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Decontamination Factors by Decontamination Agents under Normal Pressure

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Document title
Decontamination Factors by Decontamination Agents under Normal Pressure
Executive summary

Decontamination studies collected in this document have been carried out on irradiated graphite samples from Magnox reactors, UNGG Reactors, MTR's (Triga, BEPO and Merlin reactors) and HT reactors (AVR).

Several techniques as Semi-dynamic long term leaching/chemical treatment experiments, Short term leaching/chemical treatment experiments with stirring or ultrasonic assitance, and Solid liquid extraction have been applied.

The chemical reagents tested are organic for several purposes: soft acidic, extractans with soft donors, complexant agents, solvents …) and inorganic, (acidic, alkaline, neutral, solvents, oxidizers…) at different temperatures.

Description on samples and their characterisation results and experimental set-up are detailed in this report.

Effectiveness of the processes applied for H-3, C-14, alpha emitters, gamma emitters, pure beta emitters, gross beta and total activity decontamination factor and/or release rate from different sample types are included and their discussion and relevance of these results.

Studies of intercalation processes found and structural correlation.

Final remarks and conclusion in function of graphite samples characteristics, nature of treatment agents and nuclide removal efficiency has been detailed in this document.

Revisions

Rev.	Date	Short description	Author	Review	Task Leader	WP Leader
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1. INTRODUCTION

1.1. General

Chemical treatment is usually carried out by decontamination procedure with specifically selected reagents. The material to be decontaminated is immersed in a flask/tank containing the reagent, which is then agitated.

When selecting a suitable chemical decontamination process, in addition to the general considerations and in view of the variety of chemical decontamination processes available, several criteria must be considered in a detailed analysis based on origin and reactor specific conditions. Most of the criteria are related to the specific features of nuclear graphite, such as:

- Structural damage in the material
- History of operation (to determine contamination profile);
- Nature of the contamination
- Effectiveness of previously used chemical decontamination processes;
- Distribution of contamination
- Requirements (e.g. recycling versus disposal);
- Quantity and type of secondary waste from decontamination and conditioning;
- Ultimate fate of decontaminated materials;
- Time;
- Costs

Chemical decontamination normally consists of consecutive treatments of contaminated materials with different chemicals that dissolve/remove the contaminant in some cases other processes could be combined with the chemical treatments.

Chemical decontamination where the concentrations of different chemicals are less than 1 % wt is called dilute (or mild) concentrate decontamination

In chemical decontamination the composition of the contaminated materials has to be known. The selected decontamination method has to be able to attack the contamination species with corrosion of the graphite under consideration.

In general, knowledge of chemical treatment methodology is a prerequisite for assessing decontamination technology as most of the procedures and chemicals used to decontaminate nuclear materials and equipment are also used for cleaning equipment and materials in the chemical process industry. Both chemical cleaning and decontamination require the same areas of knowledge and experience: chemistry of fouling, corrosion technology, and waste generation/removal techniques. Furthermore,, the same engineering knowledge is required to devise suitable procedures for mixing, pumping, as well as heating solvents and other chemical cleaning constituents. Compliance with basic health and safety practices regarding chemical agents is required, in addition to the radiological safety aspects.

The main advantages and disadvantages of chemical decontamination can be listed as:

Advantages

- Chemical decontamination is relatively simple and similar to classical cleaning in the conventional industry for which a lot of experience exists. It may also be relatively inexpensive where additional equipment is not required.

- Chemical decontamination is a known practice in many nuclear plants and facilities. With proper selection of chemicals, almost all radionuclides not included in the structure may be removed from contaminated graphite.

- With strong mineral acids, a decontamination factor of more than 100 (defined as the ratio of activity after and before treatment) reduction of activity may be achieved, and in many cases, the item may be decontaminated up to releasable levels.

- Chemical decontamination may also remove radioactivity from internal and hidden surfaces. However, in this case, its effectiveness may be low, and measurement at release levels will be a problem.

- Chemical decontamination involves relatively minor problems of airborne contamination, similar to those of the closed system approach.

Disadvantages

- The main disadvantage of chemical decontamination is the generation of secondary liquid waste, resulting in relatively high volumes compared to other processes. The treatment and conditioning of this secondary waste requires appropriate processes to be considered when selecting the decontamination option. Moreover, in some cases the effectiveness of the decontamination may be relatively low.

- Usually the solution must be heated up to 70 to 80°C in order to increase the rate of the decontamination process.

- A further disadvantage in obtaining high decontamination factors is that corrosive and toxic reagents may need to be handled.

1.2. Objectives of the Task & Motivation

Treatment of graphite with liquid decontamination agents is an alternative option to the gas phase reactions. Mineral acids, alkaline solutions, dissolved oxidising agents, organic washing detergents or such combinations may dissolve the contamination in the graphite. Chemical treatment tests will be undertaken to determine decontamination factors.

The graphite samples will be characterised before and after treatment to determine the decontamination by radioanalytical methods (γ-spectrometry, liquid scintillation counting and α-spectrometry).

The main objective of decontamination of i-graphite is to remove the radiocarbon in such a way that the potential risk associate with this nuclide is reduced allowing further treatment of the i-graphite for recycling or/and safe geological disposal as L&ILW. Beyond the problem of radiocarbon content of irradiated graphite there are other activation products that have to be removed in order to properly categorised, treated and condition. Isotopes in i-graphite of main concern include H-3, Co-60, Cl-36 and non negligible amounts of Ni-63, Europium isotopes and alpha emitters (Am-241, Pu isotopes and U isotopes).

The techniques studied in this task not only concentrate efforts in isotopic removal, they test the efficiency in which C-14 removal occurs and implications of the process of other activation products are also tested applying several techniques and methods to decontaminate i-graphite coming from UNGG reactors, Magnox reactors, as well as MTR and HTR graphite.

The studies are focused in for main techniques from five labs FZJ, CIEMAT, ENEA, INR and University of Manchester:

- Long term semi-dynamic Chemical Treatment testing (Inorganic Agents)
- Soxhlet (solid –Liquid Extraction) (Organic and Inorganic Agents)
- Chemical Treatment with Inorganic Agents
- Exfoliation processes with organic agents with Ultrasonic application

2. EXPERIMENTAL

2.1. Test Samples

2.1.1. LONG TERM CHEMICAL TREATMENT SAMPLES (UOM)

Two types of irradiated graphite material were used in this project. Irradiated graphite samples where collected from the British Experimental Pile Zero (BEPO) Energy Reactor and made available for research by the University of Manchester. The second irradiated graphite material was sourced from the Wylfa Magnox Reactor 1.

BEPO Reactor

The British Experimental Pile Zero (BEPO) Energy Reactor was commissioned in 1948 and closed in 1968. BEPO was graphite moderated, air cooled and initially fuelled with natural uranium metal in aluminium cans.

BEPO reactor shut down in 1968 resulting in 43 years of decay to date. Upon receiving this material into the university significant quantities of activity have already decayed leaving behind the long lived isotopes commonly found in all i-graphite. This helps with The availability of this material was also a high priority and its reduced isotopic inventory made it can ideal choice for use prior to receiving the significantly more active Magnox material.

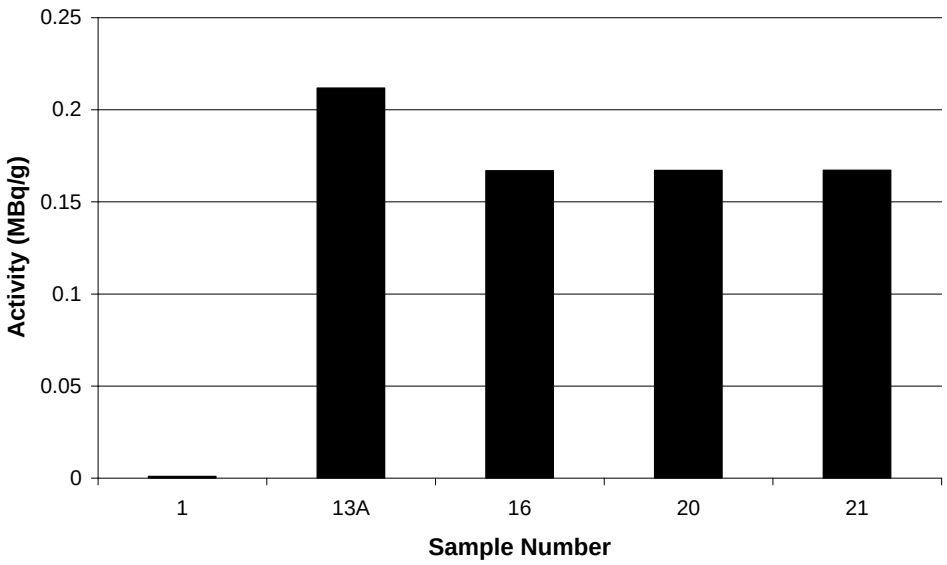


Figure 1 Graph showing total activity of each graphite sample in MBq/g.

The sample number indicates the channel from which the graphite sample was taken, therefore sample 1 (channel 1) was furthest away from the centre of the core and

sample 21 (channel 21) was at the centre of the BEPO reactor core. Figure 1 shows graphically the total activity measured for each sample data provided by Nirex.

Wilfa Magnox

Wylfa Magnox reactors were commission in 1971 and consist of two reactors with a combined capacity of 980 MW. The samples issues to UoM for this research where trepanned from the fuel channel wall of reactor 1 Two samples were collected for sending to UoM; Sample 1413/02 9U comes from an upper position in brick nine and sample 1319/12 8U comes from an upper position in brick eight

Along with the irradiation history of the two trepanned Wylfa Magnox samples provided to the University of Manchester the isotope inventory detailed in Table 1 was also provided, graphically the vast difference in quantities between each isotope present is observed.

Table 1 Isotopic inventory data provided by National Nuclear Laboratory

Nuclide	Wyfla 1413/02 Specific Activity Bq/g 9th June 2009	Wlfya 1319/12 Specific Activity Bq/g 9th June 2009
^{14}C	22100	22300
^{60}Co	123600	124000
^{137}Cs	2377	2480
^{55}Fe	890000	890000
^{3}H	5465000	5480000

Initially upon staring this program of work approximately 300 grams of BEPO graphite was offered to the University of Manchester for research into decommissioning. This material with its decreased half life was deemed suitable to provide excellent data on proof of concept experiments as well as the chance to used irradiated material with a low inventory to ensure laboratory procedures and best practices were suitable and safe. It was towards the end of this program of study that two trepanned samples from the Wylfa reactor were supplied totalling 7 grams. Wyfla sample 1413/02 9U was crushed into granules and used for leaching/chemical treatment test focusing on ^{3}H and ^{14}C analysis whereas Wlfya sample 1319/12 8U was kept intact and used for gamma spectroscopy and microstructural analysis.

2.1.2. SOXHLET EXTRACTION SAMPLES (FZJ)

Merlin:

The samples used in this study were thoroughly analysed in 2000. This section briefly details the work performed in preparation of and the results of this analysis.

The samples used in the Soxhlet Extraction tests were removed from the thermal columns during the reactor block's demolition.

Ten individual graphite bricks were removed from the bottom right channel of thermal column II in the reactor block. A sample was removed from each one of these graphite bricks.

Each of these 10 samples was analysed for radionuclides by LSC and γ spectrometry. The results of this analysis showed that the samples contain the following radionuclides: ^{3}H, ^{14}C, ^{60}Co, ^{133}Ba, ^{152}Eu, ^{154}Eu and ^{155}Eu

The reactor graphite's total inventory of contaminants was determined using ICP-MS measurements.

The analysis of the ten samples showed that sample T10 of the reactor graphite, from the part of the thermal column that was closest to the reactor's core, contained the greatest number of radionuclides (see table 2).

Table 2 Radionuclides in sample T10 (Merlin)

Nuclide	Sample [Bq/g]	
	TS 10/1	TS 10/2
H-3	4700	4760
C-14	505	449
Fe-55	<0.05	<0.003
Co-60	983	956
Ba-133	5.83	4.71
Eu-152	986	959
Eu-154	89.8	88.3
Eu-155	5.74	5.51
Total - α	<0.003	<0.003
Total - β,γ	2210	-*

AVR:

The samples for the second series of tests were taken from the core's graphite jacket.

The coordinates of the samples are not available so that it is not possible (due to confidentiality) to correlate the results with the neutron flux or neutron history of the reactor.

The samples available for selection comprised 11 samples from previous test series. This series of tests were performed in order to create a database about the AVR's HTR's activity inventory. The samples for the following tests were selected on the basis of their activity concentrations and dose output (by ALARA criterion).

Lowest dose sample was AVR-G-19 that is a black, powdered solid material and 8 sub-samples were subsequently removed from this sample and put into a test tube and were labelled AVR-1 to AVR-8. The mass of these sub-samples ranged from 0.037 to 0.043 g.

Before the start of the wet chemical tests, each one of these samples was analysed by γ-spectrometry and then compared with the previous analysis values. The results of this analysis showed that the samples contained the same radionuclides as shown by the previous measurement, and which are as follows: ^{60}Co, ^{133}Ba, $^{134/37}$Cs, ^{154}Eu and ^{155}Eu

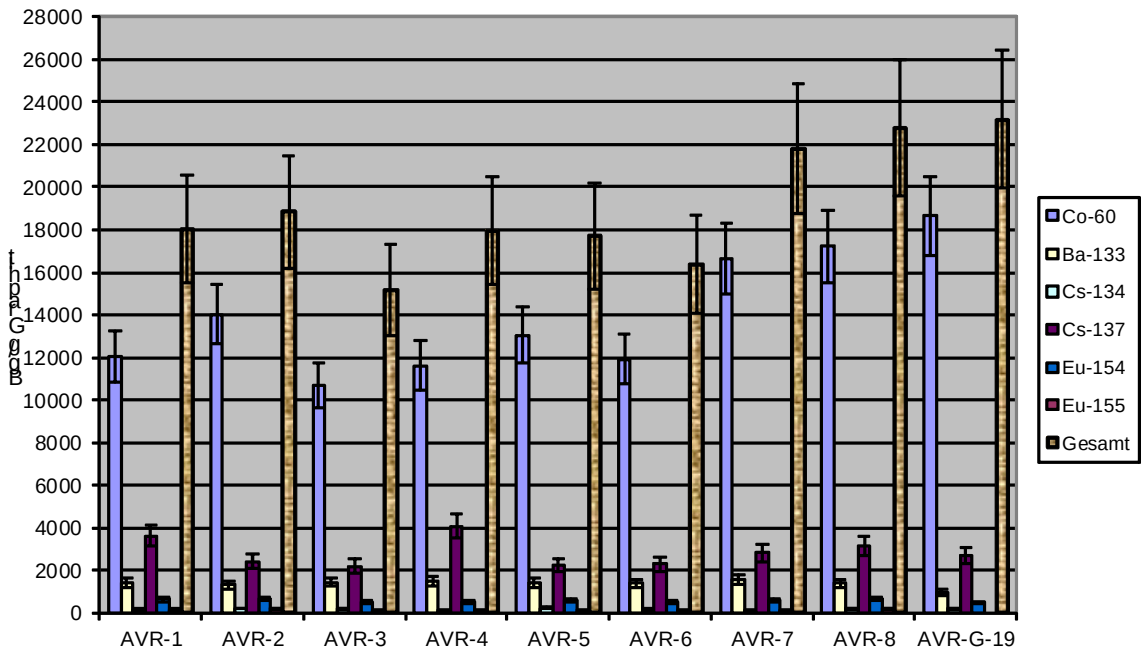


Figure 2 Sample comparison: AVR 1 - AVR 8 with AVR-G-19 (Gesamt = Total)

The activity values of samples AVR-1 –AVR-8 deviated in some cases by more than 50% from the reference specimen AVR-G-19 (see figure 2). This is an indication either of the heterogeneity or the individual samples' different quantitative compositions. This deviation has to be taken into account in the following tests.

2.1.3. INORGANIC AGENTS TREATMENT

The decontamination of graphite by chemical treatment with liquids agents depends on several factors like chemical composition of the leachant, temperature or the state of the graphite (block or powder).

2.1.3.1. INR Approach Samples

Irradiated graphite samples used in experiments comes from TRIGA reactor at Pitesti. According to the analyses performed by gamma ray spectrometry, respectively gamma spectrometry and the analyses performed by proportional counter, the irradiated graphite from TRIGA reactor (referring to the samples used in these experiments) contains the following inventory:

Table 3 Specific activity of Triga-INR samples used for leaching experiments

Activity	Co-60	Eu-152	Eu-154	Cs-137	C-14	Gross Beta

(Bq/g)						
sample A	70.75	1163	66.65	Not detected	1090	3440
sample B	52.35	1333.2	67.85	3.3	unanalyzed	328.83
sample C	52.67	1178.4	69.12	Not detected	unanalyzed	unanalyzed

2.1.3.2. CIEMAT Approach Samples

CIEMAT studied the influence of several factors on the decontamination of i-graphite powder from sleeves of an Uranium Natural Graphite Gas reactor (UNGG) by chemical treatment with liquid agents and then the decontamination of i-graphite block.

Initial activity was characterised in a homogeneous sample of sleeve powder, the inventory of which is shown in table 4:

Table 4 Specific activity of UNGG samples used for leaching experiments

A_0 (Bq/g)							
$^{239/40}$Pu	^{241}Am	^{94}Nb	^{137}Cs	^{154}Eu	^{14}C	^{60}Co	^{3}H
4.50E01	6.69E01	8.76E01	1.50e02	2.25e02	2.07e04	2.30e04	7.10e04

2.1.4. ORGANIC TREATMENT (ENEA)

2.1.4.1. Original Sample

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

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

In table 5 the masses of the samples, after the outer layer removal, are reported; the mean diameter is 1.7 cm and the mean height is about 1.0 cm (see Figure 3).

Table 5 Irradiated-Graphite Samples weights in grams (g)

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

As mentioned, 7 samples came from the Channel 8 (08F08), while the other 8 samples from Channel 7 (07S07); For each of these 2 groups, the samples came from different level origins named: *S,* Superior, *C*, Central and *I*, Inferior.

Figure 3 One of the i-Graphite samples from Latina NPP

2.1.4.2. Sample for chemical treatments

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

2.2. Methods

2.2.1. LONG TERM CHEMICAL TREATMENT (UOM)

The long term leaching experiments were performed at University of Manchester and constituted part of the PhD thesis of Lorraine McDermott [McDer12] and the summary of the experimental setup and results presented under this point have been collected from the corresponding Carbowaste Technical report.

2.2.1.1. Experimental Setup

First step is to setting-up the Laboratory conditions and the fulfilment of the safety and good practices rules and methods apply at the University of Manchester for the irradiated samples and technology used.

The determination of release of radiocarbon and tritium carried out in this investigation is making by LSC selecting the cocktails between two options (Prosafe HC and Goldstar) for best determination conditions in combination with aqueous phase 2.5 M in hydrogen peroxide. The results of the quenching (tSIE) in background measurements point out to Goldstar as the suitable scintillation cocktail to be use.

Table 6 Analysis results showing the swamping nature of the LSC cocktail

Volume addition of 2.5M H_2O_2	CPMA	DPMA	SIS	tSIE
GOLDSTAR				
1ml	35	38	37.49	386.43
2ml	32	35	25.93	354.43
3ml	30	33	29.48	330.36
4ml	31	34	21.98	312.88
5ml	41	45	27.30	292.49
10ml	27	31	24.94	221.51
PROSAFE HC				
0ml	32	34	42.83	449.65
1ml	33	36	42.14	358.25
2ml	30	33	45.05	326.30
3ml	31	34	33.11	301.16
4ml	49	54	44.89	277.94
5ml	30	33	33.97	267.94

2.2.1.2. Chemical Treatment Parameters Investigated

There are many possible options available when performing a leaching experiment on radioactive material. The leaching conditions used are often driven by repository environment or ground water systems. Sample history, size and availability also affect

the number of experiments and repeats that can be performed. This gives rise to many different approaches to the experimental conditions and length of test. However often water conditions are used as a standardised method of comparison with amount leached at 100 days also used. This gives a good comparison to the chemical treatment environments and provides more balanced conclusions on the effect of the chemical agents used.

The chemical treatment experiment focuses on ^{3}H and ^{14}C removal with minimal damage and weight loss to i-graphite. This PhD research aims to focus on reducing the isotopic inventory of the i-graphite and provide data on the mobility of ^{3}H and ^{14}C within this material. This will provide data on whether acidic treatment and isotope mobility can contribute to a reduction in environmental barriers need for geological repository conditions. Release rates and the mobility of the isotopes present has been determined and a reduction in isotopic inventory achieved.

In the test performed following a semi-dynamic testing (IAEA environmental procedure) with constant monitoring room temperature between 20-25ºC over a well known inventory and irradiation history i-graphite samples. Homogeneity of samples was accessed by autoradiography and beta determination for ^{3}H and ^{14}C were validate in the RRT performed in the framework of CARBOWASTE programme.

Short term (< 90 days) and Long term (> 90 days) experiments were performed according to IAEA methodology as well as the applied frequency of sampling and leaching/release rates (cumulative and fractional leaching rates).

Both solid and powder samples were used and the surface area for leach rate calculations was determined by BET analyses. Acidic, alkaline, oxidising, water and pH buffers (pH1 and pH13) were the chemical environments the i-graphite was analysed under.

Chemical reagents used were:

- Acidic,
- Alkaline,
- Oxidising,
- Water and
- pH buffers.

2.2.1.3. Experimental Program

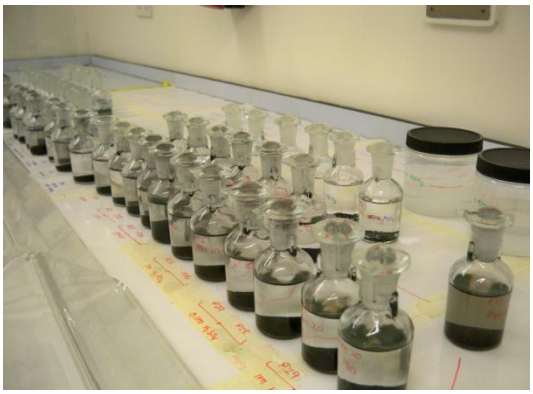


Figure 4. Leaching flasks

The leaching program involved two stages, stage One focusing on proof of concept and stage Two utilising other treatment options in addition to leach testing Magnox Wylfa graphite. Testing frequency employed was once weekly until leach rate remained steady then once every two weeks, then monthly as deemed appropriate.

In stage 1 for BEPO graphite was leached with the following conditions:

Water (solid and powder): 85 days
$KBrO_3$ 0.1 M, 0.2M, 0.3M, 0.4M, (powder and solid with 3M): 85 days
H_2O_2 0.5M, 1.0M, 1.5M, 2.0M, 2.5M (powder and solid with 1.5M): 85 days

In Stage 2 BEPO and MAGNOX graphite were leached with the following conditions:

- Water (MAGNOX: solid and BEPO: powder): 190 days
- Buffer pH 1 (MAGNOX: solid and BEPO: powder): 190 days
- Buffer pH 13 (MAGNOX: solid and BEPO: powder): 190 days
- H_2O_2 0.5 M (MAGNOX and BEPO: powder):190 days
- H_2O_2 1.5 M (BEPO: powder):190 days
- $KBrO_3$ 0.5 M (MAGNOX and BEPO: powder):190 days
- H_2SO_4 0.1M (BEPO: powder):190 days
- HCl 1M (BEPO: powder):190 days
- H_3PO_4 1M ((MAGNOX and BEPO: powder):190 days

Chemical treatment conditions were testing using liquid scintillation cocktails to ensure chemiluminescence, quenching and counting efficiency would not be affected by the chemical environments used both stages. SIS and tSIE values (quenching) are used to determine the suitable LSC cocktail of measurement.

The results shown in Sections 3.3.5 and 3.3.6 represent how aggressive each of the leaching/chemical treatment conditions employed in this research were. Using the tSIE values the following raking system can be applied to the leachants used:

Water < Potassium bromate < pH13 < pH1 < Sulphuric Acid < Hydrogen peroxide < Phosphoric Acid < Hydrochloric Acid

More concentrated molarities of the acids where tested however these proved incompatible with all the cocktails available.

Chemical leach treatments within this study focused on removing of ^{3}H and ^{14}C from i-graphite. In phase one a standardised treatment methodology was developed and employed. For each chemical environment, 0.5 grams of graphite were tested in 50 ml of leachant and each test was performed in duplicate. Each sample pair was accompanied by a standard water baseline. All chemical tests were performed at 20 ± 5°C. Samples were powdered in order to maximise the geometrical surface area and compared against solid samples for both stages. The testing methodology has been adapted according to IAEA standard for 'Semi-dynamic leach test' in which a 5ml leachant sample is removed every 7 days and replaced with a fresh 5ml of leachant. Figure 4 shows the glassware and laboratory set-up employed during both stages of chemical treatment

2.2.2. SOXHLET EXTRACTION OF IRRADIATED GRAPHITE (FZJ)

Soxhlet extraction is a distillation-based solid-liquid extraction method. It entails heating the liquid phase to boiling point inside a round-bottomed flask using a heating mantle. The resulting steam travels through the riser pipe into the condenser, where it condenses and drips into the extraction thimble to which the Soxhlet extractor is fitted. The extraction thimble contains the solid material. The extracting agent will continue to rise inside the Soxhlet extractor until it reaches the level of the drain and the solvent flows back into the flask. During the filling phase, the solvent can extract the soluble substances from the solid material. This process is continuously repeated.

Soxhlet extraction has the advantage of being able to achieve a high level of concentration of the substance being extracted using only a small amount of solvent. Its only disadvantage is its high energy consumption.

2.2.2.1. Experimental set-up

For Merlin and AVR samples the system was similar but not the same:

A Soxhlet extraction apparatus respectively comprises:

- 100-mL round-bottomed flask (triple neck flask when using argon)
- 30-mL Soxhlet extractor
- 30-mL paper or fibre glass extraction thimble
- Condenser
- Heating mantle
- Filter, clamps, stoppers, condenser hoses, Teflon ground joint sleeves

If gas is introduced, the apparatus also includes:

- Glass capillaries
- Washing bottles

Figure 5: Experimental set-up for the Soxhlet extraction for the Merlin graphite
From left: Test apparatus no. 1, 2, 3 and 4. No. 3 and 4 with an argon supply line

The Soxhlet extraction was performed with both organic and inorganic agents:

INORGANIC:

- Neutral:
- H_2O deionised
- Acidic (Different concentrations):
- HCl
- HNO_3
- H_2SO_4
- Alkaline (Different concentrations):
- NaOH solution

Organic:

- **Alcohols**:
  - C_2H_5OH ethanol
- **Ketone** (aprotic, dipolar):
- CH_3COCH_3 acetone
- **Carboxylic acids**:
  - CH_3COOH acetic acid 6 M and 12 M
- **Aromatics**:

  - Toluene
- **Halogenated hydrocarbons**:
  - CCl_4
  - 1-Bromobutane
- **Hydrocarbons**:
  - cyclohexane
  - n-hexane
  - n-pentane

2.2.2.2. Test procedure

Merlin:

Soxhlet extraction was used. The amount of solvent used was 60 mL respectively. The test period was approx. 5 hours. In the tests in which HNO3 was used as the extracting agent, the resulting gasses were transferred into a water flask filled with 20 mL 0.1 M NaOH by means of an argon stream (p = 1 bar). For comparison, some of the tests were performed without introducing argon. These tests showed that the period of time required to complete each leaching cycle was 2 to 3 times as long when using argon (duration of the extraction process using 4 M HNO3 approx. 18 min) than it was when not using argon (duration of the extraction process using 4 M HNO3 approx. 7 min). This increase is due to the triple neck flask's large volume and the longer time needed to heat the flask for each leaching process.

Following the completion of the tests, the leaching solutions were filled into appropriate glass or PE flasks. An aliquot of the leaching solution was removed and analysed by LSC and γ-spectrometry.

The extraction thimbles that were used for solvents with low-volatility at room temperature were rinsed with water and dried. After this, the solid material samples were removed from the extraction thimble.

The samples were subsequently heated at 70°C until there was no longer any detectable difference in their weight.

After the tests, approx. 0.15 g were taken from each solid material sample respectively, transferred into a test tube and, just as with the liquid samples, measured by γ-spectrometry.

AVR:

The experimental set-up used for the AVR graphite differed from the Merlin tests in the following points:

The volume or the size of the condensers, the Soxhlet extractors and the extraction thimbles were adjusted to the sample volume and were 5-mL instead of 30-mL. The

amount of solvent used was 50 mL respectively. The temperature control (3 steps) of the heating mantle was adjusted in accordance with the acids' boiling point.

In each of the tests, the gasses that developed during the tests where transferred into three washing bottles (by means of an argon stream p = 1 bar). The first washing bottle was filled with 20 mL 0.1 M HNO3 for capturing tritium and chloride, the second and third washing bottles contained 20 mL 0.1 M NaOH each for capturing C-14 in the form of $^{14}CO_3^{2-}$.

Liquid extraction with sulphuric acid (differences compared to a) only):
The extraction thimble with the sample was suspended in a vial in the round-bottomed flask. A hot plate with a magnetic stirrer was used to heat the sample. The sulphuric acid was thoroughly mixed with the magnetic stir bar. The flask temperature was kept at 80°C by means of a water bath. The water bath's temperature was kept constant with the aid of an adjustable hot plate.

Following the completion of the tests, the leaching solutions were filled into PE bottles. An aliquot of each of the leaching solutions was removed and analysed by LSC and γ spectrometry. The solvent contained in the quartz wool from the extraction thimbles was removed and added to the leaching solutions.

The extraction thimbles were subsequently rinsed with water and dried. The liquid used to rinse them was collected and its level of activity determined by LSC.

After the drying process, the solid material samples were removed from the extraction thimbles the samples rinsed with water to remove the solvent residues and then transferred into measuring test tubes.

They were subsequently placed into a glass beaker and carefully heated at 70°C to remove the residual moisture until their weight remained constant.

2.2.3. INORGANIC AGENTS TREATMENT

The decontamination of graphite by chemical treatment with liquids agents depends on several factors like chemical composition of the leachant, temperature or the state of the graphite (block or powder).

2.2.3.1. H-3 & C-14 (CIEMAT)

The study of the decontamination of ^{14}C and ^{3}H in irradiated graphite powder was carried out with several leachants: 0.1M sodium hydroxide, 0.1M sodium hydroxide with hydrogen peroxide, 3M nitric acid and mixtures of nitric, hydrochloric and sulphuric acids. In all the experiments a mixture of 0.15 g of graphite powder and a solution

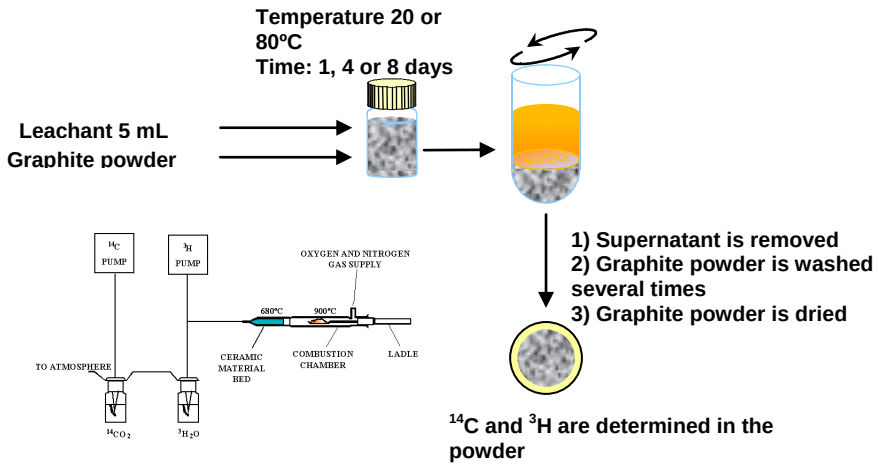


Figure 6: Experimental set-up for leaching experiment for tritium and radiocarbon including separation procedures for determination.

2.2.3.2. Beta-Gamma Emitters

Leaching of beta-gamma emitters (INR)

The experiments for removal of Co-60, Eu-152 & Eu-154 consisted in contacting the i-graphite (under the powder form) with different acids and mixtures of acids.

Table 7 The experiments performed for radionuclide chemical removal

No. exp.	mass (g)	Volume acids (decontamination solution)	Contact time	Sample type
1	1.53	5 ml HNO_3 65%	6 days	B
2	1.50	5 ml HNO_3 65%+ 5 ml apa demi	6 days	B
3	1.50	5 ml HCl 37%	6 days	B
4	1.51	5 ml HCl 37%+ 5 ml apa demi	6 days	B
5	1.48	5 ml H_2SO_4 98%	6 days	B
6	1.49	5 ml H_2SO_4 98%+ 5 ml apa demi	6 days	B
7	1.47	5 ml H_3PO_4 85%	6 days	B
8	1.51	5 ml H_3PO_4 85%+ 5 ml apa demi	6 days	B
9	1.48	5 ml HNO_3 65% + 5 ml H_3PO_4 85%	6 days	B
10	1.47	2.5 ml HNO_3 65% + 2.5 ml H_3PO_4 85%+ 5 ml apa demi	6 days	B
11	1.48	2.5 ml HCl 37%+ 2.5 ml HNO_3 65%	6 days	B
12	1.51	2.5 ml HCl 37%+ 2.5 ml HNO_3 65%+ 5 ml apa demi	6 days	B
13	1.49	2.5 ml HCl 37%+ 2.5 ml H_2SO_4 98%	6 days	B
14	1.50	2.5 ml HCl 37%+ 2.5 ml H_2SO_4 98%+ 5 ml apa demi	6 days	B
15	1.52	5 ml acid oxalic 10%	6 days	B
16	1.51	5 ml acid citric 10%	6 days	B
17	1.52	2.5 ml acid oxalic 10%+ 2.5 ml acid citric 10%	6 days	B
18	1.41	5 ml H_2SO_4 98%	24 hours	C

No. exp.	mass (g)	Volume acids (decontamination solution)	Contact time	Sample type
19	1.47	5 ml H_2SO_4 98%	3 days	C
20	1.67	5 ml H_2SO_4 98%	7 days	C
21	1.49	5 ml H_2SO_4 98%	14 days	C
22	1.58	2.5 ml H_2SO_4 98%	24 hours	C
23	1.53	2.5 ml H_2SO_4 98%	3 days	C
24	1.50	2.5 ml H_2SO_4 98%	7 days	C
25	1.53	2.5 ml H_2SO_4 98%	14 days	C
26	1.50	10 ml water	24 hours	C
27	1.53	10 ml water	3 days	C
28	1.44	10 ml water	7 days	C
29	1.55	10 ml water	14 days	C
30	1.43	2.5 ml H_2SO_4 98%+2.5 ml HCl 37%	24 hours	C
31	1.47	2.5 ml H_2SO_4 98%+2.5 ml HCl 37%	3 days	C
32	1.43	2.5 ml H_2SO_4 98%+2.5 ml HCl 37%	7 days	C
33	1.61	2.5 ml H_2SO_4 98%+2.5 ml HCl 37%	14 days	C
34	1.43	1.5 ml H_2SO_4 98%+1.5 ml HCl 37%	24 hours	C
35	1.50	1.5 ml H_2SO_4 98%+1.5 ml HCl 37%	3 days	C
36	1.53	1.5 ml H_2SO_4 98%+1.5 ml HCl 37%	7 days	C
37	1.35	1.5 ml H_2SO_4 98%+1.5 ml HCl 37%	14 days	C
1.1	2.00	10 ml HNO_3 65%	2 days	A
2.1	2.00	10 ml HCl 37%	2 days	A
3.1	2.00	5 ml HNO_3 65% +5 ml H_3PO_4 85%	2 days	A
4.1	2.00	10 ml NaOH 3M	2 days	A
1.2	2.00	5 ml HNO_3 65% +5 ml apa demi	2 days	A
2.2	2.00	5 ml HCl 37% +5 ml apa demi	2 days	A
3.2	2.00	5 ml HNO_3 65% +5 ml H_3PO_4 85%+ 10 ml apa demi	2 days	A
4.2	2.00	5 ml NaOH 3M +10 ml apa demi	2 days	A
a	2.01	15 ml water	30 days	B
b	1.99	15 ml water	3 days	B
c	2.02	15 ml water	5 days	B

The vials were periodically mechanically shaken. After the contacting period a known quantity of demineralised water was added and then they were centrifuged for 7 minutes and filtrated. The both, filtrates and graphite samples, were measured.

Measuring the graphite

Known quantities of wet graphite were add on the experimental plates and the layer was homogenised by adding 2-3 drops of etilic alcohol. The samples were dried under the UV lamp and an incrustation was given (protecting layer of toluene + polystyrene. The samples thus prepared were measured.

Leaching of beta-gamma emitters (CIEMAT)

It has been studied the decontamination of irradiated graphite powder with several leachants: nitric, hydrochloric, phosphoric, sulphuric acids at different concentrations and their mixtures with citric and oxalic acids. In all the experiments a mixture of 0.15g of graphite powder and a solution volume of 5 mL was put into a vial and was shaken for 24 hours. Then, the mixture was centrifuged and the supernatant was removed and passed through a 0.20 μm filter. The leaching procedure was carried out at three different temperatures 20, 60 and 80 ºC and using different solutions. In all cases the filtrate was measured by high resolution gamma spectrometry.

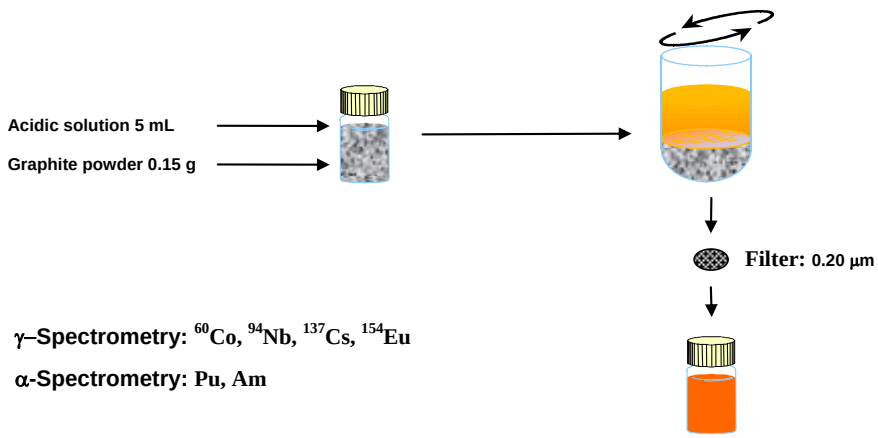


Figure 7: Experimental set-up for leaching experiment for alpha and gamma emitting nuclides.

Leaching of beta-gamma emitters (ENEA)

The procedures for leaching beta-gamma emitters with inorganic agents are the same described in section 2.2.4. In this section have been studied classic strong acid mixtures decontamination approaches for testing for future works the possibility of "combined" organic solvent/acid mixtures processes to obtain satisfying results and complete the overall decontamination steps.

At this purpose, 3 i-graphite samples coming from Latina NPP and similar to the ones used in this work as describe in section 2.1.4, have been divided in 3 sections named S1, S2 and S3.

On the first section S1 of each sample a characterisation of ^{60}Co and ^{137}Cs were performed in order to know the exact quantity of each radionuclide before the different treatments. On the latter two sections acid mixtures leaching tests were tested according to 2 different approaches:

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

The instruments used for the measurements and their characteristics are described in section 2.2.4.2

Leaching Test at 200°C with acid mixtures was performed with sections S2 of each sample were first grinded to powder and then put in a reflux system composed by a glass Pyrex flask and a water circulation refrigerator together with the different acid mixtures for 20 min. The acid mixtures were as follow:

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

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

The leaching test at room temperature with acid mixtures was performed only 2 sections were used instead of the 3 as in the previous test.

Each section (S3) of the former sample has been leached with different acid mixtures as follow:

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

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

2.2.3.3. Alpha Emitters (CIEMAT)

Experimental conditions for performing the leaching test for alpha emitters decontamination is already explained in the method of CIEMAT for beta-gamma decontamination process, being the measurement in the case of alpha emitting nuclides by alpha spectrometry.

2.2.4. ORGANIC TREATMENT (ENEA)

2.2.4.1. Radiocarbon Determination

Radiocarbon has been measured by Liquid Scintillation Counting after pre-treatment of an aliquot of each samples (about 0.12g/sample) by acid digestion with H_2SO_4-HNO_3-$HClO_4$ mixture at 200°C in closed equipment under inert gas-flow (N_2). The $^{1}4C$ (as CO_2) were trapped with washing bottles with NaOH 0.1M. The solutions obtained are completely clear and colourless. An aliquot of each solution is taken has been added with Scintillation Cocktail and measured by Liquid Scintillation Analyser in dual-label mode with $^{3}H/^{14}C$ reference standards

Table 8 Radiocarbon characterisation of the Latina NPP (by LSC)

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

2.2.4.2. Gamma-Spectrometry

In order to identify gamma radioactive isotopes and to determine the amount of radioactive material, the samples has been characterized by means of a gamma spectrometry system

2.2.4.3. Method

The i-graphite from Latina NPP, like as all the graphite coming from moderators exposed to a neutron flux (for Latina NPP is up to 5x1022 n/cm2), presents a wide range and amounts of activation products.

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

Principle

The main idea is to apply an exfoliation-like process on the graphite by organic solvents (liquid-phase exfoliation) to produce un-functionalized and non-oxidized graphene layers in a stable homogeneous dispersion. This process, helped by mild sonication, consists in separating the individual layers in a more or less regular manner. Such a separation, being sufficient to remove all the inter-planar interactions, thanks to the dipole-induced/dipole interactions between graphenes and organic solvents, results in a dispersion of the graphite in a workable media. This facilitates processing, treatment and easy characterization for the contaminants recoveries (Figure 8).

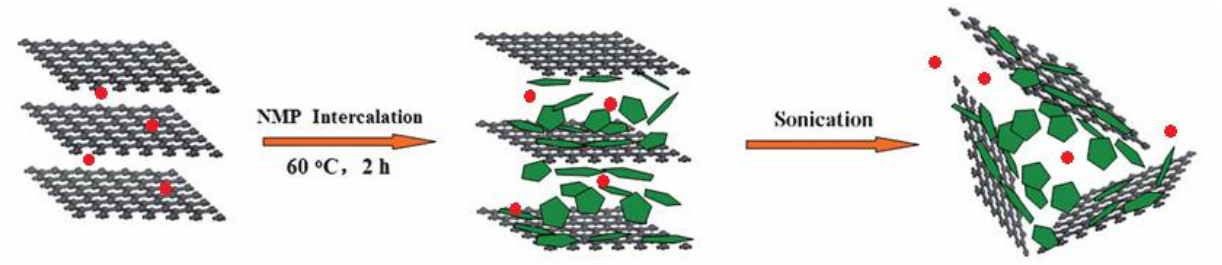


Figure 8 Representation of the main steps for the graphite exfoliation process promoted by organic solvents and ultrasound assisted

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

Procedure

The main steps in this process are:

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

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

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

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

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

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

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

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

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

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

3. RESULTS

3.1. Decontamination Factors in Mid-term Leaching Experiments (UoM)

The isotopic release rates have been calculated for ^{14}C and ^{3}H and are given as cumulative fraction of isotopic released as a function of time and takes into account the sum of isotopic release taken to reach a steady state and beyond which not further significant release is exhibited. The Cumulative Fraction Released equations are shown in equations 3 and 4 and also take into account the dilution factor experienced by the replacement of fresh leachant at testing intervals.

$$\sigma_d = A_n - (0.9A_{n-1})$$

Equation 1

σ_d = Actual activity released at time point with dilution factor/Bq
A_n = Activity at time point/Bq
A_{n-1}= Activity at previous time point/Bq

$$CFR = \sum \frac{\sigma_d + \sigma_{n-1}}{A_0}$$

Equation 2

CFR= Cumulative Fractional Release
σ_{n-1} = Activity released at previous time point /Bq
A_0 = Activity present in sample being analysed and corrected for half life /Bq

3.1.1. CHEMICAL TREATMENT PHASE ONE

The phase one leaching/chemical treatment testing was carried out using a deionised water baseline with H_2O_2, $KBr0_3$ reagents. Samples from BEPO reactor channels 16 and 20 were used throughout the 84 day test. An 8% error is associated with this leaching data which is based on LSC counting error, ±1% weight distribution and electronic pipette standard deviation. All equipment was calibrated before testing was carried out but errors are associated with the equipment are included in the assessments. All calculations include half life correction and weight correction for solid samples due to machining limitations on active material, all solid sample used where 0.5 grams ±1%.

3.1.1.1. ^{3}H release under Phase One Conditions

Water

The cumulative fraction of ^{3}H released from BEPO Channel 16 under water conditions for 84 days indicates that ^{3}H release began quickly the release of ^{3}H was extremely low as 3.1% of the total tritium inventory from the powdered sample and 1.8% from the solid sample. These release rates illustrate both the mobility of HTO species within the graphite is likely to be bound to the surface groupings which are susceptible to

exchange with hydrogen atoms in the water and that the differences observed between solid and powder material may be due to a function of exposed surface area.

The steady-state leach rate appears to have been achieved for ^{3}H after 60 days. The low reactive nature seen in this experiment leads to the conclusion that any activity removed under water conditions was surface contamination and easily removed regardless of the conditions employed. These samples had >97% of the ^{3}H and remaining at the end of this experiment.

Potassium bromate

$KBrO_3$ was used in concentrations ranging from 0.1M – 0.5M. The results obtained for ^{3}H release from leaching BEPO channel 16. All samples were powdered in order to maximise the surface area and treated under varied potassium bromate concentrations. As with water the ^{3}H results show a very slow release, this is only marginally increased with increasing concentrations. 4.2% of the total ^{3}H inventory was released under 0.1M $KBrO_3$ conditions, compared with 5.4% of the total ^{3}H inventory released under 0.4M $KBrO_3$ conditions and 5.6% of the total ^{3}H inventory was released under 0.5M $KBrO_3$ conditions. Compared to leaching release in water which resulted in a 3.4% ^{3}H release it could be concluded that the oxidising environment provided by the potassium bromate and notably the $BrO_3(^-)$ ion, has little effect on leach rate and on ^{3}H interaction and promotes the HTO exchange theory which is examined with water.

Hydrogen peroxide

H_2O_2 was used in concentrations ranging from 0.5M – 2.5M. The ^{3}H release under hydrogen peroxide conditions for powdered BEPO Channel 16 samples.began quickly and 9.7% of the total ^{3}H was released under 0.5M H_2O_2 conditions, compared with 16.2% of the total ^{3}H inventory released under 2M H_2O_2 conditions. A maximum of 17.4% of the total ^{3}H inventory was released under 2.5M H_2O_2 conditions. It is clear by the significant increase in the rate of ^{3}H released is observed under hydrogen peroxide conditions that radiolysis and isotopic exchange of the ^{3}H with the hydrogen peroxide is considered to be the mechanism behind this increased release rate. Hydrogen peroxide promotes radiolysis and the exchange of HTO from the graphite to the leachant in comparison to the water condition results where only the 3.1% of the total ^{3}H inventory released

$H_2O_2 \rightarrow OH^{\bullet} + OH^{\bullet}$ Hydroxyl radicals
$H^{\bullet} + OH^{\bullet} \rightarrow H_2O$ Isotopic exchange – Radicals
$H^{+} + OH^{-} \rightarrow H_2O$ Isotopic exchange – Hydroxyl ion

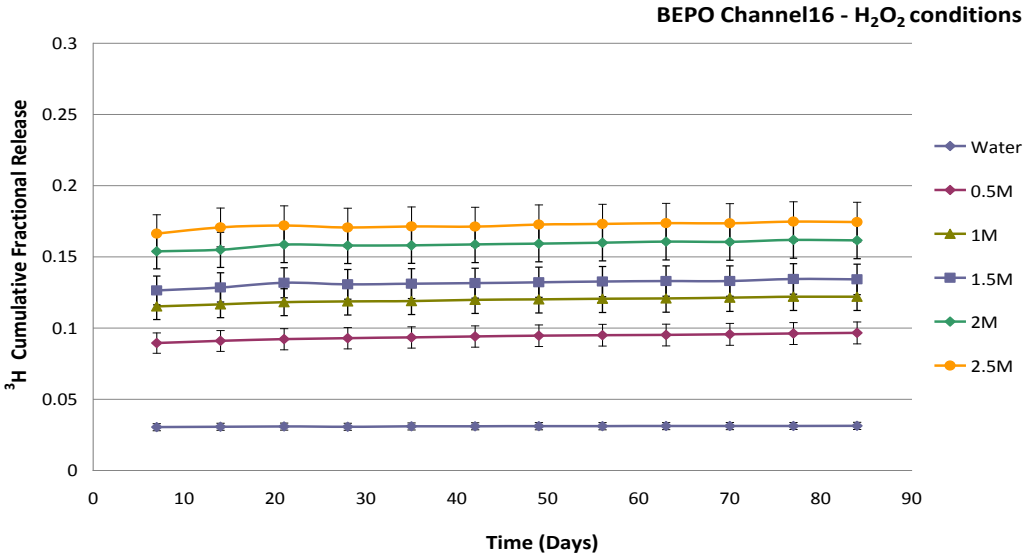


Figure 9 Powder BEPO Channel 16 ^{3}H release under hydrogen peroxide conditions

Surface area effect on tritium release

To compare the release rates of ^{3}H for solid versus powder BEPO channel 16 samples. All data has been corrected for the weight of each sample used.

BEPO Channel 16 ^{3}H release under 0.3M $KBrO_3$ conditions. removes 2.1% of the total ^{3}H inventory for the solid sample and 5.2% of the total ^{3}H inventory for the powdered sample was released.

BEPO Channel 16 ^{3}H release under 1.5M H_2O_2 conditions. presents 13.4% of the total ^{3}H inventory for the powdered sample and 4.7% of the total ^{3}H inventory for the solid sample was released under 1.5M H_2O_2 conditions

Comparing powder to solid release rates of tritium surface area has enabled a significant increase in isotopic release of ^{3}H. Under 0.3M potassium bromate conditions the solid release rate after the initial few time points is minimal showing a decrease in release towards 84 days. The powder however is increasing still at day 84, this result was one of the driving factors behind extending the phase two leaching experiment to over 100 days to observe when all the mobile or reactive forms of ^{3}H are released

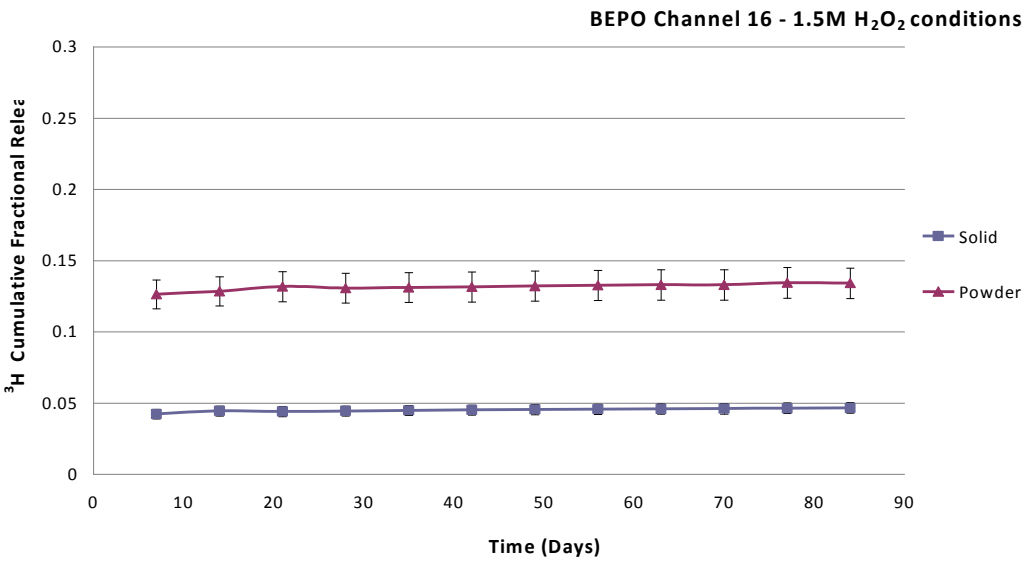


Figure 10 BEPO Channel 16 ^{3}H release under 1.5M hydrogen peroxide conditions

3.1.1.2. ^{14}C release under phase One Conditions

Water

BEPO Channel 16 ^{14}C results under water conditions released a very slow rate of ^{14}C with 0.87% of the total ^{14}C inventory released from the powdered sample and 0.34% of the total ^{14}C inventory from the solid sample, Less ^{14}C mobility is observed under water conditions for BEPO Channel 16 . The speciation responsible for this release indicates dissolved $^{14}CO_2$ as there is approximately 0.04% by volume of CO_2 is present in the atmosphere and water typically contains less than 10 mg/L, however several hundred mg/L of CO_2 can be dissolved into water should the appropriate conditions be met the limited release of ^{14}C under water conditions is most probably derived from dissolved $^{14}CO_2$ species.

Potassium bromate

The results obtained for ^{14}C release from leaching BEPO channel 16 powdered samples under potassium bromate conditions indicates a maximum of 5.7% released from the total ^{14}C inventory under 0.5M $KBrO_3$ conditions. This can be compared to release under water conditions (approximately 1% of the total ^{14}C inventory). Bromine is well known as an intercalation element capable of separating the graphite layers, the bromate ion BrO_3^- present in potassium bromate has had little effect on the graphite structure which is observed through the limited release of ^{14}C.

Lower release rates for ^{14}C than expected where achieved under potassium bromate conditions, which leads to the conclusion that mobile/weakly bound isotopes are being removed/release, however due to the large size of the bromate ion and the reduced

concentration there is little further interaction occurring between the graphite and the potassium bromate solution after 60 days.

Hydrogen peroxide

The ^{14}C released under hydrogen peroxide conditions for powder BEPO Channel 16 samples presents 11.7% of the total ^{14}C inventory and a maximum of 15.4% under concentrations >2M H_2O_2

The mechanism behind the release of ^{14}C by hydrogen peroxide is thought to be chemical oxidation by intercalation of any surface bound ^{14}C .With 15 % of the inventory has been released the bulk of the activity has remained locked within the graphite micro-structure.

Samples taken from BEPO channel 20 were found to release less ^{3}H and ^{14}C under all conditions when compared with samples taken from BEPO channel 16. The inventory and reactor history of these two channels is reported as being similar [96] however isotopic determination via thermal analysis has shown that this distribution of ^{3}H and ^{14}C is not uniformed throughout the bulk of the material supplied. BEPO channel 20 samples under hydrogen peroxide conditions were also found to turn the leachant solution grey in colour. As coloured samples interfere with LSC counting efficiency this will have lead to additional inaccuracy due to the opacity of the liquid which should be accounted for when analysing this data. Therefore BEPO channel 20 data has had a correction factor added and the 84 incremental leach rates have been reported which considers surface area and cumulative release up to 84 days Section 3.1.3 for leach rate data.

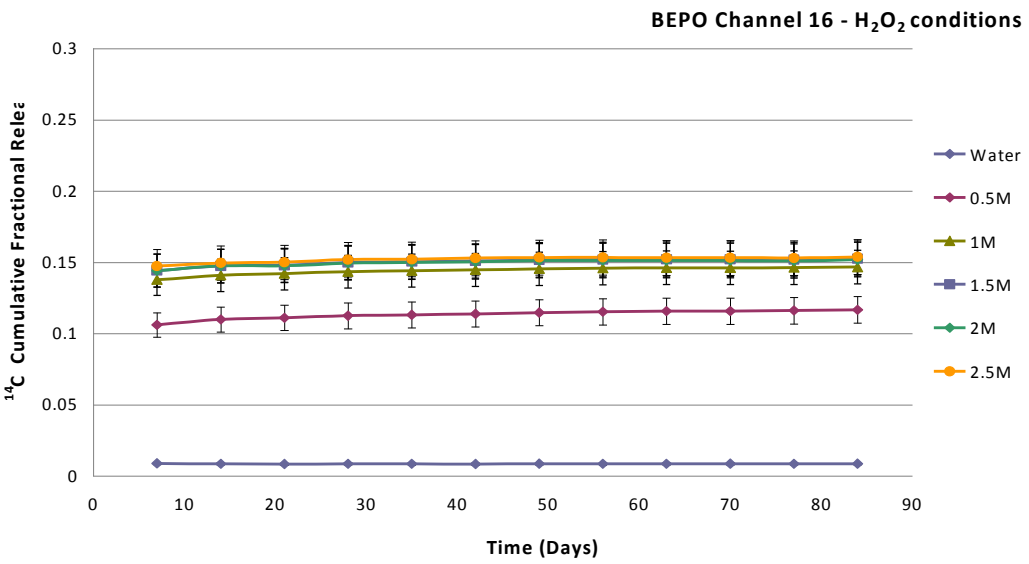


Figure 11 Powder BEPO Channel 16 ^{14}C release under hydrogen peroxide conditions

Surface area effect on radiocarbon release

^{14}C release under 0.3M $KBrO_3$ conditions solution from a sample of BEPO Channel 16. presents 0.9% of the total ^{14}C inventory for the solid sample was released and 4.9% for the powdered sample.

A steady state of ^{14}C release is achieved by day 60 for both solid and powdered material under 1.5M hydrogen peroxide conditions. Surface area has increased the mobility and availability of the ^{14}C. Given the aggressive environment of 1.5M hydrogen peroxide and the powdered structure of the material only 15% of the ^{14}C was leached out provides interesting results regarding the structure and bonding of the ^{14}C which remains. A possible conclusion would be that to remove the remaining ^{14}C from the graphite the material it must be destroyed. Employing more aggressive environments for long periods of time will provide further data to support such a statement.

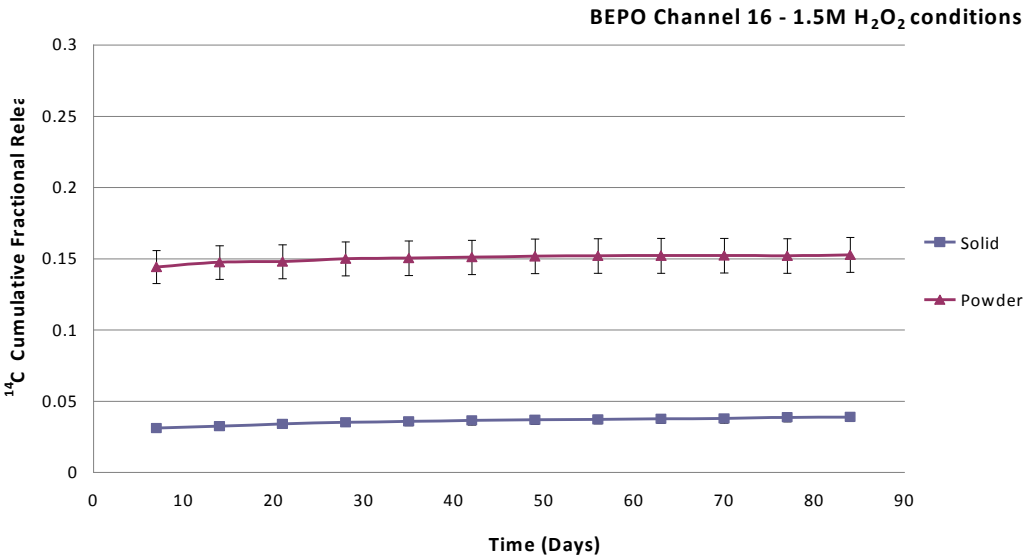


Figure 12 BEPO Channel 16 ^{14}C released under 1.5M hydrogen peroxide conditions

3.1.1.3. Leaching/Chemical Treatment Discussion

The leaching results and experimental techniques and conditions taken forward into stage two leaching experiment are summarised below:

The oxidising environment of Hydrogen peroxide yielded the highest release activities for both of ^{3}H and ^{14}C removal.

Graphite taken from channels 16 and 20 behaved differently under all leaching conditions, BEPO Channel 20 graphite provided a murky solution which interfered with

the LSC counting efficiency. The trend of release rate of ^{3}H and ^{14}C versus leaching environment were consistent with BEPO Channel 16 results.
Levels of ^{3}H and ^{14}C removal under water conditions were at the LOD limits for the LSC.

The highest values of release where achieved under 2.5M hydrogen peroxide. Hydrogen peroxide reacted with the graphite promoting ^{3}H and ^{14}C releases.

Hydrogen peroxide and potassium bromate were considered from this experiment as an aggressive oxidising environments leading to the promotion of significant isotopic release. Comparing 0.5M conditions of both solutions hydrogen peroxide is noted to give the greater release rates. Some bubbles were observed within the hydrogen peroxide solutions which may be associated with ^{3}H-labelled gaseous species being released.

An average overall weight loss of 12% was recorded, with 4% attributed to transfer between containers and filtering the material at the end of the experiment.

Leach rates calculated for all conditions are summarised in the report Characterisation and Chemical Treatment of Irradiated UK Graphite Waste CW- T-4.3.3.b this allows a comparison of amount of activity released with exposed surface area of the material on test.

3.1.1.4. Phase one Leach Rate Results Summary

Leach rate results are detailed in Tables 9 and 10 for all leaching parameters tested in the phase one research. For phase one leaching the majority of leach rate has reached a steady state by day 84 however it must be noted at 0.3M potassium bromate is still slightly increasing at day 84.

Table 9 Leaching phase one BEPO channel 16 Leach rates

Leachant condition	Type of material		Leach Rate at 84 days		Leach Rate at 84 days
Water	powder	^{3}H	$4.15E^{-6}$	^{14}C	$1.15E^{-6}$
Water	solid	^{3}H	$1.70E^{-4}$	^{14}C	$3.17E^{-5}$
0.1M Potassium Bromate	powder	^{3}H	$5.59E^{-6}$	^{14}C	$2.99E^{-6}$
0.2M Potassium Bromate	powder	^{3}H	$6.44E^{-6}$	^{14}C	$5.13E^{-6}$
0.3M Potassium Bromate	powder	^{3}H	$6.94E^{-6}$	^{14}C	$6.45E^{-6}$
0.3M Potassium Bromate	solid	^{3}H	$2.00E^{-4}$	^{14}C	$8.25E^{-5}$

0.4M Potassium Bromate	powder	^{3}H	$7.22E^{-6}$	^{14}C	$6.97E^{-6}$
0.5M Potassium Bromate	powder	^{3}H	$7.49E^{-6}$	^{14}C	$7.51E^{-6}$
0.5M Hydrogen Peroxide	powder	^{3}H	$1.28E^{-5}$	^{14}C	$1.55E^{-5}$
1M Hydrogen Peroxide	powder	^{3}H	$1.62E^{-5}$	^{14}C	$1.95E^{-5}$
1.5M Hydrogen Peroxide	powder	^{3}H	$1.78E^{-5}$	^{14}C	$2.02E^{-5}$
1.5M Hydrogen Peroxide	solid	^{3}H	$4.35E^{-4}$	^{14}C	$3.63E^{-4}$
2M Hydrogen Peroxide	powder	^{3}H	$2.14E^{-5}$	^{14}C	$2.01E^{-5}$
2.5M Hydrogen Peroxide	powder	^{3}H	$2.31E^{-5}$	^{14}C	$2.04E^{-5}$

Table 10 Leaching phase one BEPO channel 20 Leach rates

Leachant condition	**Type of material**		**Leach Rate at 84 days**		**Leach Rate at 84 days**
Water	powder	^{3}H	$6.57E^{-7}$	^{14}C	$3.88E^{-6}$
Water	solid	^{3}H	$8.79E^{-6}$	^{14}C	$1.16E^{-5}$
0.1M Potassium Bromate	powder	^{3}H	$1.20E^{-5}$	^{14}C	$7.60E^{-6}$
0.2M Potassium Bromate	powder	^{3}H	$1.64E^{-5}$	^{14}C	$1.06E^{-5}$
0.3M Potassium Bromate	powder	^{3}H	$1.53E^{-5}$	^{14}C	$1.26E^{-5}$
0.3M Potassium Bromate	solid	^{3}H	$1.77E^{-5}$	^{14}C	$3.90E^{-4}$
0.4M Potassium Bromate	powder	^{3}H	$1.86E^{-5}$	^{14}C	$1.60E^{-5}$
0.5M Potassium Bromate	powder	^{3}H	$1.79E^{-5}$	^{14}C	$1.59E^{-5}$
0.5M Hydrogen Peroxide	powder	^{3}H	$2.54E^{-5}$	^{14}C	$1.41E^{-5}$
1M Hydrogen Peroxide	powder	^{3}H	$3.57E^{-5}$	^{14}C	$1.80E^{-5}$
1.5M Hydrogen Peroxide	powder	^{3}H	$4.05E^{-5}$	^{14}C	$1.88E^{-5}$

1.5M Hydrogen Peroxide	solid	^{3}H	$8.11E^{-5}$	^{14}C	$4.25E^{-5}$
2M Hydrogen Peroxide	powder	^{3}H	$4.80E^{-5}$	^{14}C	$2.16E^{-5}$
2.5M Hydrogen Peroxide	powder	^{3}H	$5.19E^{-5}$	^{14}C	$2.53E^{-5}$

3.1.2. CHEMICAL TREATMENT STAGE TWO

Stage two leaching/chemical treatment experiments were carried out at room temperature, with a weekly testing frequency up to 190 days. Samples from BEPO reactor channels 1, 16 and 20 and Magnox Wylfa were used. An 8% error is associated with this leaching test; this is based on LSC counting error, ±1% weight distribution and electronic pipette standard deviation. All equipment was calibrated before testing was carried out but some errors are associated with the equipment are accounted for in the 8% error. All calculations include half life and weight corrections taking into account that for the solid samples due to machining limitations on active material not all solid sample used where 0.5 grams ±1%. Some of the solid samples used weighed more and there weight and activity per gram was taken into account.

Phase two leaching test were carried out at room temperature, with a weekly testing frequency up to 190 days. Samples from BEPO reactor channels 1, 16 and 20 and Magnox Wylfa were used. An 8% error is associated with this leaching test; this is based on LSC counting error, ±1% weight distribution and electronic pipette standard deviation. All equipment was calibrated before testing was carried out but some errors are associated with the equipment are accounted for in the 8% error. All calculations include half life and weight corrections taking into account that for the solid samples due to machining limitations on active material not all solid sample used where 0.5 grams ±1%. Some of the solid samples used weighed more and there weight and activity per gram was taken into account.

3.1.2.1. BEPO Channel 1 Results - All Conditions

I-graphite from BEPO channel 1 was leached under water, pH1, pH13, 1M H_3PO_4, 0.5M H_2O_2 and 0.5M Potassium Bromate $KBrO_3$. Very limited quantities of BEPO Channel 1 graphite was available so these conditions where chosen to provide a comparison to leaching phase one data as well as to provide information on the mobility of the isotopes under an acidic environment. A solution of 1M phosphoric acid (H_3PO_4) was chosen as the acidic environment and was kept remain constant throughout leaching phase two program this was to provide a contrast to the pH1 buffer which contained 0.2M Hydrochloric acid (HCl). Figure 13 shows the cumulative release rates achieved by BEPO Channel 1 graphite for ^{3}H release. In this test 4.4% of the total ^{3}H inventory was released under water conditions, 7.8% of the total ^{3}H

inventory was released under pH1, 4.3% of the total ^{3}H inventory was released under pH13, 9.6% of the total ^{3}H inventory was released under 1M H_3PO_4, 4.7% of the total ^{3}H inventory was released under 0.5M $KBrO_3$ conditions and 23.2% of the total ^{3}H inventory was released under 0.5M H_2O_2 conditions.

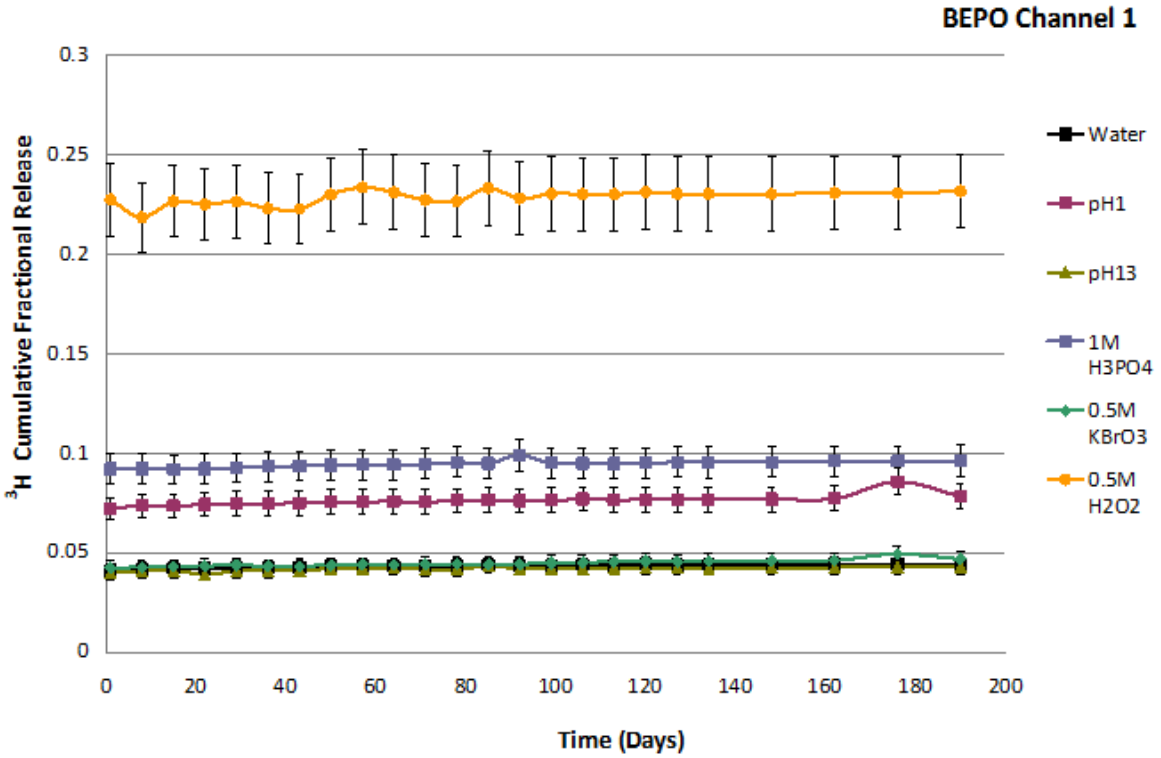


Figure 13 BEPO Channel 1 graphite ^{3}H release

Water and pH13 release rates for ^{3}H are comparable, this was expected for pH13 conditions, the mobility of the tritium is determined by the amount that is mobile. No additional ^{3}H activity compared to water has been released under pH13. 0.5M potassium bromate conditions did not produce an increase in release rate, as was previously observed in phase one. The 1M Phosphoric acid and pH1 solutions gave similar results with concentration of the acid contributing to release rate, the aggressive nature of the acid is known to breakdown the graphite structure. The aim of using weaker acidic solutions was to promote isotopic removal without the complete destruction of the graphite. The 0.5M Hydrogen peroxide solution resulted in a very high release rate of ^{3}H; this supports a hydrogen ion isotopic exchange mechanism.

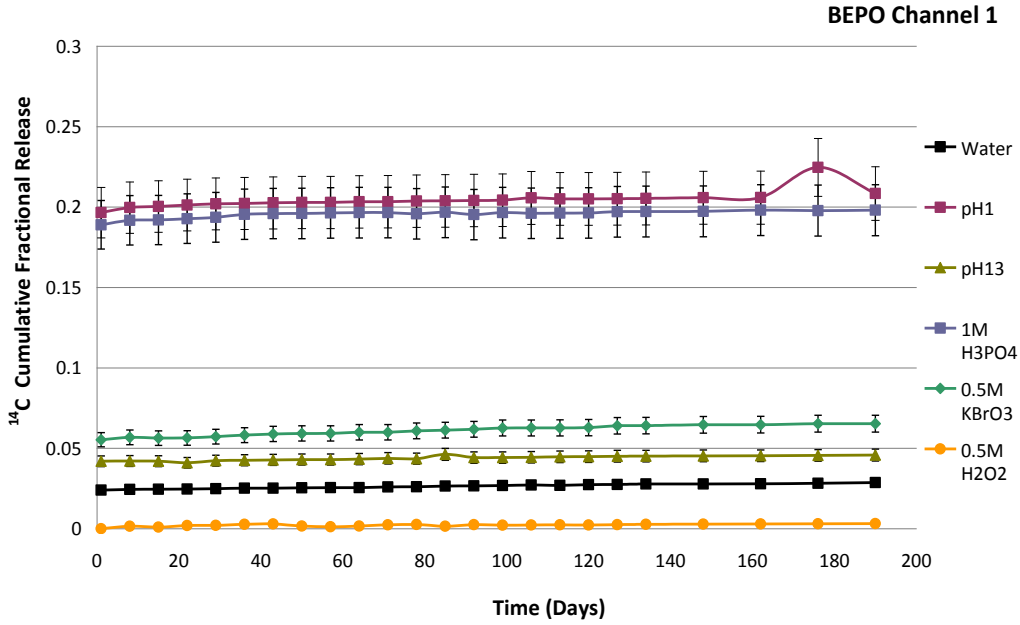


Figure 14 BEPO Channel 1 graphite ^{14}C release

Figure 14 shows the cumulative ^{14}C leaching results for BEPO channel 1. Under water conditions 2.9% of the total ^{14}C inventory was released, under pH1 conditions 20.8% of the total ^{14}C inventory was released, under pH13 conditions 4.6% of the total ^{14}C inventory was released, under 1M H_3PO_4 conditions 19.8% of the total ^{14}C inventory was released, under 0.5M $KBrO_3$ conditions 6.5% of the total ^{14}C inventory was released and under 0.5M H_2O_2 conditions 0.31% of the total ^{14}C inventory was released.

Under phase one lower release of ^{14}C under Hydrogen peroxide conditions where observed, however such an extremely low result as seen in Figure 14 should be viewed with cautious that some of the ^{14}C represent in the sample is not accounted for and therefore the author considers this result to be inaccurate.

The data shows that limited amounts of ^{14}C have been released under pH13 and 0.5M Potassium bromate solution there in an increase in release compared to water which was observed under phase one. Interestingly the acidic environments have removed more ^{14}C from the graphite material than previously observed under any other conditions. The mechanism behind this acidic attack is thought to be intercalation of the surface material (penetration of interlayer spaces within the graphite structure), which is a significantly different process to the mechanism behind ^{3}H release. This ^{14}C release under acidic conditions is thought to be due to intercalation.

3.1.2.2. BEPO graphite at pH 1 and pH13 Conditions

This section shows the results for cumulative fractional release for BEPO Channels 1 and 16, including BEPO Channel 16 solid samples under pH1 and pH13 buffered solution. Figure 15 shows that 7.8% of the total ^{3}H inventory was released from BEPO channel 1 powdered graphite, 11.2% of the total ^{3}H inventory was released from BEPO channel 16 powdered graphite and 3.2% of the total ^{3}H inventory was released from BEPO channel 16 solid graphite released under pH1. Under pH13 4.3% of the total ^{3}H inventory was released from BEPO channel 1 powdered graphite, 3.4% of the total ^{3}H inventory was released from BEPO channel 16 powdered graphite and 0.27% of the total ^{3}H inventory was released from BEPO channel 16 solid graphite.

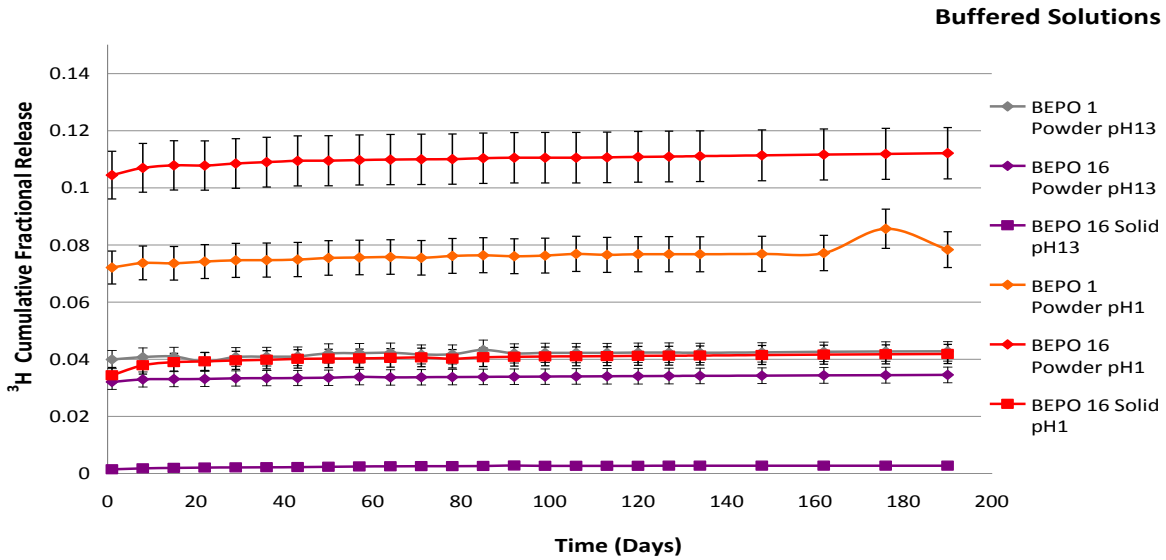


Figure 15 BEPO graphite ^{3}H release under pH1 and pH13 conditions

Figure 16 shows the ^{14}C cumulative release for BEPO Channels 1 and 16, including BEPO Channel 16 solid samples under pH1 and pH13 conditions. 20.8% of the total ^{14}C inventory was released from BEPO channel 1 powdered graphite, 25.4% of the total ^{14}C inventory was released from BEPO channel 16 powdered graphite and 6.1% of the total ^{14}C inventory was released from BEPO channel 16 solid graphite under pH1. Under pH13 solution 4.6% of the total ^{14}C inventory was released from BEPO channel 1 powdered graphite, 3.5% of the total ^{14}C inventory was released from BEPO channel 16 powdered graphite and 0.30% of the total ^{14}C inventory was released from BEPO channel 16 solid graphite.

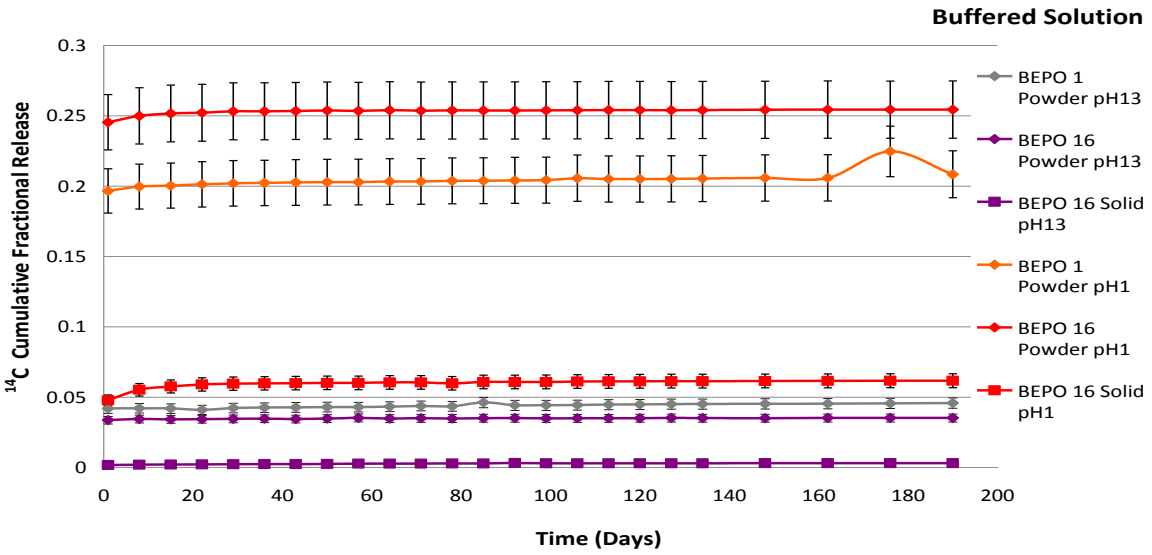


Figure 16 BEPO graphite ^{14}C release under pH1 and pH13 conditions

A significant increase is observed for ^{14}C release under pH1 conditions, the mechanism of intercalation is thought to promote this release. This proposed mechanism behind ^{14}C release is based on the acid intercalation with the graphite, this requires the anion of the acid to penetrate the interlayer spaces within the graphite structure allowing the release of loosely bound ^{14}C species.

3.1.2.3. BEPO graphite under all Acidic Conditions

Figure 17 shows BEPO Channel 16 powder graphite ^{3}H release under all acidic conditions. In these tests 10.5% of the total ^{3}H inventory was released under 1M phosphoric acid (H_3PO_4) and 0.1M Sulphuric Acid (H_2SO_4), 11.8% of the total ^{3}H inventory was released under 1M Hydrochloric acid (HCl) and 11.2% of the total ^{3}H inventory was released under pH1.

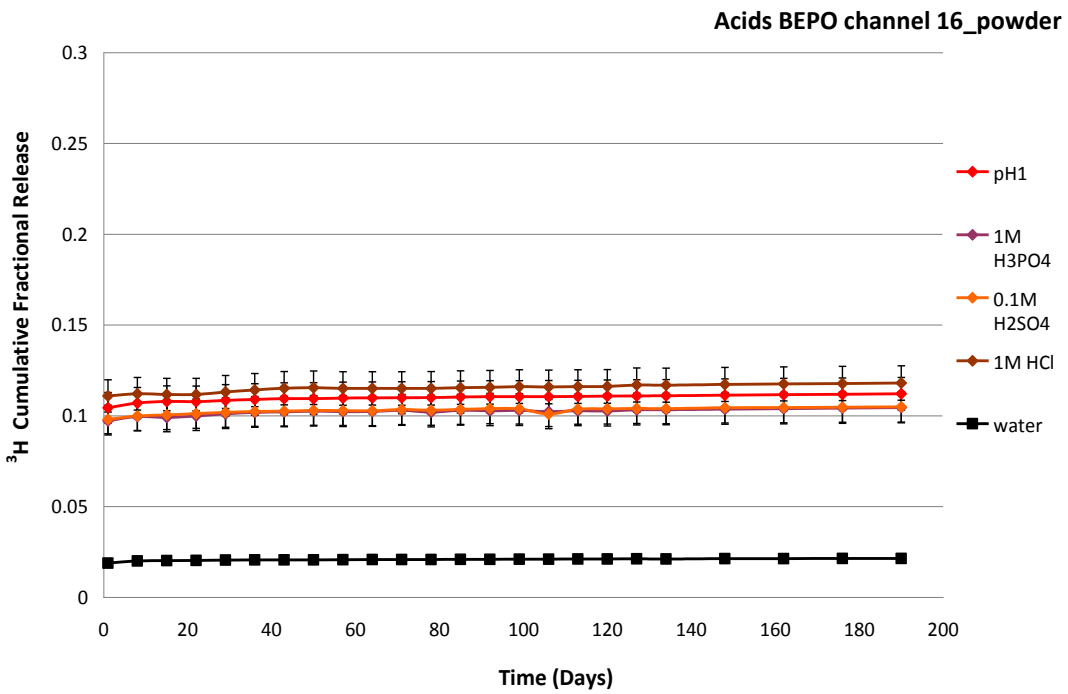


Figure 17 BEPO Channel 16 graphite ^{3}H release under acidic conditions

The data represented in Figure 17 supports the previous results for isotopic exchange being the mechanism behind ^{3}H removal as long as there is hydrogen atoms present in the right environment isotopic exchange with ^{3}H will occur. The other species present such as Cl^{-}, SO_4^{2-} and PO_4^{3-}may promote the availability of ^{3}H through intercalation within the graphite structure but they do not appear to be directly responsible for the release rate. The water data is shown on the graph is used as a comparison tool. The data achieved for BEPO Channel 20 is shown in the leach rate results.

Figure 18 shows BEPO Channel 16 powder graphite ^{14}C release under acidic conditions. 23.8% was released under 1M Orthophosphoric acid (H_3PO_4), 24.8% released under 0.1M Sulphuric Acid (H_2SO_4), 26.5% ^{14}C released under 1M Hydrochloric acid (HCl) and 25.4% released under pH1.

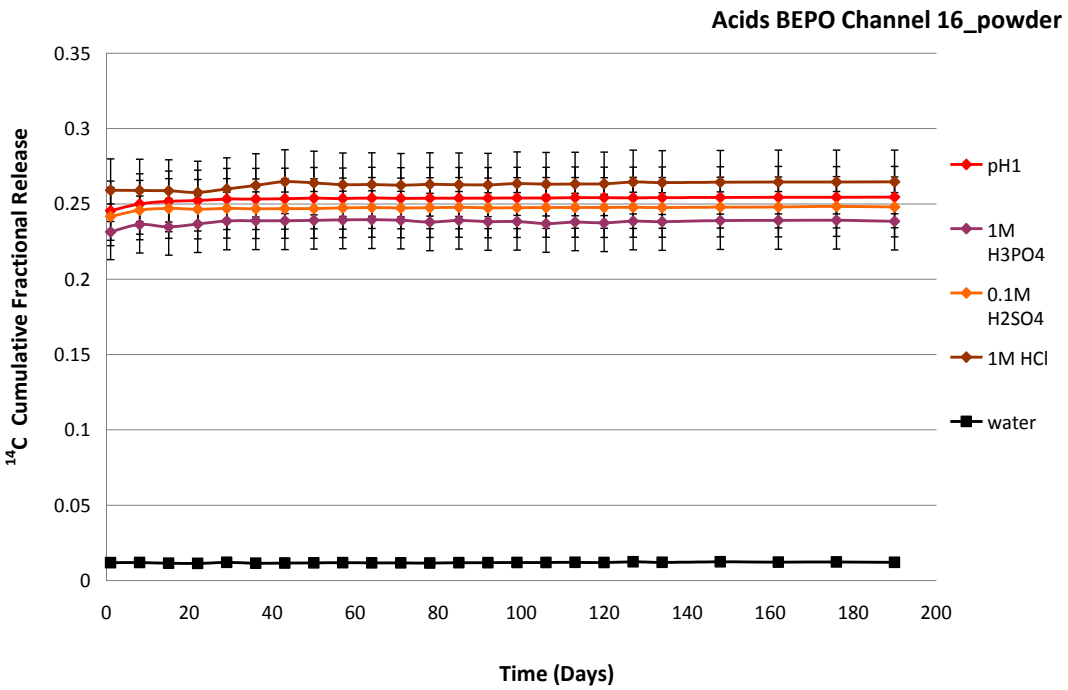


Figure 18 BEPO Channel 16 graphite ^{14}C release under acidic conditions

The data represented in Figure 18 supports the previous results for intercalation being the mechanism behind ^{14}C removal. The species present in the acids such as Cl^- ,SO_4^{2-} and PO_4^{3-} are all capable of intercalation. Using stronger concentrations of these acidic would result in the complete breakdown of the graphite structure, an interesting experiment would be to analyse how much ^{14}C is released under such conditions however the dilution required and the incompatibility of the environment with the LSC cocktail hold some limitations for this experiment and the focus of which is slightly different to the research detailed here. The water data is shown on the graph is given for comparison. The data achieved for BEPO Channel 20 is shown in the leach rate results in section 3.1.3.

3.1.2.4. MAGNOX graphite leaching

The same conditions utilized for BEPO Channel 1 material was tested on Magnox Wylfa graphite. Figure 19 shows the results achieved for ^3H release this leaching experiment. In these tests 0.13% was released under water conditions, 9.3% was released under pH1, 0.11% was released under pH13, 19.0% was released under 1M H_3PO_4, 0.09% was released under 0.5M $KBrO_3$ conditions and 0.47% was released under 0.5M H_2O_2 conditions.

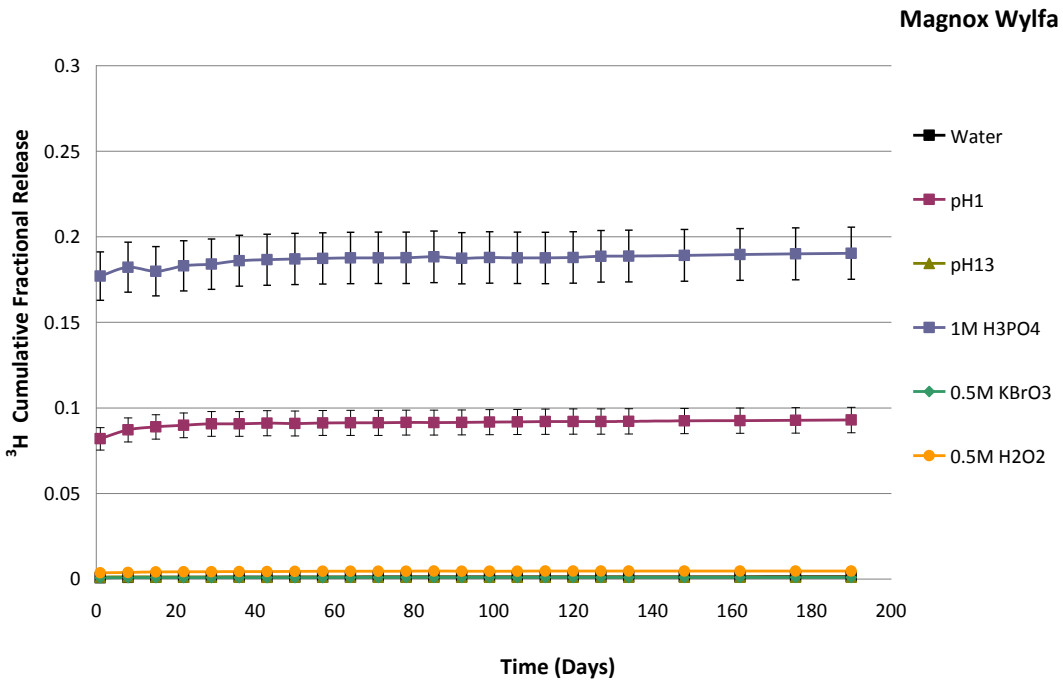


Figure 19 Magnox Wylfa ^{3}H release under all leaching conditions

Limited amounts of ^{3}H were released under water, 0.5M hydrogen peroxide and potassium bromate conditions. The Magnox material was supplied in a granulated form with a smaller surface area than the powdered BEPO graphite. From this data the conclusion can be drawn that as seen previously for tests with solid graphite samples, which are that under these three conditions hydrogen ion isotopic exchange, can only occur if the ^{3}H is easily accessible. Limited release is consistently observed under pH13 as well as ^{3}H release under acidic conditions gives results in the same order of magnitude as previously achieved.

Figure 20 shows the cumulative release rate for ^{14}C from Magnox Wylfa graphite. In these tests 2.5% was released under water conditions, 18.4% was released under pH1, 1.1% was released under pH13, 26.8% was released under 1M H_3PO_4, 1.6% was released under 0.5M $KBrO_3$ and 3.5% was released under 0.5M H_2O_2 solution.

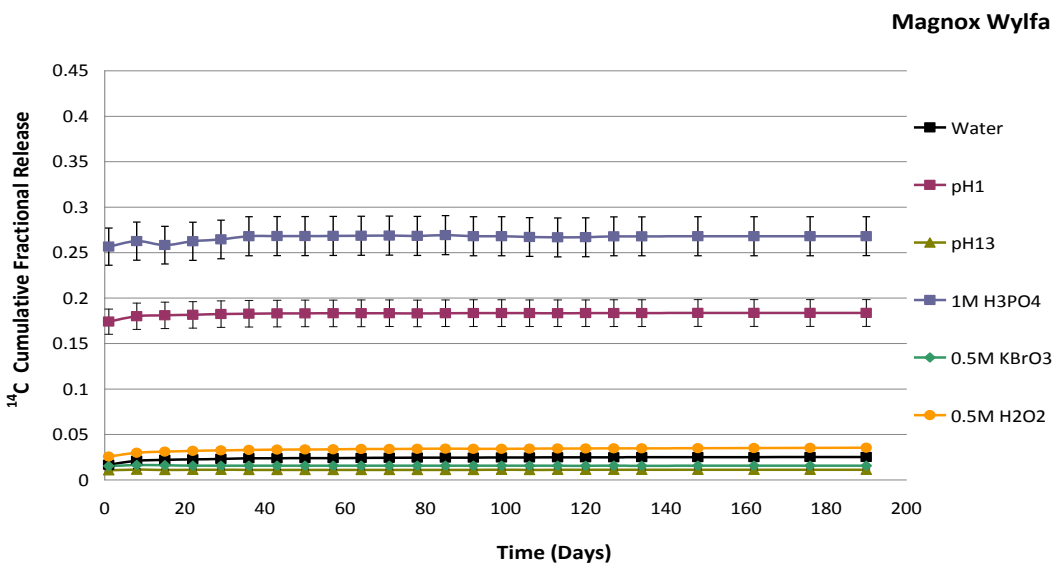


Figure 20 Magnox Wylfa ^{14}C release under all leaching conditions

Figure 20 shows that limited release of ^{14}C occurred under water, pH13, 0.5M Hydrogen peroxide and potassium bromate. However, ^{14}C releases under acidic conditions are similar to that achieved under BEPO Channel 1 and 16 powdered graphite. The pH1 solution contains 0.2M Hydrochloric acid which maybe the reason why this solution gives a lower release compared to 1M phosphoric acid. The Magnox Wylfa graphite contains significantly more activity per gram compared to the BEPO graphite which maybe why the concentration gives a significantly higher isotopic release for ^{14}C. In addition the surface area reduction may have limited the pH1 intercalation effectiveness. From these results ^{14}C appears to be present within the graphite structure in two forms, leachable and non-leachable ^{14}C species. This could well be related to the two main production pathways of ^{14}C origin.

3.1.2.5. Phase two Leach Rate Results Summary

Phase two leach rate results are detailed in Tables 11 to 14

Table 11 Leaching phase two leach rates for BEPO Channel 1 samples

Leachant condition	Type of material on test		Leach rate at 99 days		Leach rate at 99 days
Water	powder	^{3}H	$1.74E^{-5}$	^{14}C	$1.07E^{-5}$
pH 1	powder	^{3}H	$3.04E^{-5}$	^{14}C	$8.14E^{-5}$
pH 13	powder	^{3}H	$1.68E^{-5}$	^{14}C	$1.76E^{-5}$
0.5M Hydrogen peroxide	powder	^{3}H	$9.18E^{-5}$	^{14}C	$8.88E^{-7}$

0.5M Potassium Bromate	powder	^{3}H	$1.79E^{-5}$	^{14}C	$2.50E^{-5}$
1M Phosphoric acid	Powder	^{3}H	$3.79E^{-5}$	^{14}C	$7.83E^{-5}$

Table 12 Leaching phase two leach rates for BEPO Channel 16 samples

Leachant condition	**Type of material on test**		**Leach rate at 99 days**		**Leach rate at 99 days**
Water	powder	^{3}H	$2.36E^{-6}$	^{14}C	$1.34E^{-6}$
Water	Solid	^{3}H	$4.21E^{-5}$	^{14}C	$5.40E^{-5}$
pH 1	powder	^{3}H	$1.24E^{-5}$	^{14}C	$2.86E^{-5}$
pH 1	Solid	^{3}H	$2.53E^{-4}$	^{14}C	$3.76E^{-4}$
pH 13	powder	^{3}H	$3.81E^{-6}$	^{14}C	$3.93E^{-6}$
pH 13	Solid	^{3}H	$2.07E^{-5}$	^{14}C	$2.33E^{-5}$
0.1M Sulphuric acid	Powder	^{3}H	$1.17E^{-5}$	^{14}C	$2.78E^{-5}$
0.1M Sulphuric acid	solid	^{3}H	$5.10E^{-4}$	^{14}C	$1.11E^{-3}$
1M Hydrochloric acid	Powder	^{3}H	$1.31E^{-5}$	^{14}C	$2.96E^{-5}$
1M Phosphoric acid	Powder	^{3}H	$1.15E^{-5}$	^{14}C	$2.68E^{-5}$
1M Phosphoric acid	solid	^{3}H	$2.37E^{-4}$	^{14}C	$3.21E^{-4}$

Table 13 Leaching phase two leach rates for BEPO Channel 20 samples

Leachant condition	**Type of material on test**		**Leach rate at 99 days**		**Leach rate at 99 days**
Water	powder	^{3}H	$1.67E^{-6}$	^{14}C	$2.02E^{-6}$
Water	Solid	^{3}H	$2.80E^{-7}$	^{14}C	$5.59E^{-6}$
pH 1	powder	^{3}H	$1.02E^{-5}$	^{14}C	$2.73E^{-5}$
pH1	Solid	^{3}H	$2.53E^{-5}$	^{14}C	$6.68E^{-5}$
pH 13	powder	^{3}H	$4.54E^{-6}$	^{14}C	$9.62E^{-6}$
pH 13	Solid	^{3}H	$2.34E^{-5}$	^{14}C	$7.54E^{-6}$

0.1M Sulphuric acid	Powder	^{3}H	$1.06E^{-5}$	^{14}C	$2.87E^{-5}$
1M Phosphoric acid	Powder	^{3}H	$1.02E^{-5}$	^{14}C	$2.77E^{-5}$
1M Phosphoric acid	solid	^{3}H	$3.07E^{-5}$	^{14}C	$8.67E^{-5}$

Table 14 Leaching phase two leach rates for Wylfa Magnox samples

Leachant condition	**Type of material on test**		**Leach rate at 99 days**		**Leach rate at 99 days**
Water	powder	^{3}H	$2.47E^{-7}$	^{14}C	$4.94E^{-6}$
pH 1	powder	^{3}H	$1.84E^{-5}$	^{14}C	$3.69E^{-5}$
pH 13	powder	^{3}H	$2.32E^{-7}$	^{14}C	$2.23E^{-6}$
0.5M Hydrogen peroxide	powder	^{3}H	$9.18E^{-7}$	^{14}C	$6.88E^{-6}$
0.5M Potassium Bromate	powder	^{3}H	$1.79E^{-7}$	^{14}C	$3.12E^{-6}$
1M Phosphoric acid	powder	^{3}H	$3.78E^{-5}$	^{14}C	$5.39E^{-5}$

3.1.3. LEACH RATE COMPARISON OF BEPO TO WYLFA GRAPHITE

Both stage one and stage two leach rate calculations have been reported in this section. This allows the comparison of amount of ^{3}H and ^{14}C released under powder and solid samples to be compared as it takes into account surface area.

The Magnox material tested has significantly difference irradiation history to that of the BEPO material. Magnox graphite has been subject to radiolytic oxidation as well have received a higher fluence than BEPO graphite. This may have contributed to the lower leach rates observed here as surface bound activity of Wylfa graphite may have already been removed due to these two processes, particularly the former. BEPO material was irradiated in an air environment with a lower fluence at a temperature around 40˚C The isotopic inventory present in BEPO material may therefore have had less processes promoting migration of interstitials and as a result more mobile surface bound species are present giving rise to increased leach rates.

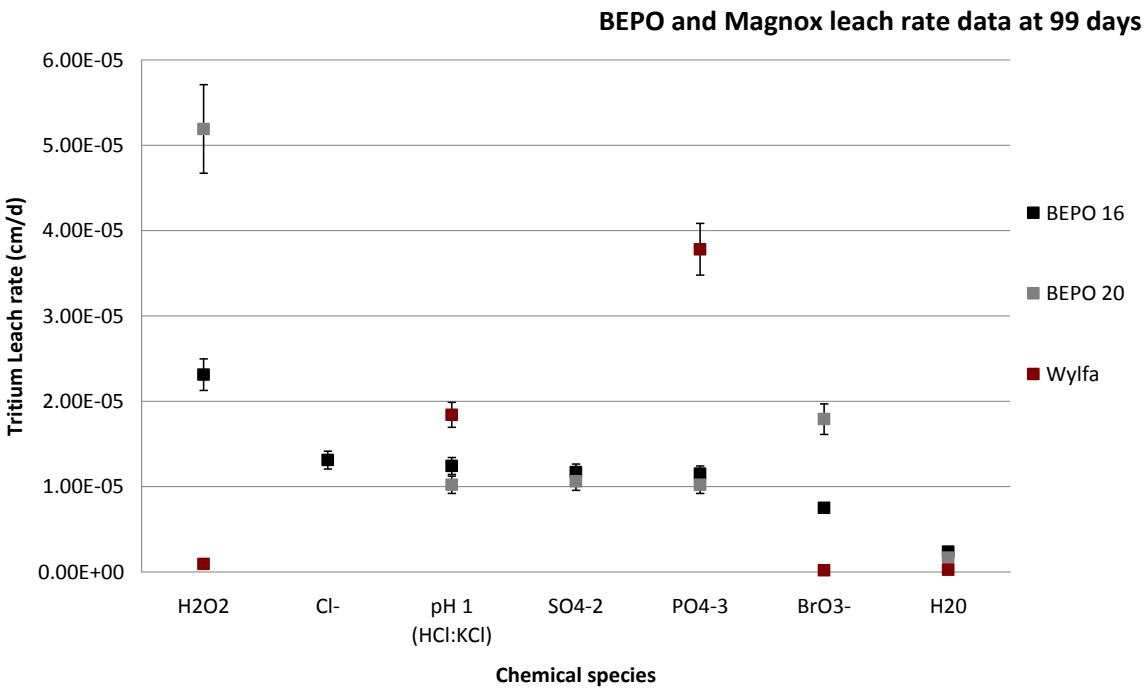


Figure 21 ^{3}H Leach rate comparison under all leaching conditions

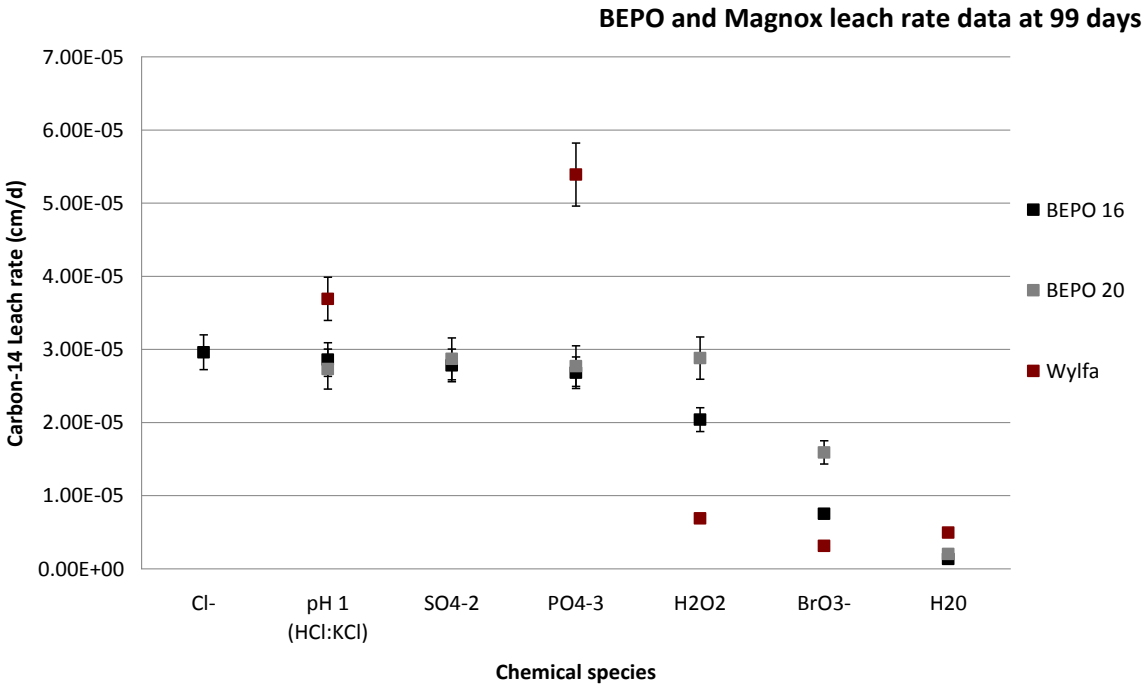


Figure 22 ^{14}C Leach rate comparison under all leaching conditions

Figures 21 and 22 show the leach rate data for BEPO graphite against speciation and

3.2. Decontamination Factors in Soxhlet Experiments (FzJ)

3.2.1. MERLIN SAMPLES DECONTAMINATION

3.2.1.1. Total Activity

The total activity was measured by LSC. When comparing the measured values, the differences in the dissolving power of the solvents used in the tests become clearly apparent (see figure 23). In contrast to the acids, all of the other solvents removed only very little or no activity at all.

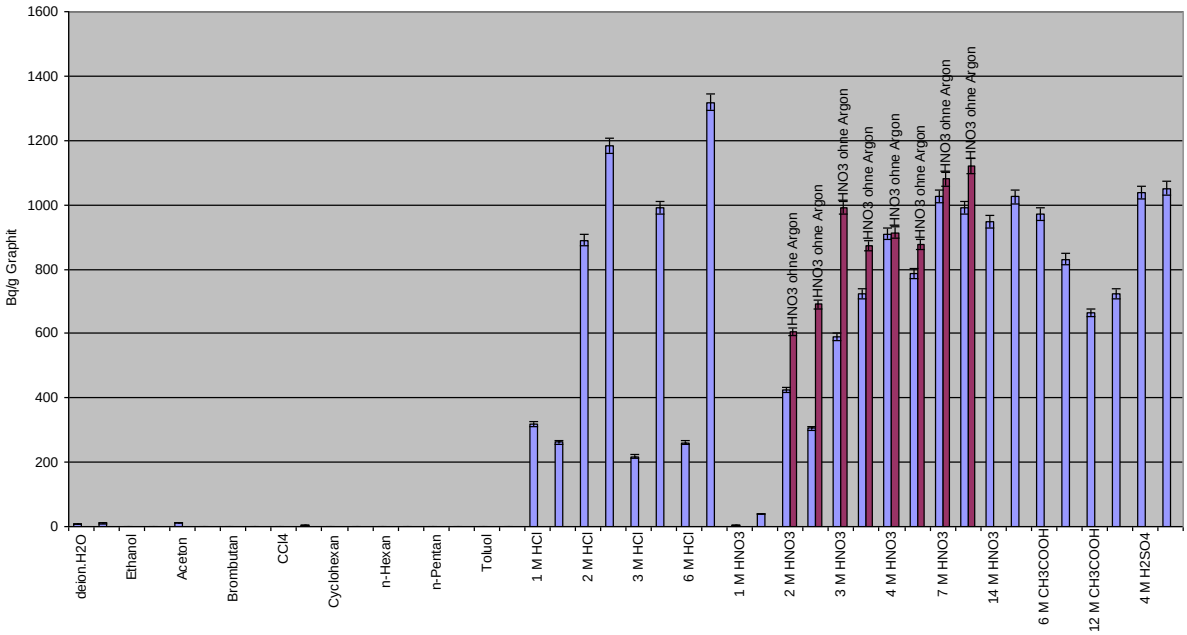


Figure 23 Overview of all of the measuring results from the Merlin leaching samples

Water, ethanol and acetone remove only very little activity (As ≤ 12 Bq/g graphite) from the graphite samples. All other organic solvents only remove small quantities (As ≤ 1 Bq/g graphite) of radionuclides from the reactor graphite. All neutral solvents are therefore not suitable for decontaminating reactor graphite and were not be given any consideration in the tests with AVR samples

Hydrochloric acid removes radioactivity from reactor graphite samples in all concentrations. In contrast to the other acids, the results for the sample duplicates fluctuated strongly. This could be the result of the graphite samples' heterogeneity with respect to structure, grain size, reactor coordinates and the location of the nuclides in the graphite. As the samples high level of activity makes measuring errors comparatively minor, measuring errors can be discounted as a potential cause.

In hydrochloric acid, it seems that any increase in concentration will generally result in greater activity removal. However, due to the strong fluctuations in the measured values, this cannot be positively verified with respect to the sample duplicates. As the 6 M HCl removes the highest level of activity, this is also the solvent that will be used for the decontamination tests on the AVR graphite.

The tests performed with the nitric acid in different concentrations show that the higher the concentration, the higher the activity remove in the samples and that the maximum level of activity is being removed at a concentration above 7 mol/L. For this reason, this is the concentration that will be used for the series of tests performed on the AVR graphite.

When leaching Merlin graphite with HNO3, a small amount (As< 3 Bq/g graphite) of ^{14}C becomes gaseous. The measured values within the sample duplicates fluctuated very strongly. This can be explained by the very small measured values, which are subject to significantly larger measuring errors than high measured values.

The other acid solvents that were used were acetic acid and sulphuric acid. The comparison of the results shows that increasing the concentration of acetic acid from 6 M to 12 M does not result in an increase in the activity count rate. Due to the problems (explosion) encountered during the extraction using 4 M sulphuric acid, no other tests with other concentrations will be performed. As with the samples with the nitric acid, the fluctuations of the measured values for the two solvents are significantly smaller within the sample duplicates than those observed for hydrochloric acid.

In order to ascertain whether repeatedly extracting radionuclides from the same sample using new solvents respectively would remove more total activity than through a leaching test, the same sample duplicate respectively will undergo extraction with the following fresh solvents four or six times for 5 hours each. The acids' concentration is selected in accordance with their effect on the extraction thimbles. The number of extraction tests is chosen in accordance with the respective result obtained from measuring the samples after the extraction. The solvents and concentrations used were: 1 M HCl, 1 M HNO_3, 6 M CH_3COOH, 4 M H_2SO_4

The test results obtained with the H_2SO_4 can only be compared within limits with the other results as, due to the problems described above, their test conditions varied.

In part, the results of the HCl and HNO_3 extraction tests follow a similar course. The course of the curves of the duplicate HCl is rather non-conclusive, only a small amount of activity was removed from the samples after the 4th leaching process. The sum of the values of the 2nd and 3rd extraction is higher than the measuring result of the 1st extraction and the total sum of all extractions is at least twice as high as the value of the 1st extraction. This trend was even more pronounced with HNO_3. During the 1st extraction, only 1 % (8% in the second replicate) of the total sum achieved by all of the extractions taken together is being removed,.

The higher amount of activity removed from the 2nd HCl and HNO_3 samples onwards can be explained by the 3-week break between the 1st and 2nd leaching test, as during that time, the solvent was able to act on the graphite

The course of the test curves obtained for acetic acid and H_2SO_4 are also similar. The results for the tests performed show that from the 3rd leaching process onwards, no significant amounts of activity are removed from the samples anymore. The continuous drop in the measured values suggests that the acids with the higher concentrations are able to remove most of the activity from the graphite during the 1st extraction step, in contrast to the weaker acids, which have to be left for a certain period of time to act in order to achieve the same results.

Overall, it can be concluded that the results obtained do not justify the efforts involved in performing multiple extractions. It is consequently more effective to immediately use acids with higher concentrations, which achieve the same results in only one single leaching test.

3.2.1.2. Gamma Spectrometry

Since only the results of the extracting agents that are capable of removing high amounts of activity are of interest for the second series of tests, only the Merlin samples of the solvents with the highest values will be analysed by γ spectrometry.

These are 6 M HCl (A_{max} = 1319 Bq/g graphite), 7 M HNO_3 (Amax = 1026 Bq/g graphite), 6 M CH_3COOH (Amax = 970 Bq/g graphite) and 4 M H_2SO_4 (Amax = 1051 Bq/g graphite). The 2 M HCl samples were also analysed in order to determine the reasons for the high activity of 1185 Bq/g graphite in one of the two sample duplicates.

The solid material samples were not analysed by γ spectrometry before the extraction tests. For this reason, the sum of the residual γ activity in the solid material sample and the sum total of the γ activity of the liquid sample are used as a comparison value.

This value is comparatively imprecise as, because of the extremely small sample size of 0.5 mL and the count rate of less than 1, it will no longer be possible to measure even relatively large levels of activities like, for example, the 154Eu value of the sample with the 6 molar hydrochloric acid in the following figure 24.

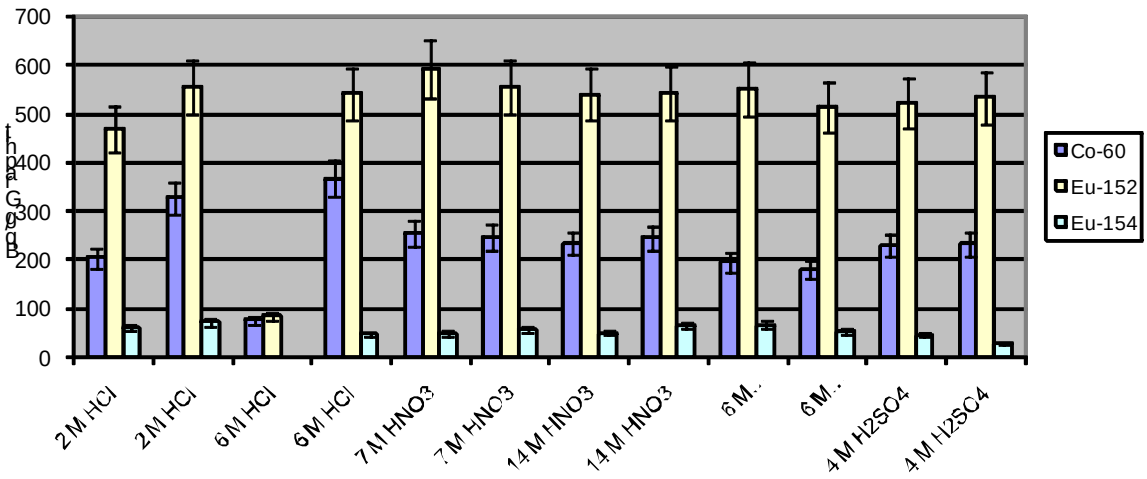


Figure 24 Comparison of the activity of the Merlin leaching samples

In the samples with high total activity, the residual activity of the solid material samples was established after the extraction tests. Just as with the liquid samples, the values of the HCl duplicates are also not conclusive when comparing the replicates.

The results of the liquid samples of the other solvents only fluctuate marginally within the sample duplicates. When taking into account a fluctuation margin that can be explained on the basis of the samples' heterogeneity and a 10 % uncertainty of measurement, they are roughly identical. The same can be also be anticipated to apply to the measured values obtained from the duplicate solid material samples.

However, there is no positive indication of a relationship between the removed amounts and remaining amounts of activity.

Removal of cobalt-60:

According to the data obtained at least 45% of the ^{60}Co content are removed, Acetic acid removes approx. 45%, nitric acid removes approx. 55%, sulphuric acid slightly more than 60% and hydrochloric acid up to 85% of the ^{60}Co content. These tests also showed that the measured values obtained with the hydrochloric acid sample duplicates fluctuated more significantly than those of the other samples

Removal of europium-152/54

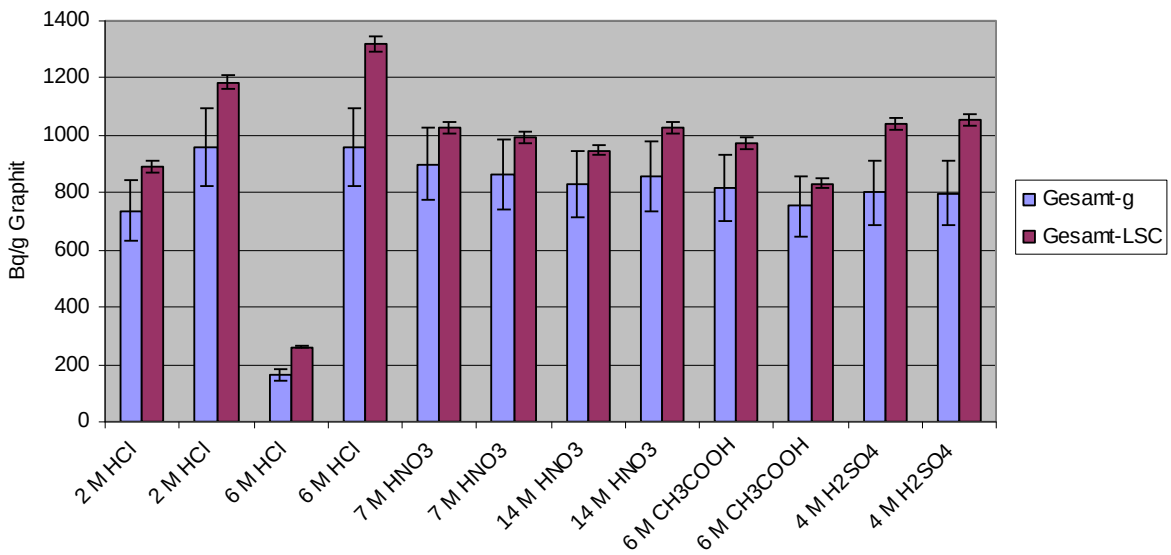
Decontamination factors of all solvents used, with the exception of 6 M HCl, remove at least 70% of ^{152}Eu. The removed activity ratio of ^{154}Eu ranges within 30% and 65%. 2 M HCl, nitric acid and acetic acid reached approx. 50%. All of the sulphuric acid and the 6 M HCl tests remain below this value.

3.2.1.3. Determination and Removal Tritium and Radiocarbon

Since, at max. 1.8 Bq/g graphite, the measured activities are too low and the concentrated acids cannot be used with the selected method of sub-boiling. Due to the high fluctuations of the measured values it is not possible to determine whether there are any significant differences between the liquid samples and the evaporated samples. This indicates that the samples only contain a very small amount of free tritium.

Determination of ^{14}C and tritium content

Comparing the activity of the total measured γ spectrometry values and the total LSC values clearly shows that the LSC values are higher than the γ values (see figure 25). As the samples do not contain any ^{90}Sr, it can be assumed that the difference between the LSC and γ values are caused by bound tritium and ^{14}C in the leaching samples. The ratio between the measured γ values and the LSC values in the liquid samples is predominantly approx. 80% (±20% errors). This indicates that the ratio between the content of pure β emitters (tritium and ^{14}C) and the γ emitters is roughly the same. The exact total bound tritium and ^{14}C content can only be estimated, but not accurately determined. Since, because of its low energy, the measured count rate of tritium is only approx. 0.3 and that of ^{14}C only approx. 0.9, the actual total activity will be higher than the measured one.



(Gesamt = Total)

Figure 25: Comparison of the total activity measured by γ spectrometry and LSC

Merlin graphite does not contain any organic 14C. Although numerous pulses were measured in some of the samples, an analysis of the spectra shows that these

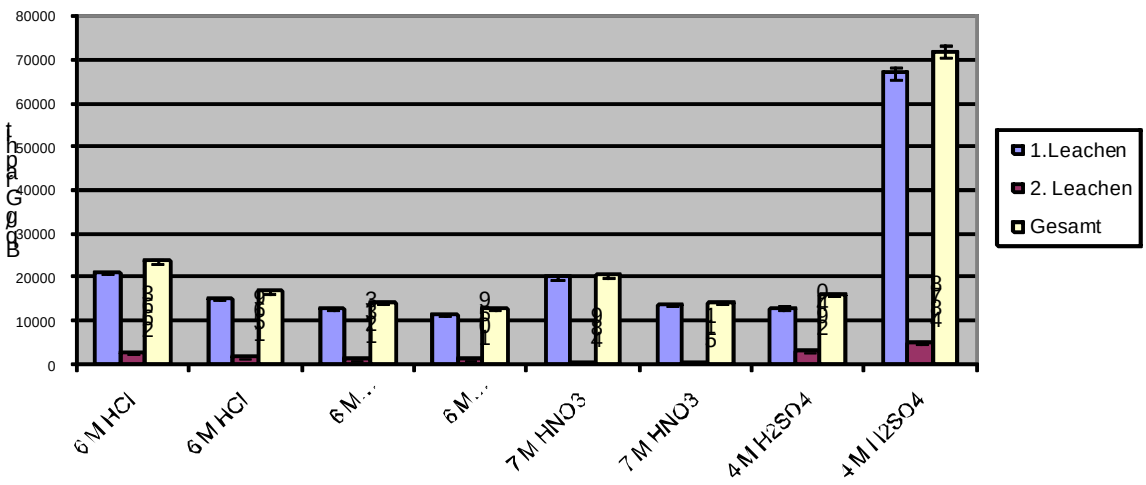
measured values are the result of luminescence interference that is caused by organic substances such as, e.g. phenolphthalein. The example spectrum also shows that the peaks of the luminescence interference do not overlap with any other peaks as they are located on the far left of the spectrum.

3.2.2. AVR SAMPLES DECONTAMINATION

3.2.2.1. Total Activity

The values of the total activities within the AVR sample duplicates fluctuated significantly with the exception of the acetic acid samples. The measured values are sum of the results obtained from the 1st and 2nd extraction of the same sample)

This clearly shows that the acids are also capable of removing more activity from the more heavily contaminated reactor graphite. This is not the result of the significantly higher amount of solvent used in relation to the quantity of reactor graphite (for Merlin 60 mL/ ≈ 0.5 g graphite Ξ 120 mL/g graphite; for AVR 50 mL/ ≈0.04g graphite Ξ 1250 mL/g graphite). This is made evident on the one hand by the results of the multiple extraction tests performed on the Merlin samples, and on the other, the fact that a significantly lower amount of activity respectively was removed during the 2nd extraction of the same reactor graphite sample than during the 1st extraction (see figure 26).



(Leachen = Leaching);(Gesamt = Total)

Figure 26 Total LSC result obtained from leaching the same sample twice

The lowest decontamination rates were achieved with the acetic acid, while the HCl tends to produce better values than the nitric acid. The results obtained with the sulphuric acid are difficult to estimate. On the one hand, the total activity measured for

the 1st sample duplicate is the average of all of the values, while, the total activity measured for the 2nd sample duplicate is about three times as high as all of the other results. Comparing the spectra of the 1st extraction and the 2nd extraction of both of the duplicates clearly shows how much of the total activity is produced by H-3 and how much by C-14.

3.2.2.2. Gamma Spectrometry

Comparing the initial activities with the residual activities of the solid material samples shows that the amount of individual nuclides that is removed does not depend on the amount of nuclides contained in the sample. This becomes evident in the case of ^{133}Ba. These values remain nearly unchanged in comparison to the values of the other nuclides

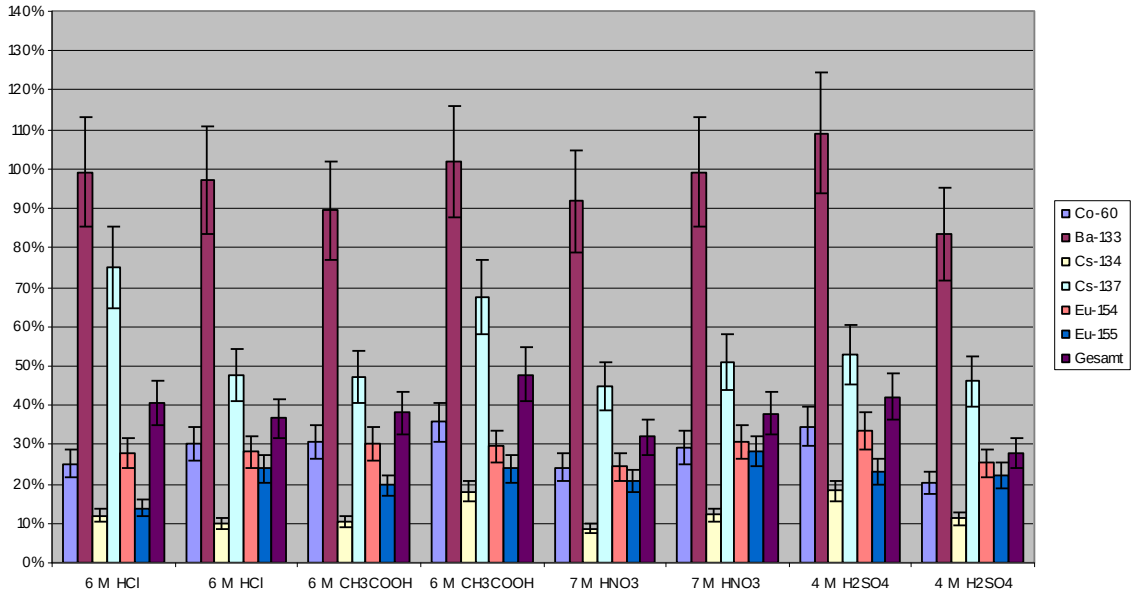


Figure 27 γ activity ratios of the solid material samples before and after leaching

- ^{60}Co decontamination factor ranging within 79% - 64%
- ^{133}Ba decontamination factor ranging within 16% - 0%
- ^{134}Cs decontamination factor ranging within 90% -80%
- ^{137}Cs decontamination factor ranging within 55% -25%
- ^{154}Eu decontamination factor ranging within 75% - 65%
- ^{155}Eu decontamination factor ranging within 85% - 70%

The barium values, some of which are higher than 100%, are an indication of measuring errors. These are at 14% and are due to the measuring device.

Comparing the solid material samples' γ activity before the tests with the total sum of all of the measuring results after the tests shows that the initial activity of the nuclides

is generally higher in the solid material samples than the total sum of the activity of all samples.

Individual Separations on Sr-90 were performed on AVR samples decontamination liquids. In the case of Sr-90 the low concentration and the background together with a short measuring time leads to a inaccurate measurement of this nuclide.

Detection of organic Carbon, as with the Merlin samples, some of the samples were found to contain numerous pulses that were higher than the background level. However, the samples' spectra show that these count rates are not the result of ^{14}C, but only of luminescence interference, which is probably caused by low-boiling organic substances (phenolphthalein), that were transferred into the washing bottles. These “ghost peaks” are so far on the left of the energy spectrum that it is clearly evident that they do not cover any other peaks

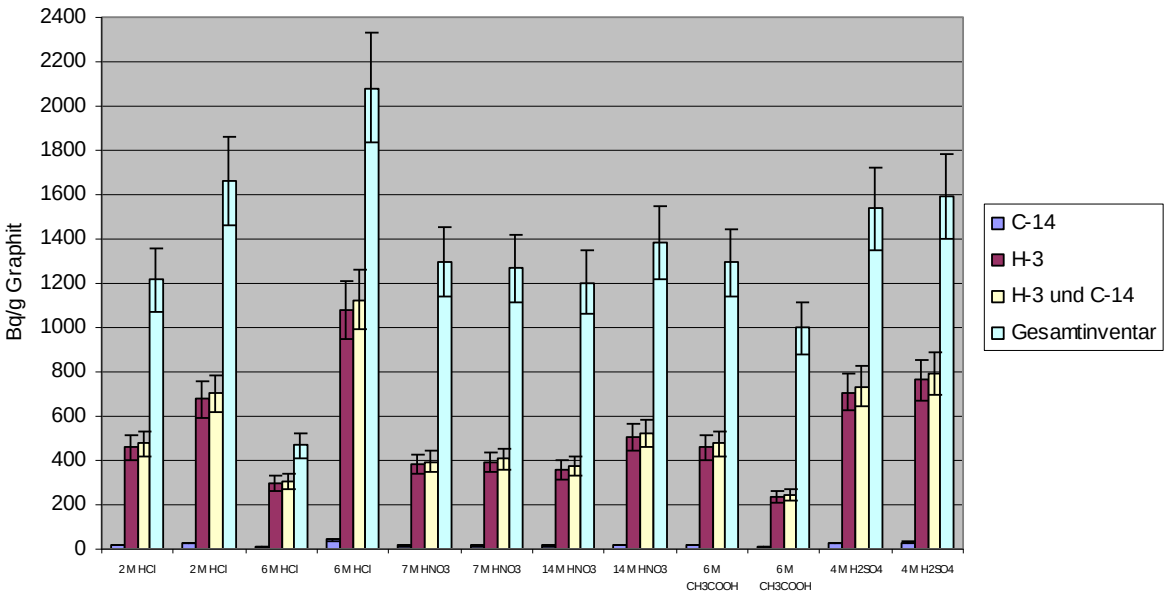
3.2.3. COMPARISON OF THE MERLIN AND AVR RESULTS

3.2.3.1. Pure β emitters:

The percentage of pure β emitters (^{3}H and ^{14}C) in the untreated Merlin graphite samples is more than 71% of the total radionuclide inventory. The percentage measured in the extraction solutions is only 20%.

If one were to assume that the ratio in the leaching solutions is the same as in the untreated leaching solutions it is possible to calculate the activity of the sample. The actual percentage of both nuclides in the total inventory would then not be approx. 20%, but approx. 44%. However, this value would still be lower than the 71% measured for the untreated samples.

The following charts show the calculated values and the ratios between the β emitters and the total inventory:



(Gesamtinventar =Total Inventory)

Figure 28 Comparison of the β activities and total activity (hypothesis)

Regarding the AVR samples, it is furthermore problematic that the quantity of pure ß emitters (^{3}H, ^{14}C and ^{90}Sr) inside the untreated samples is an unknown. For this reason, the radionuclide ratios of known AVR samples were used for comparison.

Despite the high differences in activities, the ratio between pure ß emitters and the radionuclide inventory is approx. 95%. In the extraction solutions, the measured percentage of pure ß activity is between 20% and 55%, and in the sample with the highest activity, more than 75%. The measured percentage of pure ß emitters in the sample solutions of both series of tests is therefore smaller than their percentage in the untreated solid material samples. However, the actual percentage of pure ß emitters in both series of tests is higher than the measured percentage, as the low count rate of ≤ 1, which is due to the weak energies, also has to be taken into account. This is also evident from the spectra of the LSC measurements.

According to the hypothesis, the total inventory contains up to 92% of pure beta emitters. The sample with the highest activity reaches this value. This sample's total inventory is made up to 88% of tritium. At approx. 41%, the Merlin samples' total inventories contain the lowest percentage of pure ß emitters (mostly 40%).

The comparison shows that more pure ß emitters are usually removed from the AVR graphite than from the Merlin graphite. There may be several reasons for why this percentage is higher in the AVR graphite, such as:

In contrast to the Merlin graphite, the AVR graphite or the leaching samples contain ^{90}strontium.

The presumably very high percentage (up to 95%) of pure ß emitters in the AVR graphite
The higher neutron radiation in the AVR reactor increases the reaction probability and the AVR graphite therefore reacts more easily with the solvents.
The higher neutron radiation has damaged the graphite lattice to such an extent as to make it easier for the solvents to remove the radionuclides from the graphite.

3.3. Decontamination Factors in Inorganic Treatment Experiments

3.3.1. H-3 AND C-14 (CIEMAT)

Both ^{14}C and ^{3}H are not removed at all with 0.1M sodium hydroxide or a mixture of 0.1M sodium hydroxide and hydrogen peroxide at 20ºC. The mixture HNO_3 65%-H_2SO_4 98% (1:4) at 80ºC dissolved the powder of graphite. The results obtained for 3M nitric acid, and mixtures of nitric, hydrochloric and sulphuric acids are shown on table 15 and expressed as % of the activity leached.

Table 15 Results obtained for the study ^{3}H and ^{14}C leaching using nitric and sulphuric acids as leachants at different concentrations and temperatures

Leachant	Temperature (ºC)	% Activity leached	
		^{3}H	^{14}C
3M HNO_3	20	0	0
H_2SO_4 98%-HNO_3 65% (4:1)	20	90	14
H_2SO_4 98%-HNO_3 65% (1:4)	20	7	3
H_2SO_4 98%	20	7	3
H_2SO_4 98%	80	10	8
HNO_3 65%-HCl 37% (1:3)	80	0	0
H_2SO_4 98%-HNO_3 65% (1:4)	80	12	7

The best results were obtained with the mixture H_2SO_4 98%-HNO3 65% (4:1) at 20 ºC. This mixture leached both 90% of ^{3}H and 14 % of ^{14}C. Also, with this mixture it was studied the influence of the leaching time. The study was carried out in the same conditions as before but with two different time points: 4 or 8 days. The results are shown on table 16.

Table 16 Results obtained for the study ^{3}H and ^{14}C leaching using a mixture of nitric and sulphuric acids as leachant at different leaching time

Mixture	Time (days)	% Activity leached	
		^{3}H	^{14}C
H_2SO_4 98%-HNO_3 65% (4:1)	1	90	14
H_2SO_4 98%-HNO_3 65% (4:1)	4	93	16
H_2SO_4 98%-HNO_3 65% (4:1)	8	93	20

The results are similar to the ones obtained when the leaching time was one day.

When the same procedure of leaching with H_2SO_4-HNO_3 (4:1) was applied six times repeatedly on the same graphite powder the decontamination for ^{14}C was 50% and 99% for ^{3}H but only 10 % of the graphite powder was recovered.

Finally, it has been study the stability of virgin graphite under the same conditions as the previous ones used for the leaching of irradiated graphite. The virgin graphite was dissolved with the mixture H_2SO_4 98%-HNO_3 65% (4:1) at 80 ºC while it was stable when it was treated with the mixture H_2SO_4 98%-HNO_3 65% (4:1) at 20 ºC. So the virgin graphite has the same behaviour as the irradiated graphite.

3.3.2. BETA-GAMMA EMITTERS

3.3.2.1. INR APPROACH

The samples prepared by INR, using the method described in 2.1.2, were measure and the results for gross beta determination are in Table 17

Table 17 The beta global activity of the graphite after chemical treatment and the removal efficiency

No. exp.	Wet graphite sample (g)	Dry graphite in sample* (g)	Beta global activity of dried graphite after decontamination (Bg/g)	Removal efficiency** (%)
1-g	0.75	0,38	243,01	26,10
2-g	0.72	0,39	207,80	36,81
3-g	0.68	0,36	197,71	39,87
4-g	0.68	0,34	242,99	26,11
5-g	0.74	0,29	125,39	61,87
6-g	0.78	0,31	133,06	59,53
7-g	0.74	0,34	119,17	63,76
8-g	0.71	0,32	145,11	55,87
9-g	0.71	0,28	227,08	30,94
10-g	0.79	0,38	229,81	30,11

12-g	0.73	0,37	244,59	25,62
13-g	0.79	0,36	183,65	44,15
14-g	0.74	0,45	95,75	70,88
15-g	0.71	0,44	241,59	26,53
16-g	0.74	0,42	257,53	21,68
17-g	0.73	0,43	282,10	14,21

g = graphite, P1- g, P2 -g = sample i-graphite powder

the samples P1-g, P2-g, b-g, c-g, 1-4g, 9-13g were measured in infinite thick source
the samples 5-8g, 13-g and 14-g were measured in infinite thin source
* the quantity of dried graphite was calculated by referring the quantity of wet graphite taken as sample at the quantities of initial dry and wet graphite (weight)
** it has been referred to the average of i-graphite activity (1g = 328.83 Bq)

The bar-diagram of figure 29 shows the effectiveness of the treatment for Gross beta activity

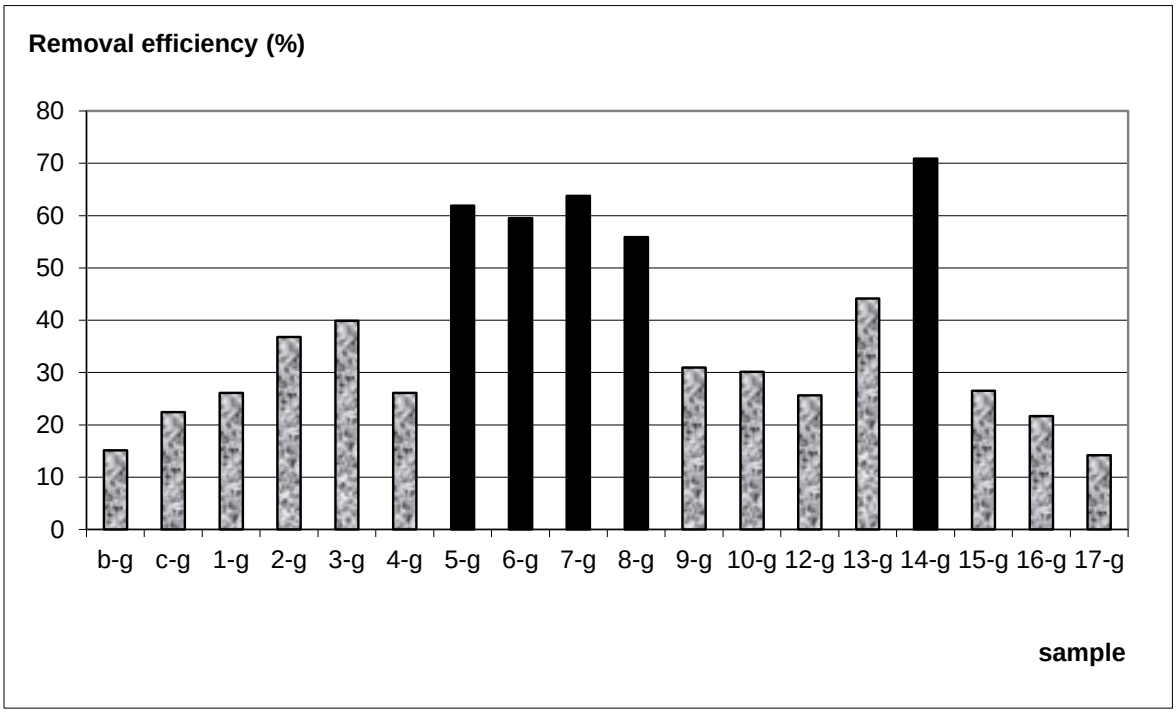
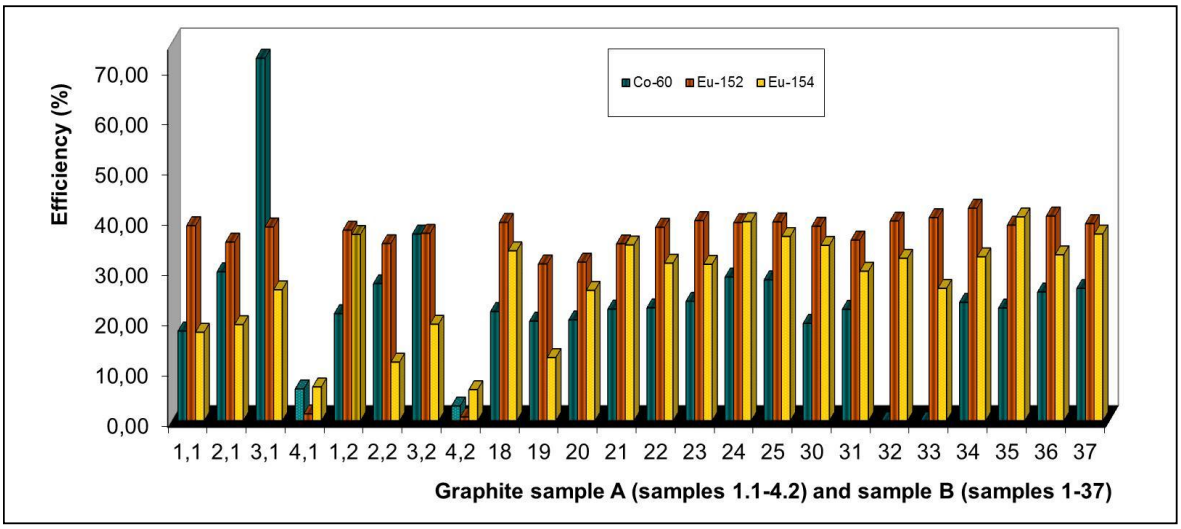


Figure 29 Beta total removal efficiency

It is shown within the set of experiments the decontamination efficiency with regards at the global beta activity is the highest (71%) in case of sample no. 14 (decontamination solution: 2.5 ml HCl 37%+ 2.5 ml H_2SO_4 98%+ 5 ml demineralized water), followed by the samples 5, 6, 7, 8 (efficiency = 59-63%) – the experiments where H_2SO_4 98% and H_3PO_4 85% were used (experiments no. 5 and 7) and in mixture with demineralized water, in volumetric ratio 1:1 in the experiments 6 and 8.

Table 18 Decontamination tests results - Co-60, Eu-152 & Eu-154 removal

No. exp.	Activity (Bq/g)				% radionuclides removed			
	^{60}Co	^{137}Cs	^{152}Eu	^{154}Eu	^{60}Co	^{137}Cs	^{152}Eu	^{154}Eu
1-g	21.52±3	4.53±3	932.65±66	50.28±6	58.89	-	30.03	25.90
2-g	22.51±3	2.81±1.4	930±63	48.56±5	57.00	15.11	30.23	28.43
3-g	9.47±2	-	900.13±60	49.43±6	81.91	100	32.47	27.15
4-g	19.02±3	8.27±4	9.6.05±65	51.29±6	63.67	-	92.79	24.41
5-g	6.2±2	-	372.94±28	20.29±3	88.16	100	72.02	70.10
6-g	5.16±1.5	-	392.78±28	20.73±3	90.14	100	70.53	69.45
7-g	8.85±2	-	526.60±38	30.65±4	83.09	100	60.50	54.83
8-g	9.17±2	-	520.36±38	28.88±4	82.48	100	60.96	57.44
9-g	7.19±2	-	479.09±33	27.68±3	86.27	100	64.06	59.20
10-g	13.38±3	-	576.81±42	32.01±4	74.44	100	56.73	52.82
12-g	17.43±2	-	863.53±62	46.98±5	66.70	100	35.22	30.76
13-g	6.43±2	3.63±2.1	551.81±40	29.89±4	87.72	-	58.60	55.95
14-g	7.95±2	-	591.87±41	33.19±4	84.81	100	55.60	51.08
15-g	17±3	4.11±3	1009.13±70	58.65±6	67.53	-	24.30	13.56
16-g	31.34±3	-	878.47±23	46.13±4	40.13	100	34.10	32.01
17-g	30.32±4	-	1148.51±82	63.9±7	42.08	100	13.84	5.82



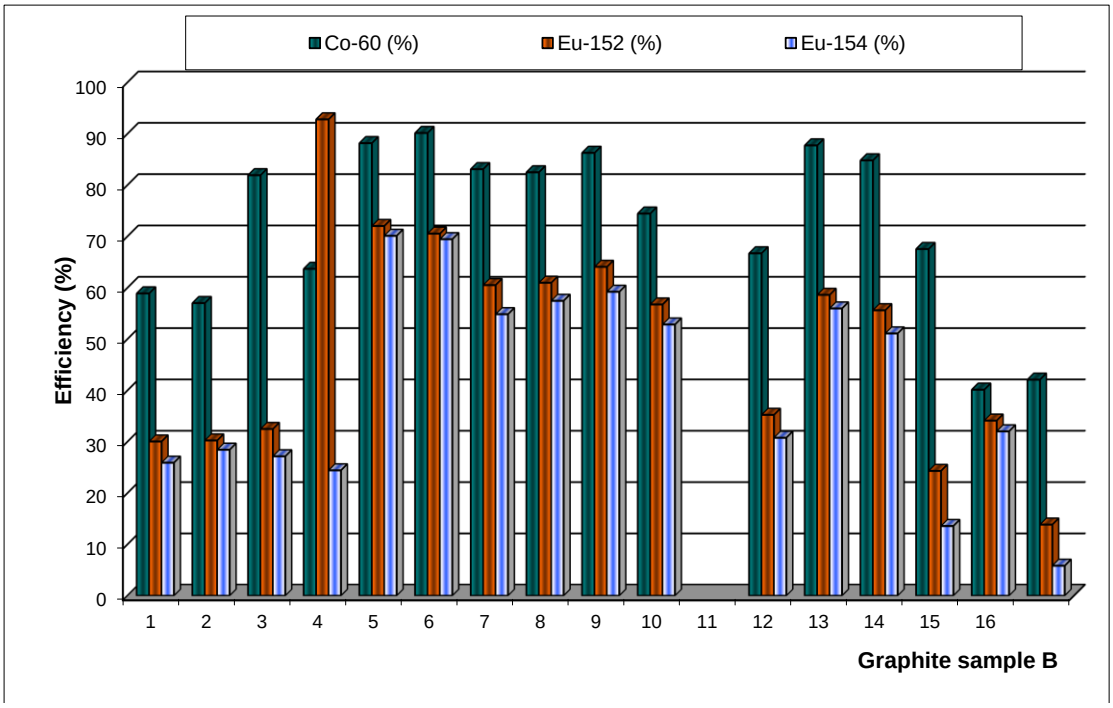


Figure 30 Gamma emitters removal efficiency

3.3.2.2. CIEMAT APPROACH

The results are shown on table 19 and 20 and expressed as % of the activity leached.

Table 19 Results obtained for the study of beta-gamma emitters leaching using acids as leachant at different concentrations and temperatures.

Reference	^{60}Co	^{94}Nb	^{137}Cs	^{154}Eu	Reference	^{60}Co	^{94}Nb	^{137}Cs	^{154}Eu
6C20	64	–	–	–	**7N20**	18	–	–	–
3C20	21	–	–	–	**3N20**	13	–	–	–

3C60	77	–	–	–	**3N60**	60	–	–	–
3C80	96	77	56	84	**3N80**	79	37	63	100
9S20	64	–	–	–	**3P20**	13	–	–	–
3S20	17	–	–	–	**3P60**	60	–	–	–
3S60	77	–	–	–	**3P80**	52	54	52	91
3S80	41	59	54	87					

First number: Acid concentration.
C: Chlorhidric N: Nitric S: Sulphuric P: Phosphoric
Second number: Temperature

Table 20 Results obtained for the study of beta-gamma emitters leaching using acids as leachant at different concentrations and temperatures**.**

Reference	^{60}Co	^{94}Nb	^{137}Cs	^{154}Eu	Reference	^{60}Co	^{94}Nb	^{137}Cs	^{154}Eu
3OC20	25	26	38	83	**3CiC20**	32	0	44	100
3ON20	17	22	35	95	**3CiN20**	11	0	36	100
3O20	15	36	42	97	**3Ci20**	9	0	31	100
3OP20	15	0	38	77	**3CiP20**	18	0	38	100
3OS20	15	0	42	67	**3CiS20**	24	0	61	100

First number: Acid concentration.
C: Chlorhidric N: Nitric S: Sulphuric P: Phosphoric O: Oxalic Ci: Citric
Second number: Temperature

In the case of Co, the amount released into the leachant increases when the temperature does and the highest leaching, around 96%, is when the leachant is a hydrochloric acid solution.

For Nb, Co and Cs the percentage of leaching decreases when the leachant is oxalic acid alone or a mixture with another acid. The highest leaching for Nb is about 77% when 3 M chlorhidric acid at 80 º C is used. For Cs the leaching is between 52 and 63 % for any acid medium at 80 º C and the percentage decreases to 40 % in presence of oxalic acid.

The highest percentage of leaching for Eu is using either dissolution of 3M nitric acid at 80 ºC, dissolution of 0.5M citric acid or a mixture of 0.5M citric acid with any acid at 20 ºC.

3.3.2.3. ENEA APPROACH

The results obtained from the leaching tests previously mentioned are shown in the Tables 21 and 22.

Table 21 Results of the tests on S2 sections at 200°C with acid mixtures

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

Table 22 Results of the tests on S3 sections at room temperature with acid mixtures

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

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

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

3.3.3. ALPHA EMITTERS (CIEMAT)

The results are shown on tables 23 and 24 and expressed as % of the activity leached.

Table 23 Results obtained for the study of alpha emitters leaching using acids as leachant at different concentrations and temperatures.

Reference	$^{239/40}Pu$	^{241}Am	Reference	$^{239/40}Pu$	^{241}Am
6C20	52	52	**7N20**	49	56
3C20	43	62,8	**3N20**	49	61
3C60	76	74,4	**3N60**	60	80
3C80	87	100	**3N80**	62	100
9S20	34	42	**3P20**	66	57
3S20	48	49	**3P60**	76	73
3S60	69	65	**3P80**	77	100
3S80	94	100			

- First number: Acid concentration.
- C: Chlorhidric N: Nitric S: Sulphuric P: Phosphoric
- Second number: Temperature

Table 24 Results obtained for the study of alpha emitters leaching using acids as leachant at different concentrations and temperatures.

Reference	$^{239/40}Pu$	^{241}Am	Reference	$^{239/40}Pu$	^{241}Am
6C20	77	100	**7N20**	77	100
3C20	66	100	**3N20**	45	100
3C60	69	100	**3N60**	57	100
3C80	84	100	**3N80**	79	100
9S20	81	100	**3P20**	82	100

- First number: Acid concentration.
- C: Chlorhidric N: Nitric S: Sulphuric P: Phosphoric O: Oxalic Ci: Citric
- Second number: Temperature

The leaching of Am is about 100% when the leachant is either an acid medium at 80 ºC, using 0.5M oxalic or citric acid alone or a mixture with any acid at 20 ºC. The leaching of Pu with any acid solution increases when the temperature does and the best result for Pu is when leaching is carried out with 3M sulphuric acid at 80 ºC

3.3.4. INTERCALATION PROCESS (CIEMAT)

An experiment was carried out to study the leaching of a virgin graphite block with a solution of H_2SO_4:HNO_3 (4:1). When a 0.7 g virgin graphite block was put into a vial with 5 mL of a mixture of H_2SO_4:HNO_3 (4:1) the block broke down into powder.

Figure 31 Virgin graphite block and graphite powder obtained after the treatment with the mixture H_2SO_4:HNO_3 (4:1)

The powder was washed with water until both sulphuric and nitric acids were removed. After several washings the water was analyzed by ion exchange chromatography in order to check the presence of sulphate or nitrate. The recovery of graphite powder was about 98 %. An examination of the structure for both the virgin graphite block and the virgin graphite powder was carried out by SEM. The images are shown on figure 32

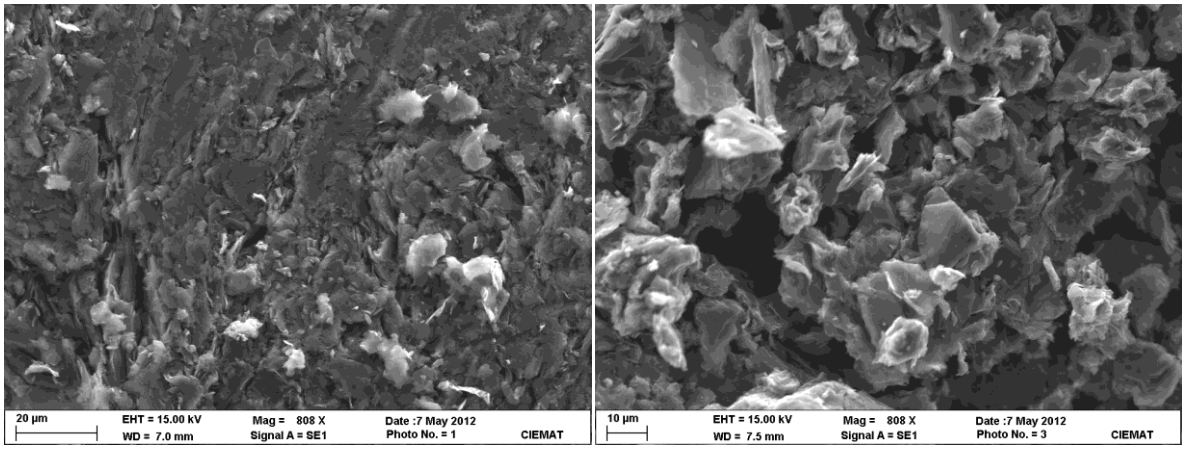


Figure 32 SEM images of a virgin graphite block (left) and its powder after treatment (right)

3.4. Decontamination Factors in Organic Treatment Experiments (ENEA)

It is started to test the process considering the three common and widely used dipolar solvents, as mentioned in the section 2.1.4.5 of this report, for their good solvency abilities:

N,N-Dimethylacetamide (DMA)

N,N-Dimethylformamide (DMF)

N-Methyl-2-pyrrolidone (NMP)

In this work, we performed a sonication bath for 10 hour in a 35W power device on sample of about 0.1g of irradiated graphite samples with 10ml of each solvents. The volume of the solvents used has been chosen for the aim described.

After sonication, the solution appear grey to dark in colour without a distinguishable sedimentation. They are left standing for a day with no changes in colour. After that, they are centrifuged for 1hour at 12000 rpm. Only the NMP/dispersion still presents dark coloration, the others were clear. All the samples/solutions were filtered on RC (Regenerated Cellulose) Filter Disk 0.2μ and undergone LSC/γ-Spectrometry.

Tables 25 and 26 Overviews of Removal Efficiencies for Radiocarbon and ^{60}Co

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

4		8					
07S07G2/I3	237,11	23,35	9,85	6,71	2,83	4,92	2,07
07S07G2/C4	238,92	7,17	3,00	6,45	2,70	23,96	10,03
08F08A1/I2	167,77	25,59	15,25	3,93	2,34	9,48	5,65
08F08A1/S2	72,12	12,03	16,68	0,88	1,21	8,10	11,23
07S07G2/I1	292,73	29,94	10,23	4,61	1,58	9,76	3,33
07S07G2/I2	1241,34	23,59	1,90	5,72	0,46	56,40	4,54

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

Although the overall results seem to be relatively low, these are the first results obtained with this new kind of decontamination process aimed to preserve the graphite as it is and avoiding both oxidation of the same and completely dissolution as acidic leaching or extraction perform.

These first and earliest results show that the removal efficiencies in the experimental conditions we used are best for N,N-Dimethylacetamide (DMA) and N-Methyl-2-pyrrolidone (NMP) for ^{14}C removal, and N,N-Dimethylformamide (DMF) in the case of ^{60}Co. The logical answer could lie in the different chemical behaviour and bonding of the two radionuclides in the graphite matrix. Anyway, further investigations would prove the possibilities to reach an overall process able to extract a wide range of radionuclides despite of the differences in chemical properties of the elements.

Another point worth to be assessed is the sonication time plus the sonication power. The energy distributed for mass unit and time in a ultrasound bath is an important point to be investigated in order to reach an exhaustive desegregation (exfoliation-like) of the graphene layers making the intercalated compounds free from the matrix and dissolved in the solvent.

Moreover, a complete ICP-MS/γ-Spectrometry characterisation of the i-GF samples will be performed to validate the destructive and non-destructive measurements carried out. This should be the starting point for the subsequent definitions of the degree of decontamination, comparing these values to those coming from the decontaminations trial and works.

4. REMARKS

4.1. Decontamination Factors in Chemical Treatment Experiments (UoM)

- Separate mechanisms for ^{3}H and ^{14}C are proposed.
- All leachable ^{3}H species have been removed prior to day 90
- The behaviour in peroxide and acidic conditions would support a hydrogen ion isotope exchange mechanism
- Commonly encountered difficulties with tritium analysis were overcome in this study by using external standards and water washes (between runs) in the post leaching thermal analysis
- There appear to be two separate ^{14}C chemical forms i.e. leachable and non-leachable because, under harsh environments and even with powdered i-graphite, no more than 30% of ^{14}C is removed
- The presence of two forms of ^{14}C provides insight in the mechanism of formation and the behaviour under continued irradiation
- Acid treatment is believed to remove ^{14}C by the penetration of interlayer spaces within the graphite structure
- Steady state of release was achieved under all conditions by day 90, after this time very limited amounts of ^{14}C were released
- The non-leachable form of ^{14}C which remains in the i-graphite structure at day 90 may require complete destruction of the material for their release

4.2. Decontamination Factors in Soxhlet Experiments (FzJ)

The results of the two series of tests (Merlin and AVR graphite) showed that the methods used, Soxhlet extraction or liquid-solid extraction, are not extremely effective in decontaminating reactor graphite. Compared to the other nuclides, tritium and ^{14}C in particular, which contribute the highest level of activity in the samples (in the Merlin samples ≈ 71% of the total radionuclide inventory, AVR samples ≈ 95% of the total radionuclide inventory) are the two nuclides of which the lowest amount is removed from the graphite. The amount of tritium and ^{14}C that is removed from the less contaminated Merlin graphite is proportionally lower than that removed from the AVR graphite (44% up to 92%).

Using strong acids, all of the other radionuclides, with the exception of ^{133}barium, are comparatively easy to remove from the reactor graphite. However, they were still not removed to a sufficient extent, as both the treated Merlin reactor graphite as well as the graphite from the AVR were still contaminated to such an extent after an intermediate storage period of 40 years that both of them would have to be disposed of in a final storage facility.
Individually nuclide comparative study of the results of Soxhlet treatment can be summarize

4.2.1.1. Pure beta emitters

The comparison between Merlin and AVR graphite shows that more pure ß emitters are usually removed from the AVR graphite than from the Merlin graphite. There may be several reasons for why this percentage is higher in the AVR graphite, such as:

In contrast to the Merlin graphite, the AVR graphite or the leaching samples contain 90strontium.

The presumably very high percentage (up to 95%) of pure ß emitters in the AVR graphite

The higher neutron radiation in the AVR reactor increases the reaction probability and the AVR graphite therefore reacts more easily with the solvents.
The higher neutron radiation has damaged the graphite lattice to such an extent as to make it easier for the solvents to remove the radionuclides from the graphite.

Tritium ^{3}H:

The leaching solutions and the washing bottles were only found to contain very small amounts of free tritium. The equipment used in this present study is not suitable for analysing the total percentage of removed tritium in the samples.

^{14}Carbon:

Inorganic ^{14}C can only be accurately analysed in the AVR samples in the washing bottles. The highest measured value of 2042 Bq/g graphite amounts to less than 4% of the sample with the lowest known ^{14}C content AVR-G-10. The leaching samples do not contain any organic ^{14}C. As with the tritium, it is not possible to precisely determine the total percentage of ^{14}C in the radionuclide inventory of the leaching samples.

^{90}Strontium:

Only the AVR samples contain 90strontium. The removed amounts are between 14% (lowest value from 4 M sulphuric acid) and 70% (highest value from 6 M hydrochloric acid), compared with sample AVR-G-7, the sample with the lowest known 90strontium content.

4.2.1.2. Gamma emitters:

Proportionally, the other nuclides, with the exception of ^{133}Ba and ^{137}Cs, were much easier to remove from the reactor graphite than tritium and ^{14}C. One of the reasons for this could be that, in contrast to tritium, these nuclides do not diffuse that strongly into and are absorbed into the graphite lattice's structure, but are located at the boundary

surfaces of the graphite lattices. Since ^{14}C, as a carbon isotope, is similarly inert as graphite, it is not as efficiently removed from graphite as other radionuclides.

^{60}Cobalt:

Only the AVR samples contain 60cobalt. The acids used in the tests remove at least 64 % of the 60cobalt. The highest amount is 79%.

Europium isotope ^{152}Eu, ^{154}Eu and ^{155}Eu:

^{152}Eu is removed to at least 70%, ^{154}Eu to between 65 and 75%, and ^{155}Eu is removed to between 70 and 85%.

^{133}Barium:

The maximum amount of ^{133}barium, which is only found in the AVR samples, removed from the samples is 16%. ^{133}barium is therefore the radionuclide of which the smallest amounts were removed from the reactor graphite.

Caesium isotopes ^{134}Cs and ^{137}Cs:

Only the AVR samples contain both of the caesium isotopes. The amount of ^{137}Cs removed is between 25 and 55%. The amount of ^{134}Cs in the solid material sample was measured as being just a small amount over the detection limit. After leaching, these values are below the detection limit for ^{134}Cs. It is therefore only possible to state that ^{134}Cs has been removed.

Hypothesis: As an alkaline earth metal, barium is deposited between the graphite lattice layers just like the alkaline metal caesium. Due to its larger ionic radius, it will be more firmly embedded at this site than caesium and is therefore harder to remove from the graphite.

4.3. Decontamination Factors in Inorganic Treatment Experiments

4.3.1. H-3 AND C-14 (CIEMAT)

Both ^{3}H and ^{14}C are not leached at all when the chemical treatment is carried out under strong oxidizing conditions without sulphuric. However, the leaching of graphite with H_2SO_4 98%-HNO_3 65% (4:1) at 20ºC during 24 hours removes 90% of ^{3}H and 14% of ^{14}C.

The treatment of a virgin graphite block with a solution of H_2SO_4:HNO_3 (4:1) at 20º C breaks down the graphite block into powder

4.3.2. BETA-GAMMA EMITTERS

4.3.2.1. INR Approach

Beta global activity efficiency:
71% - using decontamination solution: 2.5 ml HCl 37%+ 2.5 ml H_2SO_4 98%+ 5 ml demi water

59-63% - using decontamination solution: H_2SO_4 98%, H_3PO_4 85% and diluted.

Table 27 Co-60, Eu-152 & Eu-154 removal efficiency:

per g i-graphite	Co-60	Eu-152	Eu-154
3.3 ml H_2SO_4 98%	88 %	72%	70%
6.7 ml H_2SO_4 ~ 50%	90%	70%	69%
6.8 ml HNO_3 65%-H_3PO_4 85% (1:1)	86.27%	64.06%	59.20%

Therefore, the removal efficiencies using sulphuric acid ranged between 70 and 90%, and as well, a mixture of nitric acid 65% and phosphoric acid 85% (1:1) ranged between 60 and 86%, each one with the most efficient removals achieved for Co-60.

4.3.2.2. CIEMAT Approach

The best conditions for the leaching of Co are 3M HCl at 80ºC. In these conditions are leached: 100% of Am, 96% of Co, 87% of Pu, 84% of Eu and 77% of Nb.

The highest percentage of leaching for Eu is using 3M nitric acid at 80 ºC or dissolution of 0.5M citric acid alone or a mixture with any acid at 20 ºC.

These results agree with ionic character of the chemical bonds of these radionuclides in the graphite.

4.3.3. ALPHA EMITTERS (CIEMAT)

The leaching of Pu with any acid increases when the temperature does and the best result for Pu, 94% leached, is when leaching is carried out with 3M sulphuric acid at 80 ºC.

The leaching of Am is about 100% when the leachant is either an acid medium at 80 ºC or using 0.5M oxalic or citric acid alone or a mixture with any acid at 20 ºC.

4.4. Decontamination Factors in Organic Treatment Experiments (ENEA)

These first and earliest results show that the removal efficiencies in the experimental conditions we used are best for N,N-Dimethylacetamide (DMA) and N-Methyl-2-pyrrolidone (NMP) for ^{14}C removal, and N,N-Dimethylformamide (DMF) in the case of ^{60}Co. The logical answer could lie in the different chemical behaviour and bonding of the two radionuclides in the graphite matrix. Anyway, further investigations would prove the possibilities to reach an overall process able to extract a wide range of radionuclides despite of the differences in chemical properties of the elements.

Another point worth to be assessed is the sonication time plus the sonication power. The energy distributed for mass unit and time in a ultrasound bath is an important point to be investigated in order to reach an exhaustive desegregation (exfoliation-like) of the graphene layers making the intercalated compounds free from the matrix and dissolved in the solvent.

Moreover, a complete ICP-MS/γ-Spectrometry characterisation of the i-GF samples will be performed to validate the destructive and non-destructive measurements carried out. This should be the starting point for the subsequent definitions of the degree of decontamination, comparing these values to those coming from the decontaminations trial and works.

4.5. Main Achievements

Decontamination studies collected in this document have been carried out on irradiated graphite samples form Magnox reactors, UNGG Reactors, MTR's (Triga and Merlin) and HT reactors (AVR).

It have been applied several techniques as Semi-dynamic long term leaching experiments, Short term leaching experiments with stirring or ultrasonic help, and Solid liquid extraction.

The chemical agents tested are organic for several proposes: soft acidic, extractans with soft donors, complexant agents agents, solvents …) and inorganic, (acidic, alkaline, neutral, solvents, oxidizers…) at different temperatures.

Decontamination of beta-gamma emitters

Decontamination factors of **Co-60** found are:

- Acidic treat with Soxhlet can remove ~80% of Co-60 inventory in 4M H_2SO_4
- Acidic Leaching treatment with H_2SO_4 50-98% can remove ~90% of Co-60
- Acidic Leaching treatment with 3M HCl at 80ºC can remove ~87% of Co-60
- Acidic Leaching treatment with HNO_3/ H_2SO_4 at 200ºC can remove ~90% of Co-60
- Organic Leaching treatment with soft donors extractantes (DMA) can remove ~9% of Co-60

Decontamination factors of **Europium Isotopes**

- Acidic treat with Soxhlet can remove ~70-80% of $^{154/55}$Eu inventory in 4M H_2SO_4
- Acidic Leaching treatment with H_2SO_4 50-98% can remove ~70% of $^{152/54}$Eu inventory
- Acidic Leaching treatment with any acid tested mixed with complexants agents at 20ºC can remove ~100% of ^{154}Eu inventory

Decontamination factors of **Caesium Isotopes**

- Acidic treat with Soxhlet can remove ~90% of ^{134}Cs and ~50% of ^{137}Cs inventory in 7M HNO_3
- Acidic Leaching treatment with H_2SO_4 98% and H_3PO_4 85% can remove ~100% of ^{137}Cs inventory
- Acidic Leaching treatment with any acid tested mixed with complexants agents at 20ºC can remove ~100% of ^{154}Eu inventory
- Acidic Leaching treatment helped with sonication and using HNO_3/ H_2SO_4 at 200ºC can remove ~70% of Cs-137

Decontamination of **Other gamma emitters**

- Acidic treat with Soxhlet remove in the better case ~16% of ^{133}**Ba** inventory in 4M H_2SO_4

- Acidic Leaching treatment with 3M HCl at 80ºC can remove ~77% of ^{94}**Nb**

Decontamination of Gross beta and Total activity

- Acidic treat with 6M HCl in Soxhlet experiments remove the maximum amount of **Total activity** inventory.

- Acidic decontamination solution with HCl 37%: H_2SO_4 98% (1:1:2) remove ~70% of **Gross beta activity**

Decontamination of alpha emitters

- ^{241}**Am** decontamination factors are ~100% with 3M H_2SO_4,3M H_3PO_4,3M HNO_3 3M HCl at 80º C or with any of this acids and 0.5 Oxalic or Citric acid as complexant at 20º C

- $^{239/40}$**Pu** decontamination factors are ~94% with 3M H_2SO_4 at 80º C

Decontamination of tritium and radiocarbon

- Acidic Leaching treatment with H_2SO_4 98%-HNO_3 65% (4:1) at 20ºC during 24 hours removes 90% of ^{3}H and 14% of ^{14}C.

- Soxhlet extraction studies can not give a decontamination factor of tritium and radiocarbon.

- Organic extractant treatment gave a removal of radiocarbon ~10% in average with maximum of 27% in a few cases.

- Phase one long term behaviour of graphite under >2 M H_2O_2 conditions (88 days) has a C-14 release of 15.4% for powder samples and 13.4% for H-3.

- Phase two long term behaviour (99 days) under 1M H_3PO_4 presents the maximum release for Magnox granulate sample tested in both case H-3 and C-14.

Acidic conditions for removal contaminants from irradiated graphite present good results. In general the use of H_2SO_4 alone or in combination with complexants or other strong acids as H_3PO_4, HCl or HNO_3 leads to a removal of contaminants with high efficiency.

Neutral, alkaline and organic agents have no relevant efficiency in the treatments tested.

Temperature of the treatment has a positive effect in the decontamination factors.

The availability of surface and pore structure of the samples have high influence in the efficiency of the process in general is found that the effectiveness of the process is scale as:

Powder> granulate>massive

The suspected ionic bounds in the surface of the graphite lattices of actinides, alkaline and transition metals can explain the efficiency of removal. Cases of alkaline-earths or Nb have to be explained.

The chemical process with H_2SO_4 98%-HNO_3 65% (4:1) at 20ºC removes 90% of H-3 in 24 hours. The behaviour of BEPO graphite in long term leaching test with H_2O_2 remove ~15% of the H-3 inventory in 88 days and ~18% of Magnox graphite H-3 inventory with 1M H_3PO_4 in 99 days.

Radiocarbon release has no effective removal with any treatment, organic solvents tested give poor results, H_2SO_4 98%-HNO_3 65% (4:1) at 20ºC removes 14% and long term leaching test of BEPO with H_2O_2 remove ~13% of the C-14 inventory in 88 days and ~27% of Magnox graphite C-14 inventory with 1M H_3PO_4 in 99 days.

This behaviour induces to evaluate the effectiveness of the process in function of availability of C-14 in the surface treated. The speciations of radiocarbon in the graphite due to the different pathways of C-14 generation during reactor operation, in addition to pore structure and neutron damage, determine the capability of the chemical process applied.

Evidences and studies of intercalation process are found with the use of acidic media that can be use in the graphite retrieval process.

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