CArbon-14 Source Term

CAST

WP5 CIEMAT Final Report on ^{14}C Leaching from Vandellós I Graphite (D5.15)

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Date of issue of this report: 19/07/2017

The project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no. 604779, the CAST project'

Dissemination Level		
PU	Public	**X**
RE	Restricted to the partners of the CAST project	
CO	Confidential, only for specific distribution list defined on this document	

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 graphite 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

CAST		
Work Package: 5	CAST Document no. :	Document type: R
Task:	CAST-2017-D5.15	R = report, O = other
Issued by: CIEMAT		Document status: Review
Internal no. :		Draft/Review/Final

Document title
WP5 CIEMAT Final Report on ^{14}C leaching from Vandellós I graphite.

Executive Summary

One of the R&D activities planned in the Spanish context for the next years should provide support and coverage for the drawing up and/or revision of the management strategies for the different types of radioactive wastes. These strategies should be based on a better understanding of such wastes, including the physical, chemical, environmental and radiological properties of the isotopes they contain. Within this framework, the understanding of the ^{14}C behaviour in waste packages could lead to a revaluation of the near surface repository for the disposal of wastes containing this radionuclide in high concentrations.

To achieve these objectives, leaching experiments have been planned considering two different scenarios. One, in which the leaching solution simulates the expected conditions in a cement based repository where a granite/bentonite mixture has been used as backfill material. The other, using deionized water as a high efficiency chemical removal agent and for reference or comparison purposes.

The development of both analytical methods and protocols to measure the release of ^{14}C from irradiated graphite samples and the speciation in the aqueous and gaseous phase has been performed throughout the CAST project. Analytical methods, suited to identify and quantify low molecular weight organic molecules, comprise Ion Exchange Chromatography and Gas Chromatography coupled to Mass Spectrometry, they are described for aqueous and gaseous samples. Also, the preparation of the leaching experiments to measure the release of ^{14}C is described in this report.

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1 Introduction

The disposal of radioactive wastes from nuclear power plants containing ^{14}C implies considerations that are, for several reasons, different from those encountered with other usual isotopes. First of all, its long half-life (5400 years) excludes any significant loss by decay during mid-term storage periods, and secondly, carbon is one of the most commonly encountered elements in living matter occurring in nature in a wide number of chemical forms.

The understanding of the mechanisms by which the ^{14}C can be released from different types of radioactive wastes under its final storage conditions (organic, inorganic, dissolved or gaseous species) can be a crucial aspect in the design of this kind of facility.

1.1 *Relate to Spanish National Program and the CAST Project*

Since 1984, the management of radioactive waste in Spain has been the responsibility of the Empresa Nacional de Residuos Radiactivos, S.A. (ENRESA), more recently, in the year 2005, ENRESA has been created as a State Business Entity (SBE) in charge of an essential public service: the management of radioactive waste, including spent fuel from the Nuclear Power Plants (NPP’s), and the dismantling and decommissioning of nuclear and radioactive facilities.

In Spain, radioactive wastes are generated at a number of facilities distributed throughout the country that use radioactive materials and substances as regulated in the specific applicable standards, these being known as Nuclear Facilities (NF’s) and Radioactive Facilities (RF’s). Radioactive wastes may also occasionally be generated in other areas, as a result of specific activities such as uranium mining.

With a view to integrated management in Spain, radioactive wastes may be classified in two major groups [1]:

- The so-called Low and Intermediate Level Wastes (LILW), which, given their characteristics, may be temporarily stored, treated, conditioned and definitively disposed of at the El Cabril facility (Córdoba), these including the sub-group of Very Low Level Wastes (VLLW).

- The so-called High Level Wastes (HLW), consisting basically of spent nuclear fuel and other specific high level wastes. This group also includes other Intermediate Level Wastes (ILW) which, in view of their characteristics, cannot be disposed of under the conditions established for El Cabril, specific installations being required for this purpose.

Although in general the LILW are conditioned by the producers, the conditioning is performed in a specific manner and with support from ENRESA on the basis of the available capacities for e.g. certain radionuclides at any one disposal facility, among which those of the El Cabril facility are fundamental. In all cases, the acceptance criteria established by ENRESA for the subsequent management must be fulfilled.

Before the storage of waste at the Near Surface Repository at El Cabril, waste producers are required to measure and report ^{137}Cs and ^{60}Co (considered as “easy to measure radionuclides”) in their operative wastes, and then ENRESA assesses the content of a number of other radionuclides, including ^{14}C, using scale factors based on statistical studies.

At the El Cabril facility, there is a limitation on the total amount of ^{14}C that can be disposed of, and that limit is 20 TBq [2]. Based on that, and the room available in the disposal cells, ENRESA derives limits for acceptance of individual waste packages.

Several works and projects at national level aiming to provide data on the content and distribution of ^{14}C in different kind of wastes [3] [4], mainly coming from nuclear reactors (‘spent’ ion exchange resins or graphite for example), have been carried out over the past years. Because of its mobility, the ^{14}C is considered as a relatively difficult to measure radionuclide in the scale factors calculations.

Due to this limited storage capacity for ^{14}C, radioactive wastes with high concentrations of this radionuclide are intended to go to interim storage in a Centralized Temporary Storage (CTS) facility or a final deep geological disposal facility together with the spent fuel and the high level wastes. Unfortunately, it should be pointed out that although there is wide agreement in relation to the deep geological disposal option and CTS, there are at present no facilities of these types and there are considerable delays in their implementation.

A large number of full commercial reactor dismantling projects are now in the execution phase in Spain. NPP dismantling and decommissioning activities may be seriously hampered (or even rendered impossible) depending on the availability or otherwise of a sufficient capacity for management of, not only the spent fuel, but materials of moderate (but appreciable) quantities of radioactive waste containing ^{14}C that, in the Spanish case, require specific temporary storage installations, such as CTS.

Because of the reasons mentioned above, one of the R&D activities planned in the Spanish context for the next years should provide support and coverage for the drawing up and/or revision of management strategies for the different types of radioactive wastes, based on better understanding of such wastes including the physical, chemical, environmental and radiological properties of the isotopes they contain [5].

Within this framework, the understanding of the ^{14}C behaviour in waste packages could lead to a revaluation of the near surface repository for the disposal of wastes containing this radionuclide in high concentrations.

To achieve these objectives, leaching experiments have been planned considering two different scenarios. In one, the leaching solution (granite-bentonite water - GBW) simulates some of the expected conditions in a cement based repository in which a granite-bentonite mixture has been used as backfill material. The other, using deionized water as a high efficiency chemical removal agent is used for reference purposes.

The particular aerobic conditions in which the tests have been made can facilitate, by comparison with the anaerobic conditions of the most of the participants in the CAST project, the understanding of the leaching and speciation processes happening in these experiments.

2 Materials and Methods

2.1 *Activation History of the Material*

Vandellós I was a Spanish nuclear power plant (460 MW) of French design operated from 1972 to 1989 which used natural uranium as fuel, graphite as moderator and CO_2 as coolant (UNGG reactor). In 1989 the plant was shut down by Ministerial Order, as a consequence of a non-nuclear accident.

The graphite in the nucleus acted as moderator and as reflector in the protector shield of the steam generator. The graphite from the nucleus was composed of pile graphite, which remains there for the whole life of the reactor, and graphite fuel sleeve which was replaced together with the fuel.

The graphite pile is located inside reactor building in a safe enclosure (25 years). The total mass produced was 2.5E+3 tons. The sleeves were extracted, crushed and stored at Vandellós I in 220 cubic containers of 6 m^3 each. The total mass of this kind of waste was 1.1E+03 tonnes.

During operation, the sleeves were placed inside the reactor pool while removing the fuel; it means that non-activation products like ^{137}Cs, transuranids, etc., have been incorporated from those present in the pool. In the leaching tests carried out in the current work, only sleeve graphite has been available.

The treatment applied to manage this waste, and the characterization processes carried out in the years of dismantling, have made it impossible to analyse volatile compounds other than ^{3}H and ^{14}C. Therefore, ^{99}Tc and ^{129}I were not measured, and ^{36}Cl was not detected above detection limit.

Figure 1. Vandellós I NPP.

2.2 *Sample Preparation*

The samples of irradiated graphite received at CIEMAT (Figure 2) were used for manufacturing fuel sleeves and presented three different sample sizes (Table 1) with the average radiological data (declared in the transport document) shown in the Table 2.

Table 1. Sleeve graphite samples from Vandellós I received at CIEMAT.

Reference	Grain Size	Quantity Available (g)	Contact Dose Rate (µSv/h)
GC-1	Ø ~ 5 mm	241,6	30
GC-2	Ø ~ 20 mm – 30 mm	523,9	14
GC-3-4	Powder	780,1	90

Table 2. Radiological data of sleeve graphite samples from Vandellós I.

Radionuclide	Activity (Bq/g)	Reference Date
^{3}H	8,91E+04	03/10/2011
^{14}C	1,35E+04	03/10/2011
^{60}Co	4,00E+04	03/10/2011
^{63}Ni	5,88E+04	03/10/2011

Figure 2. Samples of irradiated graphite received at CIEMAT.

The reference sample selected for leaching was the GC2, which corresponded to the biggest fragments of graphite. The procedure developed to obtain core samples from this small graphite pieces is detailed below:

- First of all, the biggest fragments of graphite available (stone-like material of around 2 - 3 cm. Ref. GC-2) were selected and wrapped in plastic (Figure 3).
- The selected pieces were put into a weighing bottle of 60 mm x 35 mm (Ø x h) containing fresh cement for at least 48 hours or until the mixture becomes set (Figure 4).
- Into a portable glove box, graphite core samples of about 11 mm x 12 mm (Ø x H) were obtained using a diamond core drill of 14 mm Ø (Figures 5 and 6).
- The upper and lower surfaces of the cylindrical blocks were polished with P120 grit paper.
- All the samples obtained were weighed and measured (diameter "Ø", height "H", volume and surface area). The physical properties of samples obtained this way are provided in Table 3.
- Most of the graphite powder produced after each drilling was contained in the weighing bottle. In this way, it could be easily collected for its radiological characterization by gamma spectrometry and, prior to its total incineration, by Liquid Scintillation Counting (LSC).

Figure 3. GC-2. Selected graphite.

Figure 4. Cemented graphite sample.

Figure 5 (Above). Graphite core 11 mm x 12 mm (Ø x H) and diamond core drill 14 mm Ø.

Figure 6 (Left). Vice clamp, drill and cemented sample.

Table 3. Specimens 1 to 6 - physical properties.

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

2.3 Microstructural Characterisation

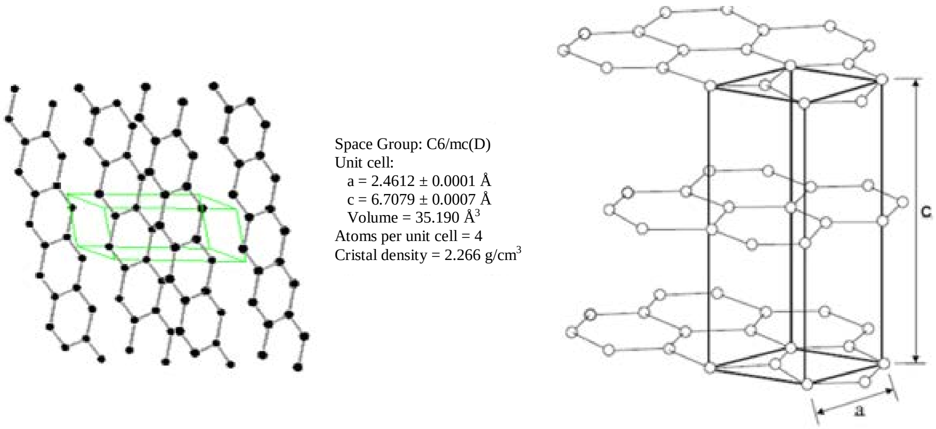
The relationship between the structural damage produced in the graphite by irradiation and the consequences on the treatment and disposal behaviour of the material is an open issue for waste management. Taking this into account, in the framework of the CARBOWASTE project, CIEMAT considered it of interest to characterize, by X-ray diffraction, diffraction laser and physisorption techniques, irradiated and virgin graphite samples from Vandellós I (among others), in order to obtain the structure in crystals and also microstructure information of material [7].

X-ray diffraction, diffraction laser and physisorption techniques permitted the obtainment of information on the structure in crystals as well as microstructural information of the material. This microstructural characterization involves among other considerations the amount of the phases in the sample, the crystallographic parameters, the crystalline size and stress.

These microstructural tests showed a correlation between microstructural changes, the graphite specific surface and the degree of irradiation, but only specific knowledge of the irradiation history of each sample studied would allow an accurate consideration of the results and relevant conclusions.

The samples analysed showed different specific surface area values for similar particle sizes. This behaviour probably could be related to different parameters such as lattice size, thermal treatment and fracture behaviour (cleavage), related to the irradiation history.

The samples from Vandellós I NPP showed a semi-Gaussian distribution related to the particle size distribution, with an average particle size of 9.02 µm (at the 50% of the sampling). This value was between 5.73 µm (at 10 %) and 12.22 µm (at 90 % of the sampling). Deviation was up to 33.44 % around the most frequent value, so the particle diameter obtained was 9.02 ± 3.02 µm and the specific surface area 1.9312 ± 0.0064 m^2/g. Figure 7 shows a representation of the crystal system for Vandellós I NPP graphite.



Space Group: C6/mc(D)
Unit cell:
a = 2.4612 ± 0.0001 Å
c = 6.7079 ± 0.0007 Å
Volume = 35.190 Å^3
Atoms per unit cell = 4
Cristal density = 2.266 g/cm^3

Figure 7. Crystal system for Vandellós I NPP graphite.

2.4 *Radiological Characterisation of Initial Sample*

To perform the characterization of the initial sample, an aliquot (ca. 20 mg) of the powdered sample produced after each drilling was introduced in a combustion oven (Harvey OX500), where the sample is burned to 900 ºC in an oxygen stream. The gases formed are passed through a catalyst bed (CuO, Pt), where the carbon compounds are converted to $CO_{2,}$ which is trapped in a specific cocktail, and finally the vial obtained was analysed by LSC in a Packard Tricarb 3110 TR/LL LSC. Figure 8 shows a representation of the initial graphite characterisation methodology for ^{14}C determination.

In this process, all the interferences coming from beta-gamma emitters different from ^{14}C are removed. The same sample is burned 3 times for 3 minutes, to be sure that there is no activity remaining in the combustion chamber. In this way, the ^{14}C activity percentage collected is about 99.9 %.

Additionally, another aliquot of the powder sample (ca. 1 g) was placed into a glass vial (counting geometry) and measured by gamma spectrometry with a Canberra BEGe 3830 HPGe Detector, to determine the activity of the high energy beta-gamma emitters present in the initial sample.

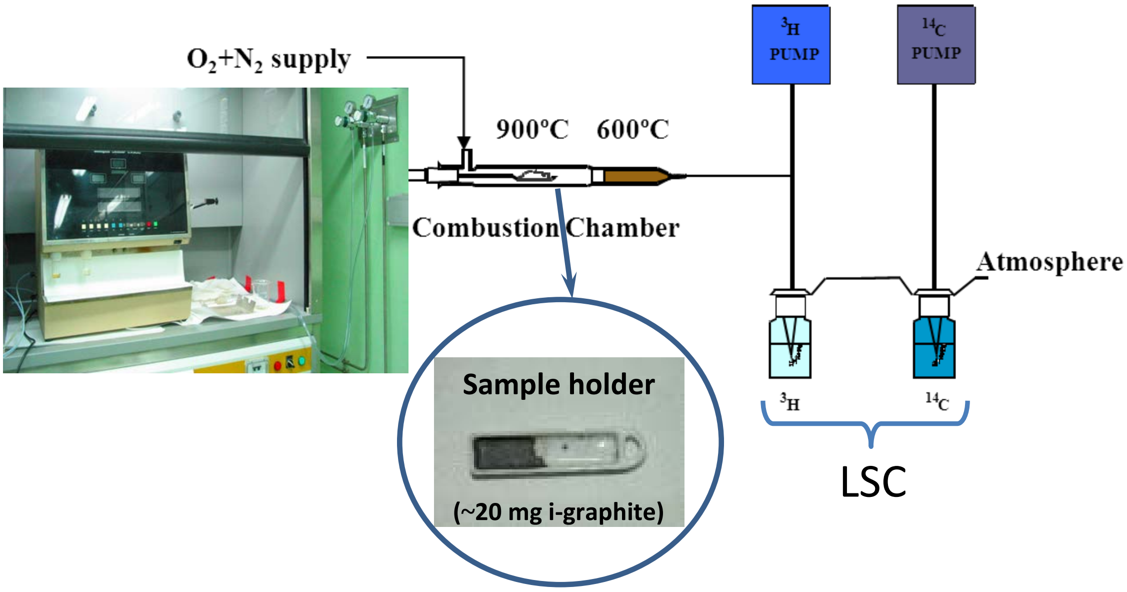


Figure 8. Initial graphite characterisation methodology.

2.5 *Leaching Process*

Once graphite cylindrical samples were obtained, the leaching process, based on the standard ISO 6961 "Long-Term Leach Testing of Solidified Radioactive Waste Forms" [6], was carried out on the basis detailed below.

2.5.1 Specimen, Leachant, Leaching Container and Temperature

The leaching experiments started on June 2016 with the V-I-1 and V-I-2 core-drilled samples, whose main characteristics are depicted in Table 3. As leachant, Milli-Q® water type 1 (pH = 5.8, EC = 0.05 µS/cm) for V-I-1, and granite-bentonite water (synthetic) for V-I-2, have been used (see Table 4 for granite-bentonite water composition).

The leachant container is made of PTFE (material recommended for its chemical inertness) and the value of the ratio provided by dividing the volume of leachant by the exposed geometric surface area of specimen is 0.2 m. Although the leaching tests were carried out at room temperature, the losses of leachant by vaporization were negligible.

Table 4. Granite-bentonite water composition.

Al	**< 0,03**	**mg/L**
B	< 0,03	mg/L
Br$^-$	15,7	mg/L
Ca	100	mg/L
Cl$^-$	6,7	g/L
$CO_3^=$	< 12	mg/L
Electric Conductivity	16,8	mS/cm
F$^-$	< 0,5	mg/L
HCO_3^-	32,4	mg/L
K	44	mg/L
Mg	580	mg/ml
Na	4,1	g/L
NO_3^-	115	mg/L
pH	7,2	
Si	4,1	mg/ml
SiO_2	11.9	mg/L
$SO_4^=$	2.0	g/L

2.5.2 Leach Container Preparation and Leachant Renewal

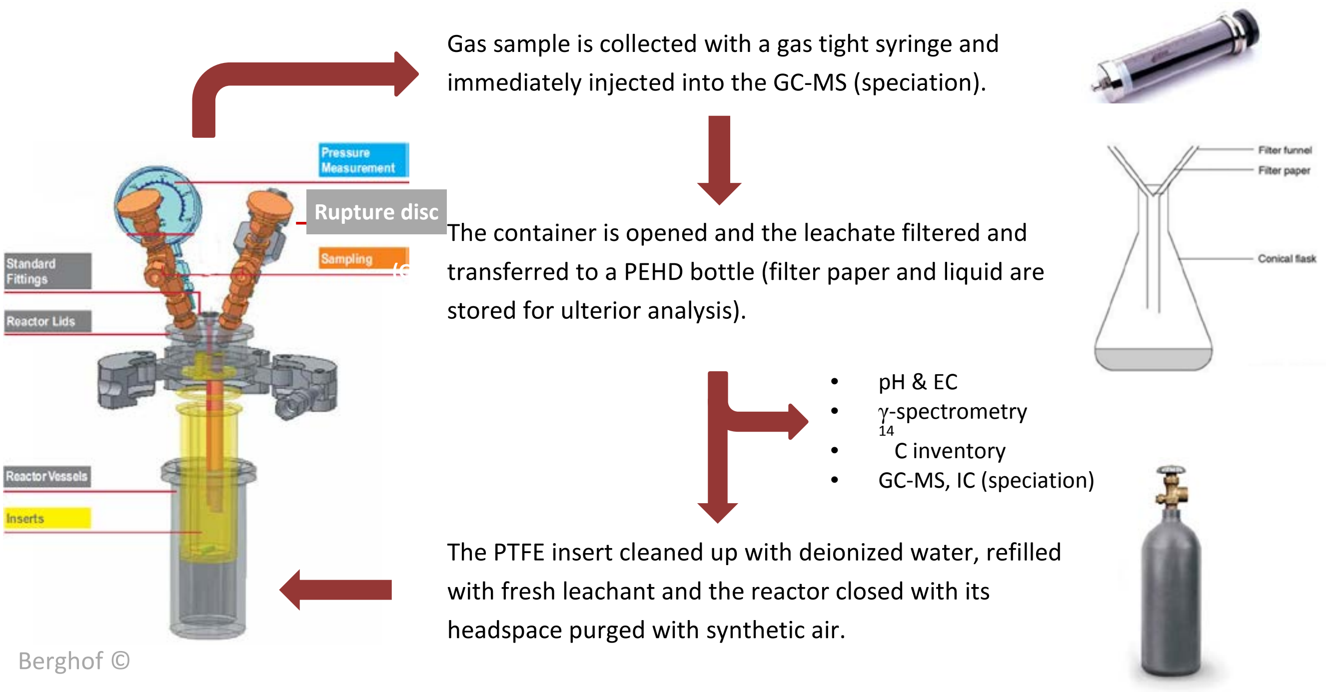
The specimen was suspended in 120 ml of leachant by means of a PTFE thread and surrounded by at least 1 cm of liquid in all directions (Figure 9). The total volume of the vessel is 150 ml, and prior to its first use, it was cleaned up with deionized water.

Figure 9. Leaching containers for deionized water and GBW.

The initial gas phase composition consists of synthetic air (21 % oxygen, 79 % nitrogen) supplied from a 5 litre compressed air cylinder. The pressure vessel was set up at 1 bar.

The leachant changing frequency is chosen depending on the material, its radioactivity levels and the availability for measurements of the different equipment needed. Based on that, both the gas and the leachate are renewed after 15, 28, 56, 90, 182 and 359 days from the start of the test.

After each interval, initially the gas sample (volatile species) is collected through the gas sample extraction valve, by means of a gas-tight syringe, and immediately injected into the GC-MS system. Once this previous step has been completed, the container is opened, the specimen is withdrawn from the leachant, the leachate is filtered using Schleicher & Schuell white ribbon filter paper, and finally transferred to a polyethylene bottle. Both the filter paper and the liquid are stored for later analysis (the whole process is depicted in Figure 10).



Gas sample is collected with a gas tight syringe and immediately injected into the GC-MS (speciation).

The container is opened and the leachate filtered and transferred to a PEHD bottle (filter paper and liquid are stored for ulterior analysis).

- pH & EC
- γ-spectrometry
- ^{14}C inventory
- GC-MS, IC (speciation)

The PTFE insert cleaned up with deionized water, refilled with fresh leachant and the reactor closed with its headspace purged with synthetic air.

Figure 10. Leaching process sampling methodology.

Once the leachate is stored, the PTFE vessel 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).

The filter paper and the filtered leachate are analysed for ^{14}C activity, first with a Packard Tricarb 3110 TR/LL LSC, and after the first results are obtained, where no ^{14}C activity has been detected, the samples are measured again with ultra-low level LSC equipment (Quantulus). For these analyses, the volume of leachate introduced in the combustion oven is 0.5 mL, where same sample is burned 3 times for 3 minutes.

The general conditions of the leaching processes carried out for core samples of graphite are depicted in the Table 5.

Table 5. General conditions of graphite leaching experiments.

Parameter	Leaching Conditions
Specimen geometry	Cylinder block 11 x 12 mm (Ø x H)
Leachant	Pure / GBW (synthetic)
Temperature (°C)	Room temperature
Vessel / Stirring	PTFE / No
$V_{leachate}/S_{specimen}$	0,18 - 0.20 m
Initial gas phase composition	Synthetic air (21 % oxygen, 79 % nitrogen)
Regime	Total renewal of the leachate (static).
Sampling	14, 28, 56, 90, 180 and 360 days from first immersion 14, 14, 28, 34, 90 and 180 leachate ages
Analyses	**Pre-leaching:** Solid phase: ^{14}C inventory & γ-spectrometry Leachant: Background ^{14}C inventory, pH & EC **Post-leaching:** Leachate: ^{14}C inventory, speciation (GC-MS, IC), γ-spectrometry, pH & EC Gas phase: Speciation (GC-MS)
Evaluation of results	Incremental leaching rate as a function of time of leaching (cm/day)

2.6 *Speciation*

Throughout the CAST Project and regarding the analytical requirements for speciation, a methodology to determine permanent gases (CO, CO_2), C1 to C5 hydrocarbons, alcohols and aldehydes has been developed using a Gas Chromatograph coupled to a Mass Spectrometer (GC-MS). To analyse permanent gases, hydrocarbons C1 to C5 and CO_2, it was decided to use a column that is a combination of Molsieve 5A and PoraBondQ, named Select Permanent Gases/CO_2 HR (Agilent).

A column to analyse different alcohol and aldehydes, in particular methanol, ethanol, formaldehyde (with a small amount of stabilizer, methanol, to suppress oxidation and polymerization), acetaldehyde and propionaldehyde was set up. The column used was DB-624UI (L = 60 m; ID = 0,25 mm and F = 1,40 mm). In this case the following temperature-time profile, used in order to separate the different peaks, was applied: 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 with a temperature of 40 ºC.

Also, the methodology to determine short chain carboxylic acids by an Ion Chromatography System using a conductivity detector has been implemented. In this case a Dionex ICS-900 Ion Chromatography System (ICS) with Ionic Reagent Free Controller (RFC) has been used. This equipment permits the analysis of short chain carboxylic acids with a AS11-HC column.

As part of method used in the experiments, a set of standard solutions of acetate, formate and oxalate were prepared, each of of 1000 mg/L. From these solutions, a mixture of diluted solutions, ranging from 0.01 ppm to 1 ppm, were prepared. The calibration was carried out by using three mixed standards with different concentrations. The chromatograms of the calibration standards in deionized water medium are shown in Figure 11, and the calibration results for each analyte are shown in Table 6.

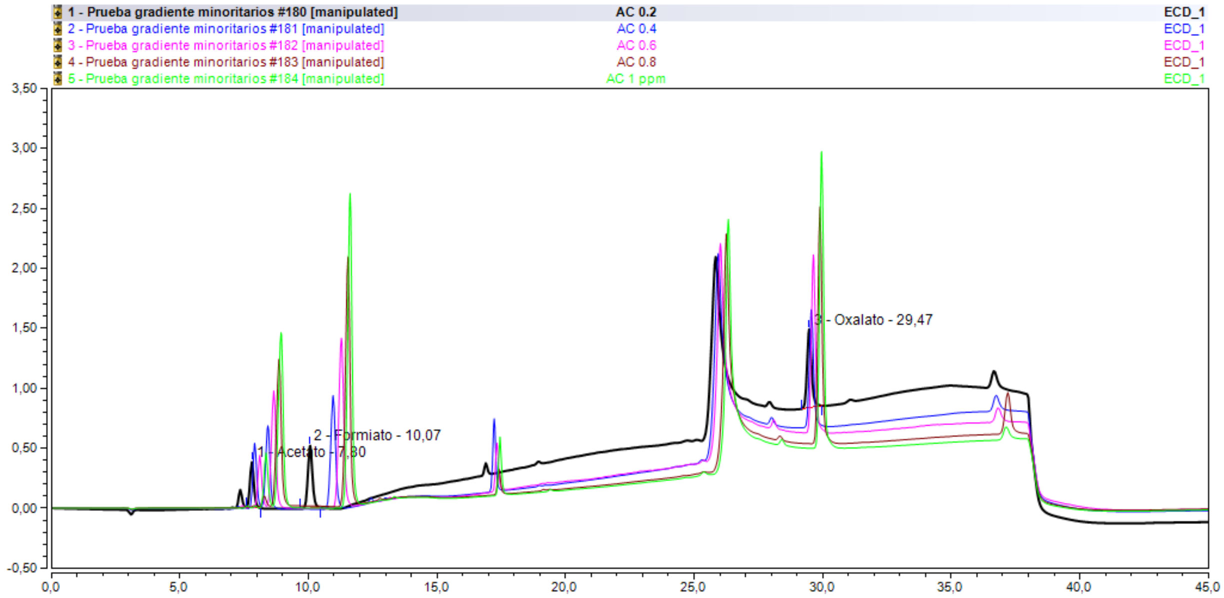


Figure 11. Chromatograms of the calibration standards in deionized water.

Table 6. Results of calibration solutions in deionized water.

Leachant: Deionized Water.						**Calibration results**			
Compound	**Concentration (mg/L)**					**r²**	**Offset**	**Slope**	**MDC**
Acetate	0.01	0.02	0.03	0.04	0.05	0.9888	0.012	0.2015	0.002
Formate	0.02	0.04	0.06	0.08	0.1	0.9947	0.0009	0.3895	0.005
Formate	0.1	0.2	0.3	0.4	0.5	0.9903	-0.0214	0.4645	0.005
Oxalate	0.02	0.04	0.06	0.08	0.1	0.9935	0.0033	0.4348	0.01

3 Results and Discussion

3.1 *Radiological Characterisation of the Initial Sample*

The results of ^{14}C and the most representative high energy beta-gamma emitters of the irradiated graphite samples are indicated in Table 7; the spectra of ^{14}C corresponding to the samples V-I-1 and V-I-2, intended for leaching in pure water and GBW respectively, are shown in Figure 12.

Table 7. Radiological characterization of graphite cylinders 1 to 6.

				Activity (Bq/g)					
Sample	**Mass (g)**	**H_{avg} (mm)**	**$Ø_{avg}$ (mm)**	**^{14}C**	**2u (%)***	**^{60}Co**	**2u (%)**	**^{137}Cs**	**2u (%)**
V-I-1	1,9688	12,68	11,28	1,22E+04	7,42	5,56E+01	3,57	2,03E+03	6,27
V-I-2	2,0222	12,51	11,09	1,35E+04	7,34	4,98E+01	3,71	3,98E+02	6,28
V-I-3	2,1861	14,07	11,11	1,08E+04	7,26	1,08E+01	5,00	2,88E+01	6,63
V-I-4	1,8077	12,15	11,08	1,13E+04	7,27	1,42E+02	3,61	2,17E+02	6,32
V-I-5	1,9102	11,70	11,07	1,12E+04	10,88	5,87E+01	3,78	4,20E+01	6,62
V-I-6	2,0964	12,51	11,05	1,10E+04	7,23	2,34E+01	4,08	1,40E+01	7,04

* The range “a ± 2u” represents a 95% level of confidence where the true value “a” would be found. The value of “U“ or “2u” is the value which is normally used and reported by analysts and is hereafter referred to as “measurement uncertainty”.

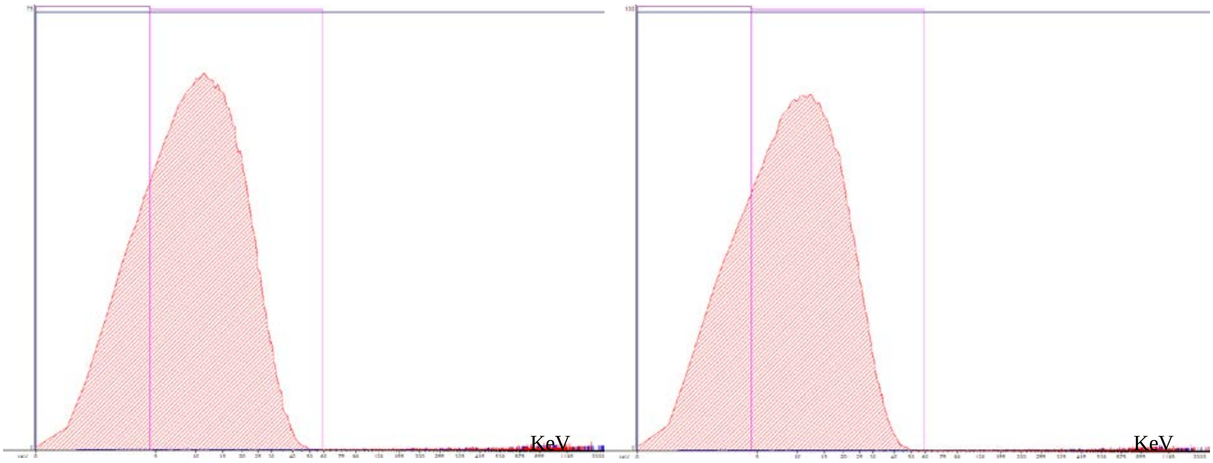


Figure 12. ^{14}C spectra corresponding to the V-I-1 and V-I-2 graphite core samples.

3.2 *Leaching Process and Speciation Using Deionized Water*

3.2.1 ^{14}C and Main β-γ Emitters Results

The results of ^{14}C and the main high energy beta-gamma emitters (^{137}Cs and ^{60}Co) found in the leachates after each leaching step are indicated in Table 8.

Table 8. Results of ^{14}C, ^{137}Cs and ^{60}Co in deonized water as leachate (Vol. = 120 mL)

Leachant: Deionized Water.			**Activity (Bq/g)**		
Leaching Step (days)	**^{14}C**	**^{60}Co**	**2u (%)**	**^{137}Cs**	**2u (%)**
15	< 3,00E-03	1,73E-03	40,93	4,74E-01	4,39
28	0,267 ± 0,1	-	-	9,33E-02	5,62
56	< 2,40E-02	-	-	9,35E-02	6,16
90	< 2,40E-02	-	-	1,25E-01	5,12
182	< 2,40E-02	-	-	7,85E-02	6,96
359	< 2,40E-02	9,33E-03	13,18	1,07E-01	5,51

Although the value of the second step is higher than the Minimum Detectable Activity (MDA), the rest of steps are below MDA. Taking this into account, it is more likely that this could be because of bad filtering of the sample or cross-contamination in the equipment than because of the leaching process itself. The spectra corresponding to this sample (G-AD-28) is presented in Figure 13.

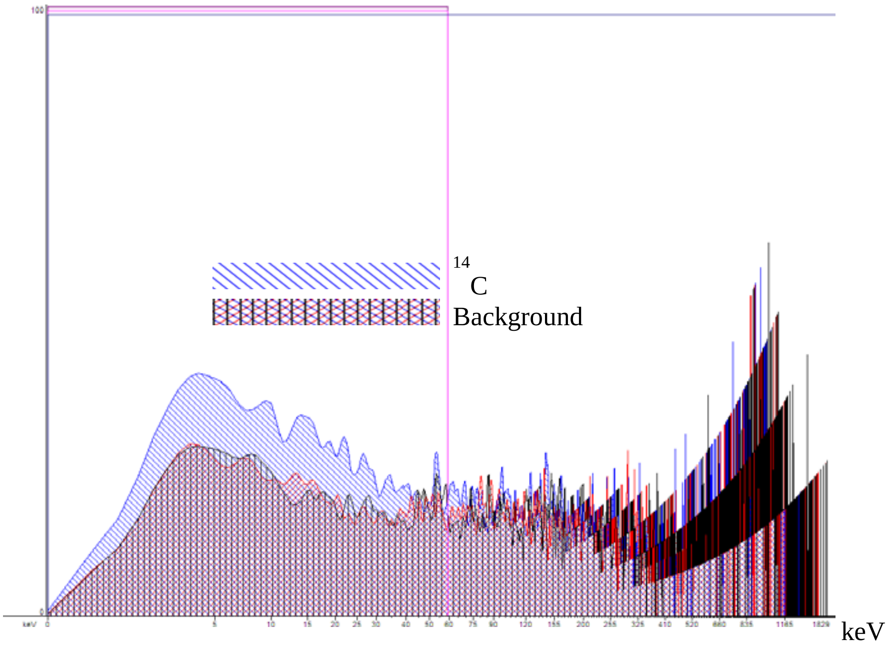


Figure 13. ^{14}C spectra of G-AG-28 leachate sample.

It was tried to obtain ^{14}C values above the MDA by concentrating, in the vial where the CO_2 is trapped, a number of aliquots of the leachate (up to 5 mL) that are introduced in the combustion oven, and subsequently measuring the trapped solution in a low background equipment (Quantulus). This procedure provided a lower MDA in the measurements (ca 5.00E-03 Bq/g), but no ^{14}C activity was detected either. In summary, using this technique and with this experimental approach, at present it is not possible to determine ^{14}C activity in the leachates.

Regarding the main beta-gamma emitters, only two ^{60}Co values have been obtained in the leachates, corresponding to 14 and 359 days, and therefore it has not been possible to establish a leaching trend for this radionuclide. The accumulated activity of this radionuclide detected in the leachates represents 0.02 % of the total ^{60}Co of the initial sample.

On the other hand, ^{137}Cs has been detected in all the leaching steps; the accumulated activity of this radionuclide detected represents the 0.05 % of the total ^{137}Cs present in the initial sample. Table 9 shows the leaching rates (R_n) and the accumulated activity ($\Sigma A_n/A_o$) for ^{137}Cs, whose values in logarithmic scale are represented in Figure 14.

Table 9. Leaching rates and accumulated activity of ^{137}Cs in pure water.

Leachant: Deionized Water. Sample V-I-1 dimensions: S = 6.49 cm^2 V = 1.27 cm^3. R_n (cm/day)

Leaching Step (days)	**Leachant (mL)**	**^{137}Cs R_n**	**^{137}Cs $\Sigma A_n/A_o$**
15	120.0	3,66E-04	2,33E-04
28	120.0	8,30E-05	2,79E-04
56	120.0	3,86E-05	3,26E-04
90	120.0	4,25E-05	3,87E-04
182	120.0	9,87E-06	4,26E-04
359	120.0	6,99E-06	4,78E-04

As can be observed in Table 9, in the 359 day leaching step, corresponding to 177 continuous days of leaching in pure water, a leaching rate value for ^{137}Cs of 6,99E-06 cm/day has been observed.

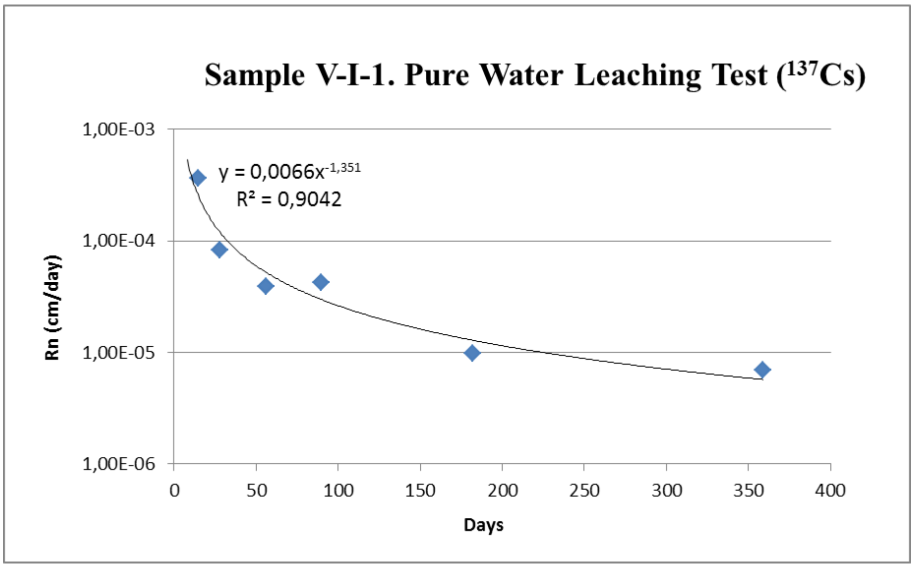


Figure 14. Leaching rates of ^{137}Cs in pure water.

3.2.2 Organic Carbon Compounds Results

3.2.2.1 Organic Carbon Dissolved Species Determination by ICS

The results of the different leachates, obtained with the column AS-11 and with concentrations gradients of 1.5 mM KOH (0-8 min); 25 mM KOH (8-30 min) and 1.5 mM KOH (30 - 40 min) and a flow of 1 mL/min, are shown in Table 10.

Table 10. ICS results obtained from deionized water leachates.

Leachant: Deionized Water.	**Concentration (mg/L±2U)**					
Compound	**Day 15**	**Day 28**	**Day 56**	**Day 90**	**Day 182**	**Day 359**
Acetate	< 0.002	< 0.002	< 0.002	0.043±0.001	< 0.002	< 0.002
Formate	0.067±0.001	< 0.005	0.08±0.02	0.21±0.01	< 0.005	< 0.005
Oxalate	< 0.01	< 0.01	0.14±0.06	0.034±0.001	< 0.01	< 0.01

As can be observed in the previous table, acetate was detected, although close to the MDC, in the fourth leaching step (90 days); formate in the 15, 56 and 90 days steps and oxalate in the 56 and 90 days steps. In Figure 15 is represented the formate and oxalate peaks detected in the 90 days step (34 days of leaching in a row).

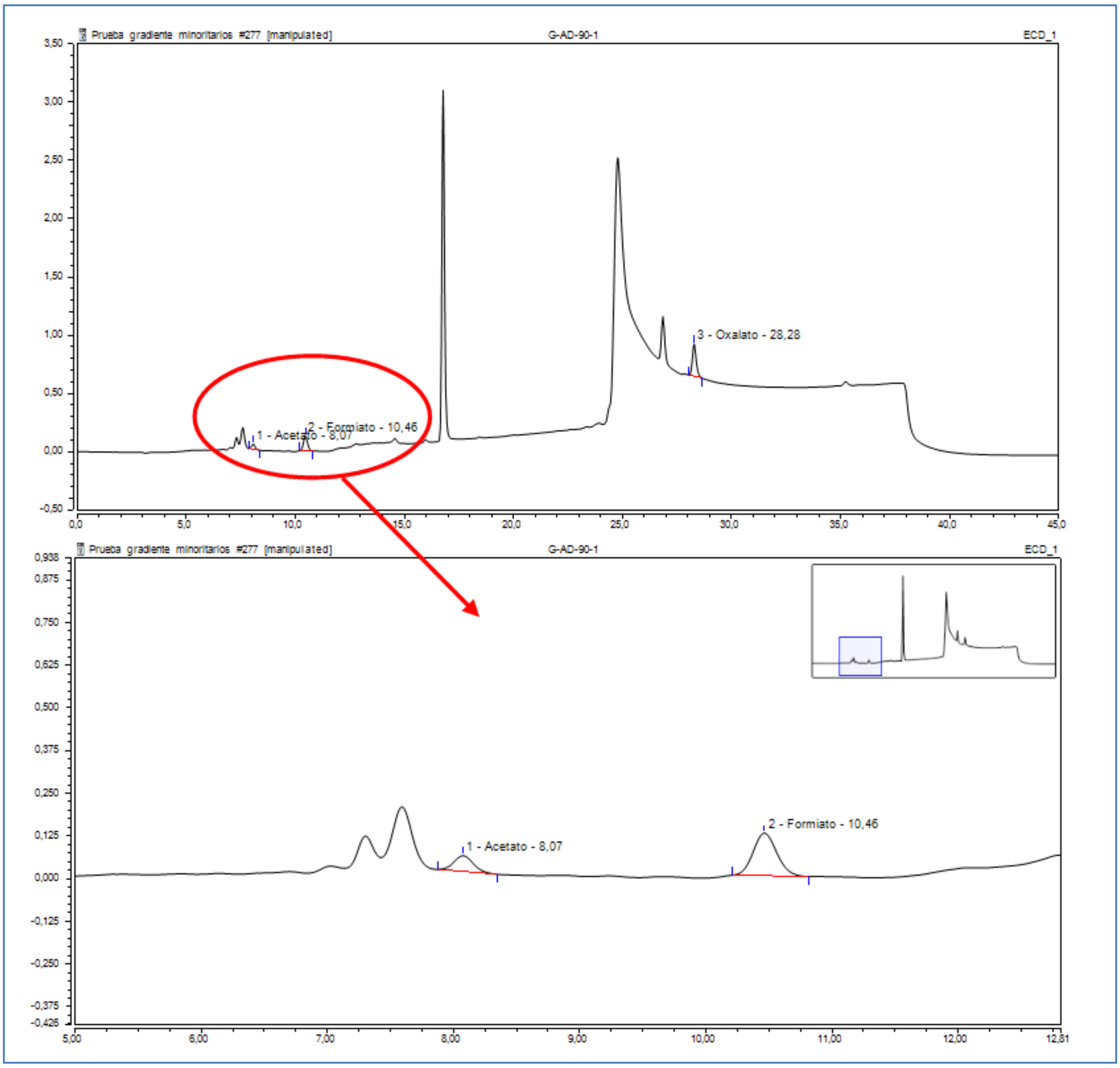


Figure 15. Acetate, formate and oxalate peaks in pure water (90 days step).

3.2.2.2 Gas and Leachate Volatile Species Determination by GC-MS

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

The assays to analyse CO have been carried out 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 have been carried out with the following temperature-time profile: 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. In this case, the technique of head space sampling was used, with 30 seconds of incubation time at 40 ºC.

Using this technique, neither alcohols nor aldehydes were detected in leachates in any step of the leaching process. Regarding gas samples, CO was not detected above MDC (3.5 ppm). The technique to trap the gas samples has not been implemented in our laboratories, so it was not possible to carry out ^{14}C determinations.

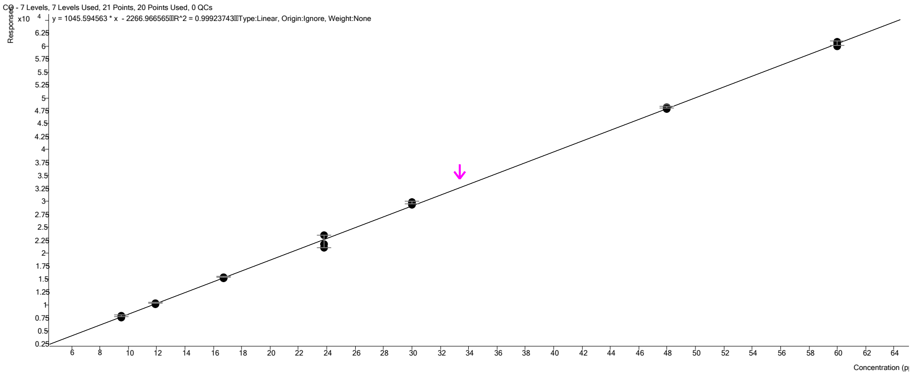


Figure 16. Calibration curve GC-MS applied for CO determination.

3.3 *Leaching Process and Speciation Using Granite-Bentonite Water (GBW)*

3.3.1 ^{14}C and Main β-γ Emitters Results

The results of ^{14}C and the main beta-gamma emitters found in the leachates after each leaching step are indicated in Table 11. The analyses were performed in the same conditions as mentioned for deionized water leachates.

Table 11. Results of ^{14}C, ^{137}Cs and ^{60}Co in GBW as leachate (Vol. = 120 mL)

Leachant: Granite-bentonite water.		**Activity (Bq/g)**			
Leaching Step (days)	**^{14}C**	**^{60}Co**	**2u (%)**	**^{137}Cs**	**2u (%)**
15	< 2,40E-02	2,15E-02	8,15	2,05E-01	4,75
28	< 2,40E-02	5,71E-03	18,14	1,22E-02	14,49
56	< 2,40E-02	6,61E-03	19,88	7,29E-03	29,36
90	< 2,40E-02	5,83E-03	16,26	7,23E-03	18,62
182	< 2,40E-02	5,41E-03	26,47	7,27E-03	35,49
359	< 2,40E-02	9,20E-03	13,04	9,30E-03	19,35

As can be observed in Table 11, all values obtained were lower than MDA, therefore, as in the case of pure water, it is not possible to obtain any conclusive results.

Regarding the main beta-gamma emitters detected in the leaching test with GBW, Table 12 shows the leaching rates (R_n) and the accumulated activity ($\Sigma A_n/A_o$) of ^{137}Cs and ^{60}Co, whose values in logarithmic scale are represented in Figures 17 and 18 respectively. The accumulated activity of these radionuclides detected represents respectively 0.06 % and 0.11 % of the total ^{137}Cs and ^{60}Co present in the initial sample.

Table 12. Leaching rates and accumulated activity of ^{60}Co and ^{137}Cs in GBW.

Leachant: GBW. Sample V-I-2. Dimensions: S = 6.29 cm^2 V = 1.21 cm^3. R_n (cm/day)					
Leaching Step (days)	**Leachant (mL)**	**^{60}Co R_n**	**^{60}Co $\Sigma A_n/A_o$**	**^{137}Cs R_n**	**^{137}Cs $\Sigma A_n/A_o$**
15	120.4	6,67E-04	4,32E-04	7,93E-04	5,15E-04
28	119.6	2,03E-04	5,46E-04	5,44E-05	5,46E-04
56	120.0	1,09E-04	6,79E-04	1,51E-05	5,64E-04
90	120.0	7,95E-05	7,96E-04	1,23E-05	5,82E-04
182	120.0	2,73E-05	9,05E-04	4,58E-06	6,00E-04
359	120.0	2,41E-05	1,09E-03	3,05E-06	6,24E-04

As can be observed in the Table 12, in the leaching step at Day 359 (177 continuous days of leaching) a leaching rate value of 3,05E-06 cm/day for ^{137}Cs and 2,41E-05 cm/day for ^{60}Co has been observed.

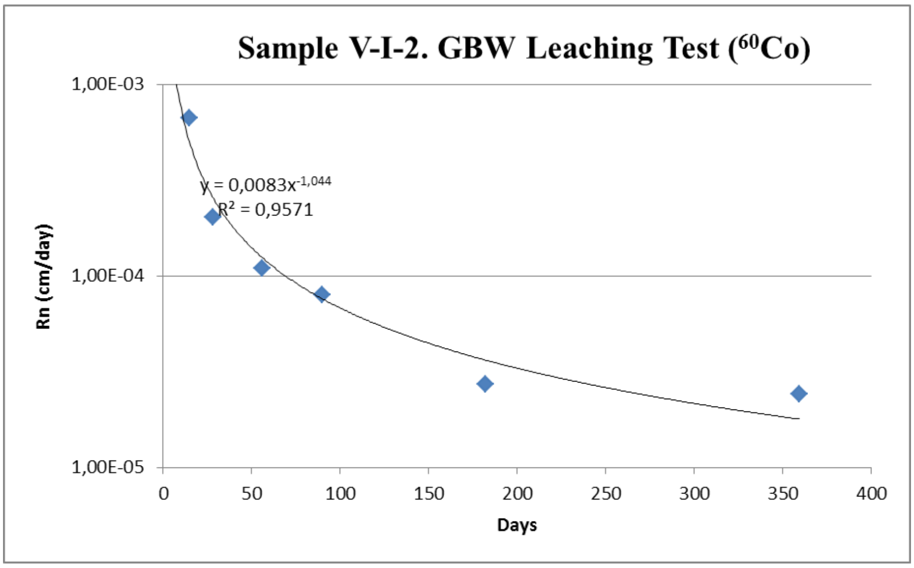


Figure 17. Leaching rates of ^{60}Co in GBW.

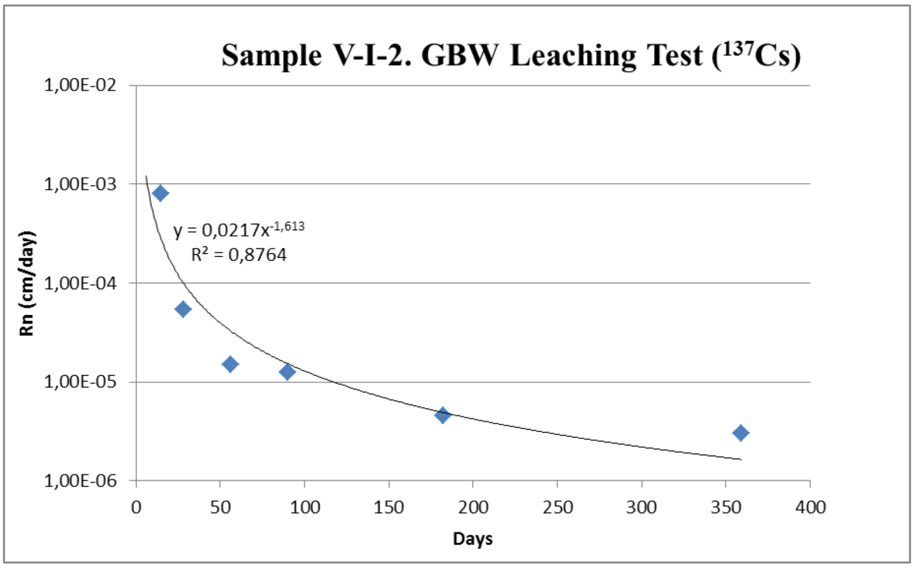


Figure 18. Leaching rates of ^{137}Cs in GBW.

3.3.2 Organic Carbon Compounds Results

3.3.2.1 Organic Carbon Dissolved Species Determination by ICS

Due to the high concentration of anions and cations in GBW, which saturates the ICS signal, it is not possible to use this technique to analyse the leachates obtained using this methodology.

3.3.2.2 Gas and Leachate Volatile Species Determination by GC-MS

To analyse GBW leachates, the same methodology as was applied for pure water was used. Both alcohols and aldehydes were not detected in leachates in any step of the leaching process, and, regarding gas samples, nor was CO (values were again below MDC (3.5 ppm)).

4 Final Remarks.

- Although significant heterogeneity has been observed both in the detection and in the activity of the high energy beta-gamma emitters, the ^{14}C content of the core samples tested shows a good correspondence, with an average specific activity of 1,17E+04 Bq/g and a standard deviation of the 8,74 %.

- Among all the analyses of leachate samples carried out, including pure water and GBW, only one value, corresponding to the 28 days leaching step in pure water, presented a value of ^{14}C higher than the detection limit. It is more likely that this could be because of bad filtering of the sample or cross-contamination in the equipment than because of the leaching process itself.

- Using pure water as leachant, in the ICS analyses, acetate was detected, although close to the MDA, after 90 days of leaching time; formate after 15, 56 and 90 days and oxalate in the 56 and 90 periods. However, this technique cannot be used to analyze GBW solutions because of the high concentration of anions and cations present in this media.

- Both alcohols and aldehydes in leachates have not been detected in any step of the leaching process, and regarding gas samples, nor was CO (whose values were again below MDC (< 3.5 ppm)).

- After 359 days of leaching, the following leaching rates has been observed: 6,99E-06 cm/day for ^{137}Cs in pure water, 3,05E-06 cm/day for ^{137}Cs an GBW and 2,41E-05 cm/day for ^{60}Co in GBW.

- After all the leaching steps were completed, the graphite core samples were dried, weighed and measured, without presenting any significant dimensional change (< 1 %), cracks or crumbles.

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