion concentration in the leachant that masked the presence of ions dissolved from the waste form. With deionized water, the pH and the conductivity increase, which means a certain amount of ions are dissolved from the IGM into the leachant.
- Organic carbon has been found in deionized water as formate ($HCOO^-$) in leachants from day 28, 91, 184 and 215. An oxalate ($(COO^{2-})_2$) could be detected, only in one leachate sample after 28 days.
- Both alcohols and aldehydes in leachates have not been detected at any time of the leaching process.
- CO was not found in the gas phase of the leaching process with a minimum detectable concentration (< 3.5 ppm), except for the first and second leaching period with granitic-bentonite water, where the concentration is 30.9 mg/l and 10.4 mg/l. This is may be also related to the carbonate content in the leachate.
- After 356 days of leaching in granitic-bentonite water the following leaching rates have been observed: 1,44E-06 cm/day for ^{60}Co and 3,52E-06 cm/day for ^{137}Cs.
- The values obtained for ^{14}C are lower than Minimum Detectable Activity, therefore it could be only concluded that the leaching rate for ^{14}C is less than 6 E-06 cm/day.
- The Leaching rate (R_n) for ^{60}Co and ^{137}Cs in granitic-bentonite water decreases with the time and after 356 days itis constant.
- The durability of the IGM glass matrix has been validated by leaching experiments.
- A methodology has been established to manufacture the IGM samples at laboratory scale.
- It is possible to close the pore system in irradiated graphite without increasing the volume of the waste.

Thermal Treatment

Regarding thermal treatment the data obtained with virgin graphite experiments have allowed refinements of the elements of the experimental system. Such a system methodology will be the basis of the system at a pilot plant scale.

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

- ✓ Collecting the nuclides of interest and allowing the mass balance of the thermal treatment process that will determine the decontamination factors in an accurate way;
- ✓ Establishing the work temperature.

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

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

Ratio ^{14}C/Total C results are not definitive or conclusive, and they have to be improved because the corrosion rate of the graphite is higher than the one desired. Reasons for this behavior are proposed to be based on the use of powder graphite which increases the surface and the corrosion kinetic due to the higher availability of ^{12}C. Further experiments can demonstrate the influence of the grain size in the corrosion kinetic.

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

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

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

Although the release of surface ^{14}C of Vandellós I graphite took place during its operation to be obtained, Experiment 2 demonstrates that oxygen saturation of the surface at 300º C allows ^{14}C to be obtained without a high corrosion rate ($^{14}C/^{12}C = 2,6$) with a thermal treatment in inert atmosphere. This indicates that surface bound ^{14}C is not completely released during operation, which can be released by chemisorbed oxygen on the surface to be decontaminated (there was a lack of oxygen on the surface of Vandellós 1 irradiated graphite). An experimental line was opened in which, at the experiments is beginning, surface saturation with oxygen is performed followed by a partial oxidation.

The set of experimental data indicates that a lower treatment temperature and lower reactivity of the oxidant agent increase the $^{14}C/^{12}C$ ratio. A series of experiments with a reduced flow less than 2 L/h of oxygen flux or the use of CO_2 as an oxidant agent and an increase on the treatment time at 700º C are planned. The use of H_2O is not planned, in order to avoid steam reforming interfering with the thermal treatment.

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