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Leach behaviour of Magnox graphite

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Document title
Leach behaviour of Magnox graphite

Executive summary

This milestone report focuses on the information currently available for irradiated graphite material taken from Magnox power stations which has undergone a leaching experimental program. This report aims to highlight the previous reports carried out on this topic within the UK as well as research done as part of the CARBOWASTE program.

This report will evaluate the current isotopic inventory present within magnox irradiated graphite as well as the interest in certain radionuclide release and there proposed mechanisms. This report will support deliverable D-6.1.6 'leaching behaviour of radionuclides from graphite' which will compare this data to that of all leaching data available to the author from every available source.

Revisions

Rev.	Date	Short description	Author	Internal Review	Task Leader	WP Leader
00	10/03/2013	1st Issue	McDermott, UoM	Jones, UoM		

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Table of Abbreviations

Symbol / Abbreviation / Acronym	Definition
α	Alpha
AGR	Advanced Gas-cooled reactor
BEPO	British Experimental Pile Zero Reactor
β	Beta
CEA	Commissariat à l'énergie atomique et aux énergies alternatives
CoRWM	Committee On Radioactive Waste Management
ε	Electron capture
EDF	Electricité de France
EDND	Equivalent DIDO Nickel Dose
ENEA	Italian National Agency for New Technologies
FNAG	Furnaces Nuclear Application Grenoble
FZJ	Forschungszentrum Jülich
γ	Gamma
GDF	Geological Disposal Facility
GLEEP	Graphite Low Energy Experimental Pile
HOPG	Highly ordered pyrolytic graphite
HAW	High Activity Waste
IAEA	International Atomic Energy Agency
ICRP	International Commission on Radiological Protection
ILW	Intermediate Level Waste
INPL	Institute of Nuclear physics of Lyon
i-graphite	Irradiated graphite
LLW	Low Level Waste
LLWR	Low Level Waste Repository
LSC	Liquid Scintillation Counting
MW	Megawatt
MW(th)	Megawatt Thermal
n	neutron
NCRP	National Council on Radiation Protection and Measurements
NDA	Nuclear Decommissioning Authority
NNL	National Nuclear Laboratory
NRG	Nuclear Research and consultancy Group
p	proton
PGA	Pile Grade A
pH	measure of the acidity or basicity of an aqueous solution
PIE	Post Irradiation Examination
σs	scattering cross-section
σa	absorption cross-section
SoGIN	SOcietà Gestione Impianti Nucleari
TRL	Technology Readiness Level
UKAEA	United Kingdom Atomic Energy Authority
UoM	University of Manchester
VLLW	Very Low Level Waste

1 Introduction

1.1 UK Magnox reactors

A total of 26 Magnox class reactors were constructed at 11 sites in the UK, the commissioning and shutdown dates for each site are given in Table 1. Magnox reactors are constructed from an array of graphite moderator and reflector bricks, Oldbury and Wylfa employed a pre-stressed concrete pressure vessel, all other reactors had a steel pressure vessel [1]. Moderator bricks were fabricated from Pile Grade-A graphite, manufactured by Anglo Great Lakes (AGL) and British Acheson Electrodes Ltd (BAEL), the coke was sourced from the Shell Oil refinery at Pernis in Holland [2]. Pile Grade-B graphite, used for reflector bricks, was initially AGXP graphite but later (due to supply issues) a variety of 'pure' graphite types were used [3]. Magnox fuel consists of a rod of natural uranium clad in an alloy of magnesium and aluminium; known as magnox. There were a total of 11 fuel element designs employed across the fleet, the diameter of the uranium rod was the only standard feature between them [4].

Table 1 Magnox Reactors in the UK [5]

Station	Reactors	Commission date	Total electrical power (MW per reactor)	Shutdown date	Weight (tonnes)
Calder Hall	4	1956-1959	200	2003	1164
Chapelcross	4	1959-1960	200	2004	1164
Berkley	2	1962	276	1989	1938
Bradwell	2	1962	246	2002	1810
Hunterston A	2	1964	300	1990	1780
Trawsfynydd	2	1965	390	1993	1900
Hinkley Point A	2	1965	470	2000	2210
Dungeness A	2	1965	440	2006	2150
Sizewell A	2	1966	420	2006	2237
Oldbury	2	1968	434	R 2 2011 R1 2012	2090
Wylfa	2	1971	980	R2 2012 R1 2014[6]	3470

In addition to use as a moderator and reflector, graphite was also employed as channel sleeves in Chapelcross reactors 2, 3 and 4, fuel struts at Berkeley and fuel sleeves at Hunterston. The graphite used in these components was initially manufactured from PGA and later NITTETSU, which was sourced from BAEL, AGL, their successors, and eventually SGL [7]. The Berkeley MK2F design included a graphite support strut (Figure 1); the Hunterston MK1C design used a graphite sleeve, as shown in Figure 2.

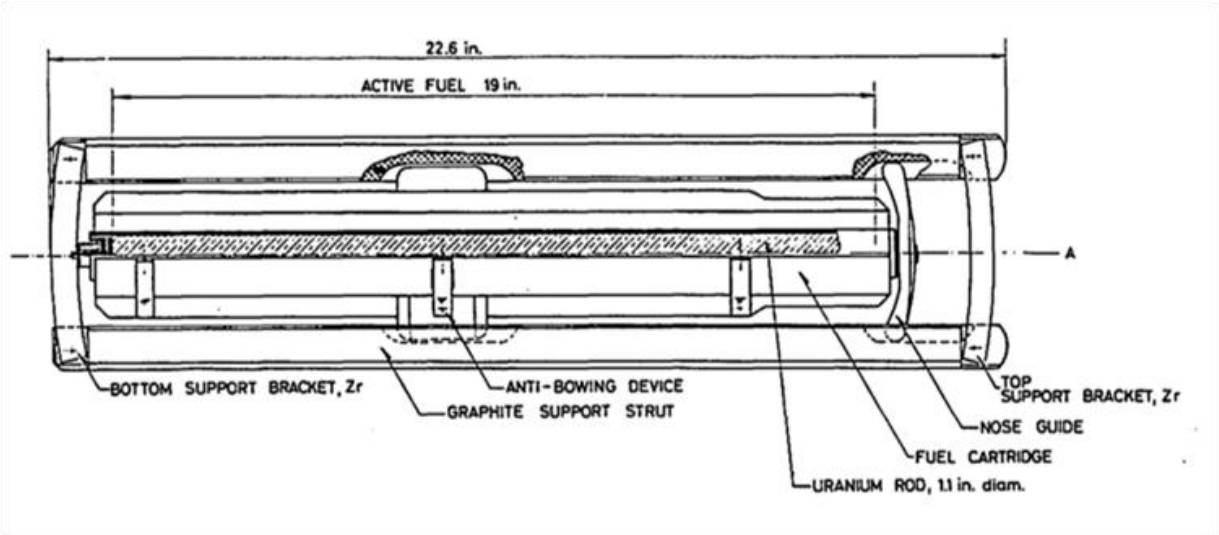


Figure 1 Schematic of the Berkeley MK2F fuel element design with graphite support strut (IAEA Reactor Data Sheets, p210) [8]

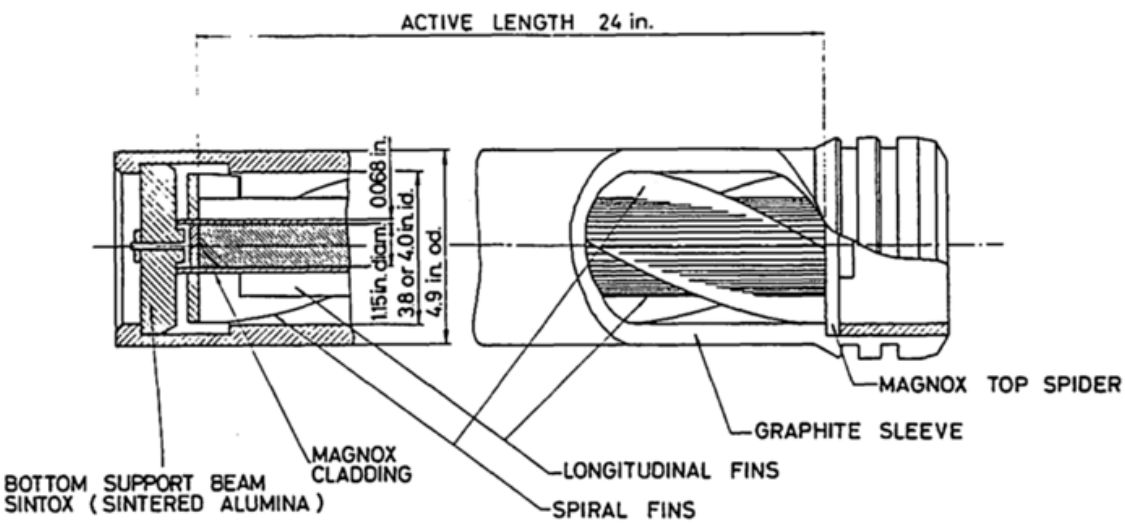


Figure 2 Schematic of the Hunterston MK1C fuel element design with graphite support strut (IAEA Reactor Data Sheets, p256) [9]

The original elemental composition of these components is not available, and the storage conditions after ejection from the core would complicate any attempts to relate the post-irradiation composition to that of the starting composition.

1.2 Pile Grade-A

The graphite used in both the Windscale piles and Magnox stations is Pile Grade-A (PGA), this consists of a petroleum coke filler phase and coal tar pitch binder. The coke particles are needle shaped and as the material is extruded during the manufacturing process these particles tend to align parallel (to the extrusion direction), which results in PGA having anisotropic properties [10], as described in Table 2.

Table 2 Typical PGA properties; both parallel and perpendicular to the extrusion axis [11]

PROPERTY	PILE GRADE A	
	Parallel	perpendicular
Density [g/cm^3]	1.74	
Open Pore Volume [cm^3/cm^3]	0.193	
Closed Pore Volume [cm^3/cm^3]	0.01	
$CTE_{20\text{-}120°C}$ [$10^{-5}K^{-1}$]	0.9	2.8
Thermal Conductivity (20°C) [W/m K]	200	109
Electrical Resistivity [µohm-cm]	620	1100
Young's modulus (20°C) [GN/m^2]	11.7	5.4
Poisson's Ratio	0.06	0.15
Tensile Strength [MN/m^2]	17	11
Compressive strength [MN/m^2]	27	27
Flexural strength [MN/m^2]	19	12

A Magnox reactor core consists of an assembly of graphite bricks which have vertical channels for fuel, control rods and coolant flow [12]. The design of the graphite bricks varies between stations, with later designs incorporating 'vertical key-ways' as identified in the schematics shown in Figure 3. These keys interlock the individual bricks and allow relative movement in both radially and vertically directions to accommodate both thermal and irradiation induced dimensional changes [12].

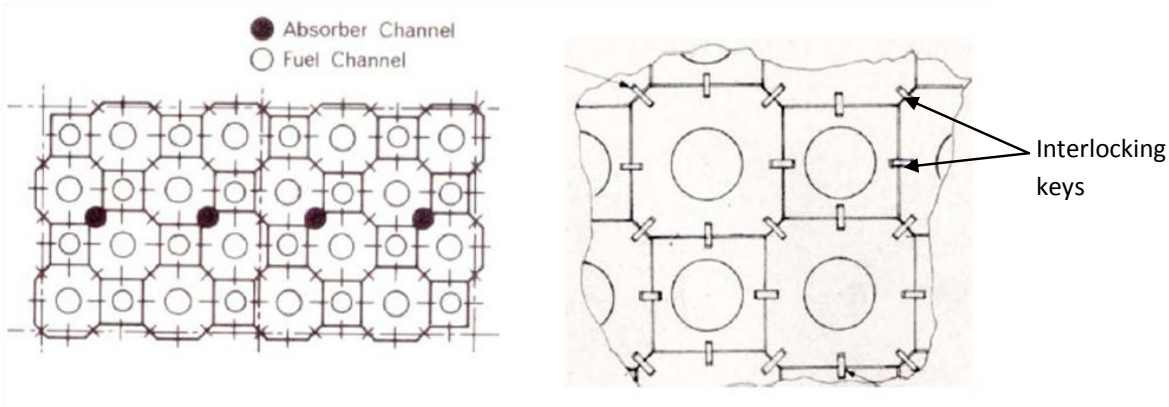


Figure 3 Example cross section of Magnox graphite moderator bricks [13]

1.3 Key radionuclides of concern in i-graphite

Particular concerns associated with disposal of this material include the presence of several long and short lived radioactive isotopes, namely ^{3}H, ^{14}C, ^{36}Cl, ^{41}Ca, ^{55}Fe, ^{60}Co, ^{63}Ni, ^{90}Sr, ^{133}Ba, ^{134}Cs, ^{137}Cs, ^{152}Eu, ^{154}Eu and some transuranics arising from trace uranium and fission products from failed fuel. The source of the radionuclides in graphite is likely to be a combination of the activation of an original impurity in the graphite (some of which may be gas trapped in the closed pores) together with general reactor operations including;

- Contamination introduced by the coolant during reactor operations
- Fuel types / changes in fuel cladding
- Fluence
- Location within reactor
- Contamination during PIE
- Contamination by damaged fuel i.e. windscale piles and one of the chapel cross reactors

An NDA report in 2010 [14] highlighted the important inventory and material information when classifying and indentifying the parameters required for decommissioning and treatment option assessment as:

- Waste classification
- Volume
- Radioactivity concentration

- Material composition
- Current or planned treatment and packaging

1.4 Long lived isotopes

One isotope of major importance is Carbon-14 due to its long half-life of 5730 years and the environmental concerns related to this isotope are partly due to the possible release of radioactive methane gas or other harmful organics whilst decommissioning or under GDF. The scientific debate on the origin of ^{14}C in irradiated graphite focuses on the ^{13}C or ^{14}N pathway. This is considered hugely important when determining the mobility of this isotope which is present in large quantities in i-graphite. This pursuit of knowledge drives forward many treatment programs and the relationship between removable ^{14}C and non-removable ^{14}C may help identify which graphite wastes are suitable for a particular treatment option.

Table 3 Activation reactions for producing ^{14}C [5, 15-17]

Reaction	Cross section (barns)		
	2200 m/s neutrons	LWR neutron spectrum	Fast reactor neutron spectrum
$^{13}C(n,\gamma) \rightarrow {}^{14}C$	0.9×10^{-3}	1×10^{-3}	0.5×10^{-6}
$^{14}N(n,p) \rightarrow {}^{14}C$	1.81	1.48	12.6×10^{-3}
$^{15}N(n,d) \rightarrow {}^{14}C$	0	0	1×10^{-3}
$^{16}O(n,{}^{3}He) \rightarrow {}^{14}C$	0	0	0.03×10^{-6}
$^{17}O(n,\alpha) \rightarrow {}^{14}C$	0.235	0.183	0.12×10^{-3}

Chlorine-36 is also of international importance due to its incredibly long half life of 301,000 ± 4,000 years and its hydrophilic nature [18-19]. The source of chlorine-36 present in i-graphite waste is expected to arise from C-Cl covalent bonds, mineral impurities (i.e. chloride ions) or as free chlorine (adsorbed species). Whilst C-Cl covalent bonds will be the stable under storage and irradiation, chlorine present as Cl_2 and ^{36}Cl is very mobile and will be liberated early in reactor operations. The current known fingerprint inventory for ^{36}Cl is small and specific activities are typically in the region of Bq/g. Previous views regarding chlorine release focused particular concern

with uncontrolled releases of ^{36}Cl due to its high solubility, mobility and sorption rates during retrieval, treatment and ground water release under long term disposal GDF environments. Presently research is being undertaken by EPRI and IPNL into determining the ^{36}Cl speciation within i-graphite waste, origin, production (recoil energies) and whether this weak emitting β isotope will have any real long term risk to the environment during decommissioning, storage and treatment. CARBOWASTE deliverable D-6.1.6 has full details of ^{36}Cl leaching experiments carried out within this EU program.

Table 4 Origins of chlorine-36

Pathway	Origin
$^{35}Cl(n,\gamma) \rightarrow {}^{36}Cl$	^{36}Cl production rate associated with thermal neutron-capture

1.5 Short lived isotopes and metallic contaminants

Isotopes considered in this remit have short half-lives <30 years and decay to insignificant levels after a few tens of years and may pose issues for handling nuclear graphite waste immediately after reactor shutdown, depending on treatment, decommissioning and storage of graphite waste reflects on whether short lived isotopic inventory requires any future assessment. Short lived radionuclide's typically present in i-graphite include, ^{60}Co (half-life of 5.3 years), ^{3}H (half-life of 12.3 years) and ^{137}Cs (half-life 30 years). These isotopes are well documented on the radiation poisoning and harmful effects they have on the environment and human population when released [20].

Tritium has a half-life of 12.3 years and is mainly produced from the neutron activation reaction ^{6}Li (n, α) ^{3}. Very small amounts of ^{3}H probably occur also from ^{3}He (n, p) ^{3}H and ^{2}H (n, γ). Tritium is a low energy beta emitter; issues with tritium are of detection and contamination. The environmental problems related to this isotope is due to the possible unexpected release whilst decommissioning (whilst i-graphite is being drilled ,crushed or moved) and detection issues [21-23].

Table 5 Origins of tritium

Pathway	Origin
$^{6}Li(n) \rightarrow {}^{3}H + {}^{4}He$	Contamination from association with tritiated material
$^{238}U(n) \rightarrow$ tertiary fission products + ^{3}H	Direct material activation Contamination from the fission process

Figures 4 and 5 show commonly found short-lived isotopes present in i-graphite post reactor closure. From this graph it is clearly visible the isotopes that will require handling considerations when decommissioning include ^{60}Co, ^{63}Ni ^{134}Cs, ^{137}Cs, ^{152}Eu and ^{154}Eu from the high energy gamma emissions. Fuel contamination of the nuclear graphite during reactor lifetime can also give rise to transuranic present in the isotopic inventory post closure. These are typically alpha emitting with a long half-life.

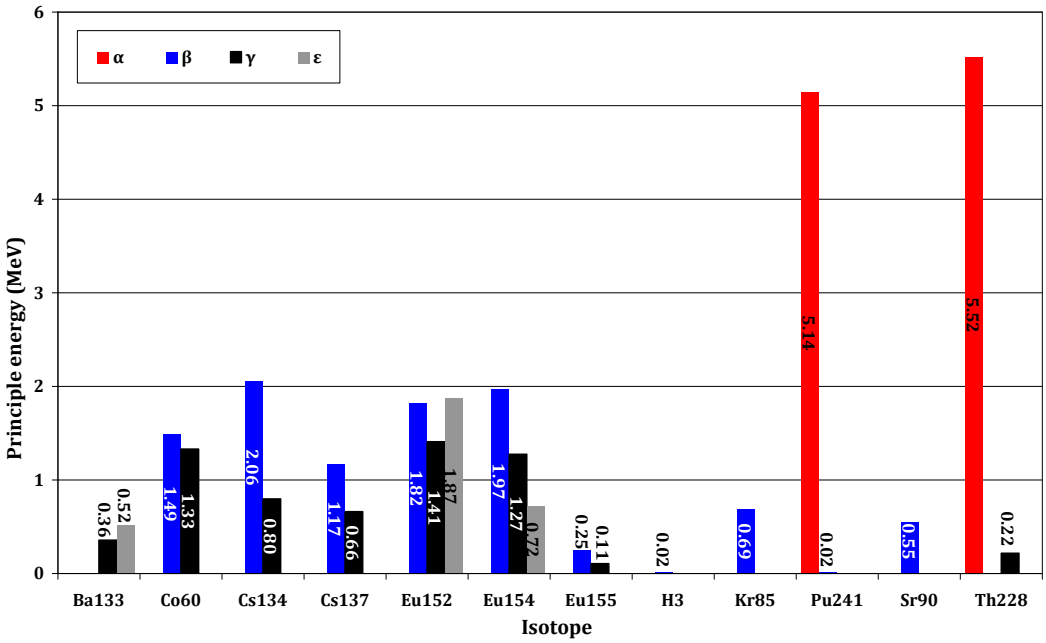


Figure 4 Graph showing principle energies commonly found short lived isotopes present in graphite waste

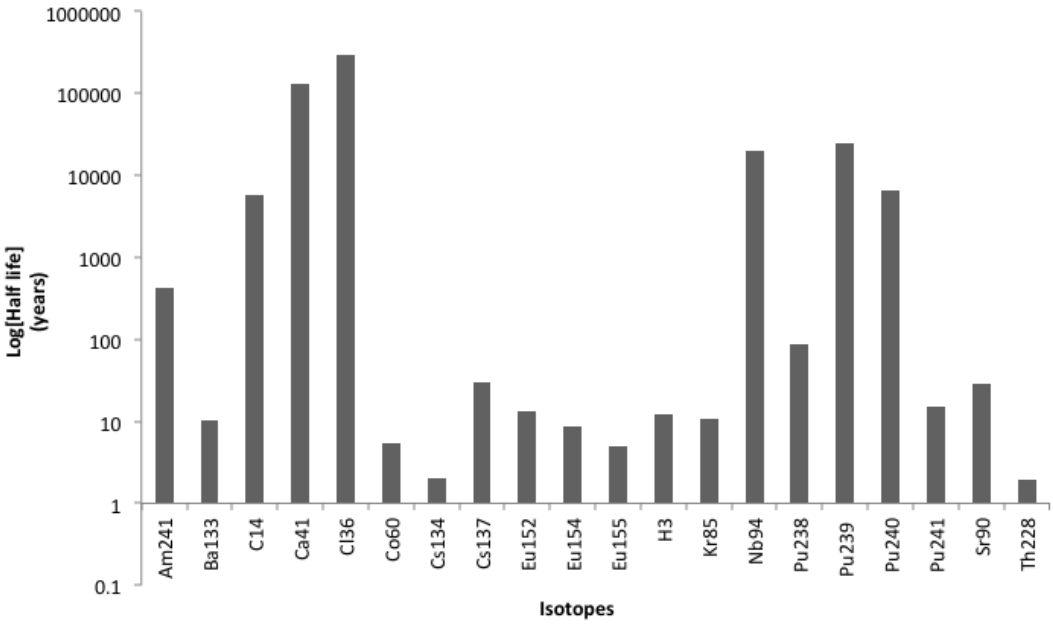


Figure 5 Graph showing the half-life of commonly found isotopes present in graphite waste

2 Leaching Review

2.1 Leaching experiments

The previous studies have focused on the decommissioning of nuclear graphite via a repository environment hence focusing on the leach ability of the isotopic inventory present within the i-graphite. Focus has been placed on the stability of the isotopic inventory within i-graphite. Leaching conditions are often driven by repository environment or ground water systems i.e. water, pH12 or pH13. 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. Various leaching parameters which are altered depending on the desired requirements:

The three most commonly used methodologies are;

- IAEA recommendations [24]
- Comparison methodology ANS-16.1(Encapsulated waste) [25]
- CEA leaching diffusion determination experiments [26]

The IAEA methodology centers on selecting the appropriate experimental methodology and always including a water standard which can be compared to other research programs in order to link up data. Experimental methodologies follow these standard formats;

- Dynamic – complete removal of total leachant solution at each time point
- Semi-dynamic – portion of leachant is removed at each time point and then replaced with fresh solution, so the total volume remains at a constant
- Static – at each time point a portion of leachant is removed and not replaced

A full detail of the approach and application considerations behind each leaching methodology is detailed in deliverable D-6.1.6.

2.2 Literature review

The first work published in the public domain on radioisotope analysis of Grade A graphite was carried out at the Argonne National Laboratories by Libby in 1946 [27], examining the radiocarbon chemical methods analysis to determine ^{14}C concentration and diffusion in the environment.

Leaching studies on radioactive material by Hespe et al [28] in 1971 focused on standardising graphite leaching methods. Hespe concluded through measuring the changes in pH, gross alpha activity and gross beta / gamma activity, the most likely method mechanism for removal for radioisotopes in graphite would be transported by water in environmental conditions. In addition Hespe found radioisotopes of significant interest including the first reports on ^{14}C. Little reported work was carried out during the 1970's, however the interest in radioisotopes release was stepped up during the 1980's where many governmental groups concentrating their efforts on radioisotope release and mechanisms.

In 1982, Bush, Smith and White [15], discussed in detail the origins, production pathways of ^{14}C in reactor graphite and ^{14}C waste arising for each reactor type in production this was based on calculations of 10ppm of N_2. Bush details analytical methods for the determination of ^{14}C and predicts both the gaseous and solid waste arising from ^{14}C from several reactor systems including Magnox and AGR. Little detail was published in the report by Bush, Smith and White[15] on leaching methodology, however the report documents conditioning of graphite waste through reduction, gaseous trapping and solid immobilisation which leads to a overview of final options of ^{14}C contain waste and radiological impact.

The oxidation of graphite in liquid water for radioactive waste storage applications was reported by Gray [29] in 1982, and provides useful background knowledge into the leaching behaviour of graphite in water. Gray found that graphite reacts with dissolved oxygen with water acting as a catalyst. In addition Gray carried out experiments on graphite irradiated by in a ^{60}Co radiation field. Gray carried out numerous experiments

to confirm and correct gaseous leakage issues during his leaching experiments and demonstrated that through using a fused quartz vessel instead of Pyrex corrected this issue. Gray also compares graphite leach rates in water with various other materials such as concrete to find that graphite is at least three orders of magnitude more durable with a reaction rate 100 times lower than concrete. Gray's results obtained from the leaching experiments under ^{60}Co radiation show H_2 and CO_2 were the only gases released and hence the graphite was degassed after irradiation and prior to analysis, in order to determine whether a direct correlation between the graphite and oxygen concentration could be found. This was not the case and it was concluded that whilst irradiation had a substantial effect on the release of H_2, it had no measurable effect on the behaviour of any of the other gases.

In 1984, White, Smith and Saunders studied the assessment of graphite management options in terms of reactor decommissioning [30]. A full radiological assessment including methodology and models for common disposal routes with costing is well documented. Characterisation parameters of graphite included elemental analysis, decay routes, neutron flux profile, reactor inventory, activation inventory and reported knowledge of the operational and irradiation history of each reactor. The group detected ^{3}H, ^{14}C, ^{133}Ba, ^{60}Co and ^{134}Cs in the leachant from Magnox graphite which had been irradiated for approximately 13 years to ~ 1600 MWd/t, the samples had been removed from the reactor three years prior to the leaching analysis. Leaching rates were in the order of 10^{-5} cm / day White et al [30] reported that leach rates decreased by factors of 50-100 after 100 days and obtained steady state release rate for ^{14}C. Data specifying graphite weight loss post-treatment and surface area measurements are also published. Other radioisotopes may have been present in the graphite however; these were below the limits of detection. White, Smith et al.[30] also concluded that any ^{134}Cs originated from the activation of ^{133}Cs, present as a trace impurity in the graphite.

2.3 Literature review summary

A summary of the published studies on the leaching of radionuclides from graphite has been comprehensively presented in the IAEA TECDOC [5]. It was reported that the leaching mechanism for carbon species is a water catalysed oxidation by dissolved oxygen to form carbon dioxide. This report documents evidence that supports ^{14}C oxidisation rate and release of oxidised species and leached at a greater rate than stable ^{12}C in the early stages.

Known leaching methods for nuclear graphite have not significantly advanced since 1940's. Leaching mechanisms have been predicted however to date have not been widely validated. There has been immense amounts of attention is placed on figure of leaching rates in the order of 10^{-5} however realistically predicting the migration and long term possible unwanted chemical reactions in deep repository conditions is no small task when a standardised universal leaching technique is not well established. Generally, leach rate experiments on irradiated graphite are initially rather erratic tend to stabilise within the experimental timescales which have been on the order of 70–140 days [5, 30-31]. An interesting observation is that the results quoted on leaching studies illustrate the differences between sample history, geometry, porosity, leaching methodology, sampling frequency and quoted leach rate. This drives a further the need for comparable data on material specific to the reactor of interest prior to decommissioning.

2.4 Leaching parameters - factors to consider

The reviewed papers detail how techniques and methodology vary from different sources, influencing the interpretation of published leach rate and in affect reduces the comparability of data. It is often difficult to compare leaching data for graphite due to the experiment been designed for a particular application or situation which is not directly transferable.

Listed below are some of the influencing parameters which have been applied in previous leach tests. Validation of the parameters can be justified through many sources including application of international Standards [32]. These Standards have been published by the IAEA [24], ISO [33] and ANS-16.1 [25]; adapted for graphite encapsulation leaching. These standards highlight important techniques and best practices to apply when considering carrying out a leaching experiment, particularly for post analysis comparison to literature data.

Factors to consider prior to carrying out a leaching experiment;

- Comparison/origin of i-graphite
- Microstructural characterisation – density, open porosity, surface area
- Radionuclide inventory – initial and final (post leaching)
- Dynamic/semi-dynamic/static approaches
- Leaching solution - locally sourced tap water/deionised water/pH12/pH13
- Room temperature
- Length of test
- Isotopes determined
- Varying time points for analysis
- Gas phase determination
- Management of sample analysis- filtered or unfiltered
- Pre-washing stages
- Data from literature
- Mechanical release of radionuclides (diffusion, surface effect, ionic exchange)
- Chemical and radiological phenomena (flux, corrosion)

3 Irradiated Graphite

3.1 Wylfa sample history

Wylfa Magnox reactors were commission in 1971 and consist of two reactors with a combined capacity of 980 MW. Wylfa reactors were the largest and last of the magnox reactors to be built in the UK see Table 11 in the introduction section. Each Wylfa core has 6,156 vertical fuel channels and contains over 49,248 natural uranium magnox-clad fuel elements; these large graphite moderated reactors typically supply 23 GW h of electricity per day. The primary coolant used in carbon dioxide.

The samples issues to UoM for this research where trepanned from the fuel channel wall of reactor 1 channels 1413/02 and 1319/12 in April 2007. Figure 6 shows the location of these two sampling points. There are twelve bricks per column in reactor 1 and they are numbered from the bottom of the core. 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. Table 6 details the irradiation history of these two samples. Sample 1413/02 was used for leaching experiments and sample 1319/12 was used for other characterisation work covered in T-4.3.3-b.

Table 6 Irradiation conditions of Wylfa samples used in this study

IRRADIATION CONDITIONS	1413/02 9U	1319/12 8U
Irradiation temperature (˚C)	352	342
Adjacent fuel dose (MWD/t)	34973	37319
DIDO equivalent dose at channel wall (10^{20} n/cm^2)	34.21	37.11

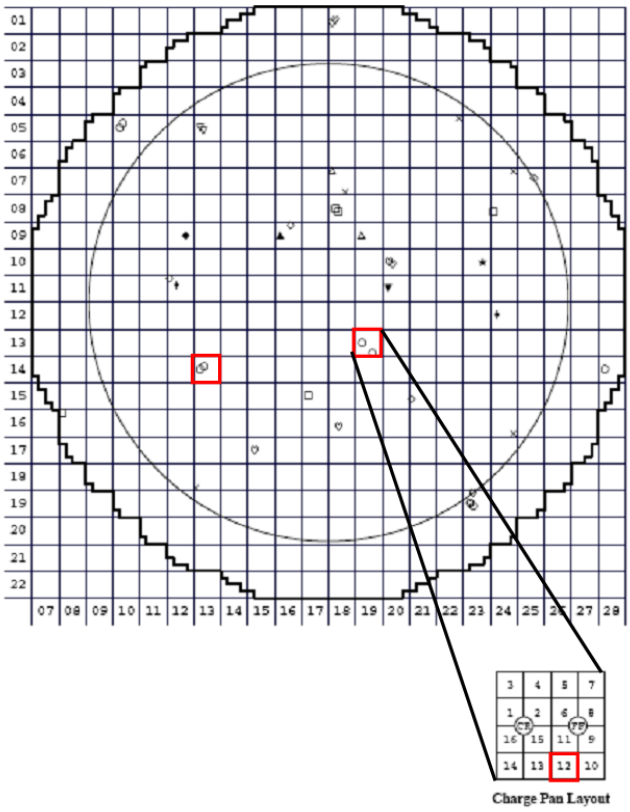


Figure 6 Highlighted in red are the samples taken in 2007 from the Wylfa reactor 1 used in this research

3.2 Wylfa isotopic inventory

The irradiation history of the two trepanned Wylfa Magnox samples was provided to the University of Manchester. Inorder to determine the ^{3}H and ^{14}C isotopic inventory present complete combustion of irradiated graphite material was carried out [34-35]. The Carbolite® MTT furnace with a copper oxide catalyst was used for thermal analysis of this irradiated graphite material. A process of using sucrose labeled ^{3}H and ^{14}C standards are used to determine the recovery and capture of ^{3}H and ^{14}C in order to apply a correction value to the final determination. The CuO catalyst ensures all inorganic and organic carbon species are converted into HTO and carbon dioxide. Two trapping bubblers are used to capture each isotopic labelled species, these bubblers contain 20 mls 0.1M Nitric acid to capture HTO and 40 mls of carbon trap is used as a trapping agent for $^{14}CO_2$. Figure 7 shows a schematic of the furnace employed.

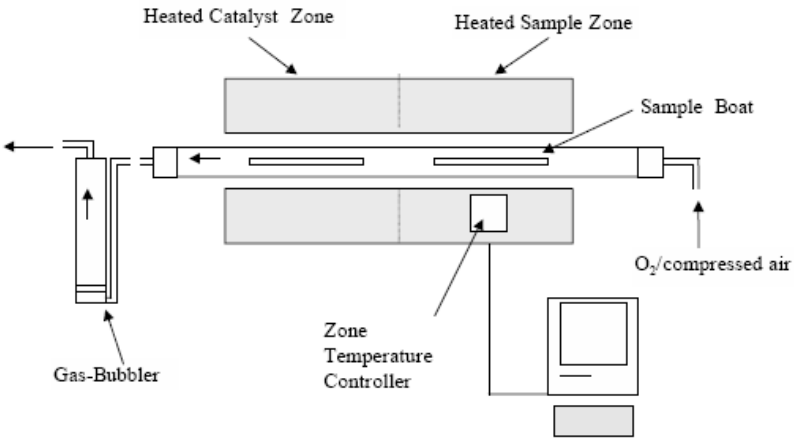


Figure 7 Schemtic of Carbolite® MTT ^{3}H and ^{14}C furnace

This methodology is estimated to have a 10% error associated with this process due to any gaseous losses that may occur during the combustion process. The recovery checks that are performed calculate any losses which may occur during analysis allowing higher levels of accuracy to be achieved. The furnace and LSC data of recovery check and unquenched standards are recorded and monitored over all analysis that is carried out. Typically ^{14}C recovery checks are between 85-90% recovery and quenched LSC standards 100% and there is a <1% carryover between bubblers.

The isotope inventory for the wylfa samples detailed in Table 7 was determined using the above methodology and gamma spectroscopy.

Table 7 Isotopic inventory for Wylfa samples determined

	WYFLA 1413/02	WLFYA 1319/12
Nuclide	**Specific Activity Bq/g**	**Specific Activity Bq/g**
^{3}H	199066	
^{60}Co		23700
^{137}Cs		1140
^{14}C	73208	

3.3 Oldbury sample history

Oldbury Reactor 2 started generating electricity in April 1968 and is scheduled for decommissioning in 2012. This reactor has a gas outlet temperature of 365 °C. Oldbury nuclear reactors where designed to produce a 600 MW electrical power however only sustained 434 MW during their lifetime. Reactor 2 produced 893 thermal power MW(t) and had a pile grade A (PGA) reactor core weighing 2061 tonnes with a reactor graphite total of 2090 tonnes. The Oldbury reactors were the first nuclear power station in the UK to have a pressure vessel made from pre-stressed concrete instead of steel.

Samples provided for CARBOWASTE research where provided by NNL. The present information is what has been made available to the auther. Installed sets from pot 634 located at position 4 in Channel S77 (BNL Channel 3) of Oldbury Reactor 2 were supplied. This installed graphite pieces have been in place continuously from start of life up until June 2005. The Mean Core Irradiation of these installed sets is 30658 MWd/t. Dosimetry calculations have not been specifically carrier out for these samples; however a suitable reference sample from Oldbury Reactor 1 trepanned in 2004 has had full dosimetry calculations performed. On this basis the following information has been provided, in table 8.

Table 8 Irradiation conditions of Olbdury i-graphite provided by NNL

IRRADIATION CONDITIONS	
Irradiation temp	543 K
Adjacent fuel dose	52827 MWd/t
DIDO equivalent dose	40.27×10^{20} n/cm^2
Calder equivalent temperature	543 K
DIDO equivalent temperature	597 K
DPA	5.28

4 Experimental Data

Progress on the characterisation of structural changes in virgin and irradiated graphite before leaching and chemical treatment has been undertaken as part of the CARBOWASTE project, additional experimental information on chemical treatment and comparison of leaching data is available in T-4.3.3-b and D-6.1.6.

4.1 Experimental program

Leaching experiments at UoM followed the IAEA semi-dynamic methodology [24] is selecting the environmental standard which aims to give minimal damage and weight loss to i-graphite whilst determining what isotopes are removable under environmental conditions (limited ground water attack). Leachant is tested is every 7 days until the isotopic removal falls to insignificant quantities justifying longer periods within the testing program, this makes this methodology one of the few driven by release rates. This methodology utilizes 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. Following this; a trend in UK data analysis has emerged using incremental day leach rate (at 100 days) when comparing leaching data as this takes into account surface area, sample geometry and activity present per sample. The equation below details how leach rate has been calculated as recommended by the IAEA.

$$R_n = \frac{(a_n / A_n)}{(F / V) t_n}$$

R_n= *Leach Rate* $cm.d^{-1}$
a_n= *Radioactivity released at renewal period*
A_o= *Radioactivity present in specimen*
F= *Exposed surface area* (cm^2)
V= *Volume of specimen* (cm^3)
t_n= *Duration of leachant renewal period*

Leaching experiments have been performed to determine ^3H and ^{14}C migration from irradiated-graphite (i-graphite). Each experiment contained 0.5 grams of i-graphite immersed in 50 ml of leachant. All leaching tests were performed at 20 ± 5°C. Samples were ground in order to maximise the accessible surface area. This testing

methodology was taken from the IAEA proposed standard for 'Semi-dynamic leach test'[24], in which a 5ml leachant sample is removed every 7 days and replaced with a fresh 5ml of leachant. All leach tests were performed at room temperature, with a weekly testing frequency and test duration of 190 days. An 8% error is associated with this leaching test; based on LSC counting error, ±1% weight distribution and electronic pipette standard deviation. All Cumulative Fraction Release (CFR) calculations include a half life, dilution and weight correction are shown in figures 8 and 9.

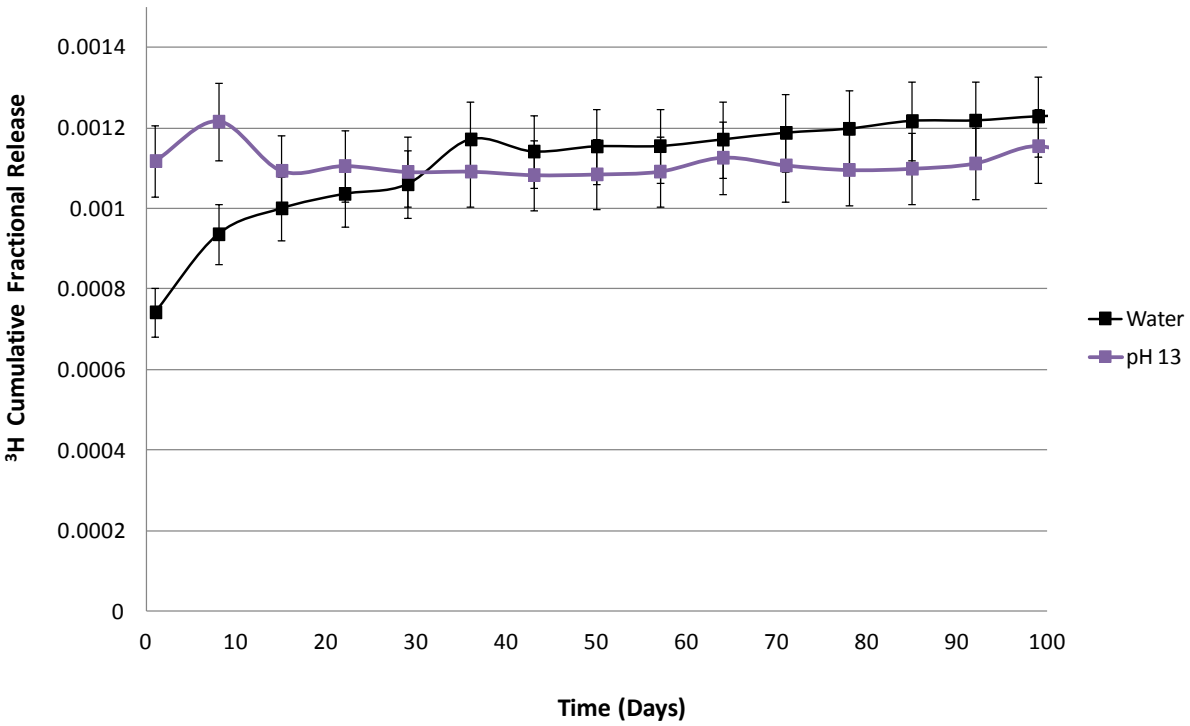


Figure 8 Tritium release under semi-dynamic leaching conditions

The tritium release from this i-graphite material reached 0.12% of the total tritium inventory after 190 days under water conditions and 0.11% under pH13 conditions. This level of activity was in the region of the LOD for the LSC equipment. As discussed earlier Tritium is an isotope of interest due to its potential for migration, however this was not observed for this material under these conditions.

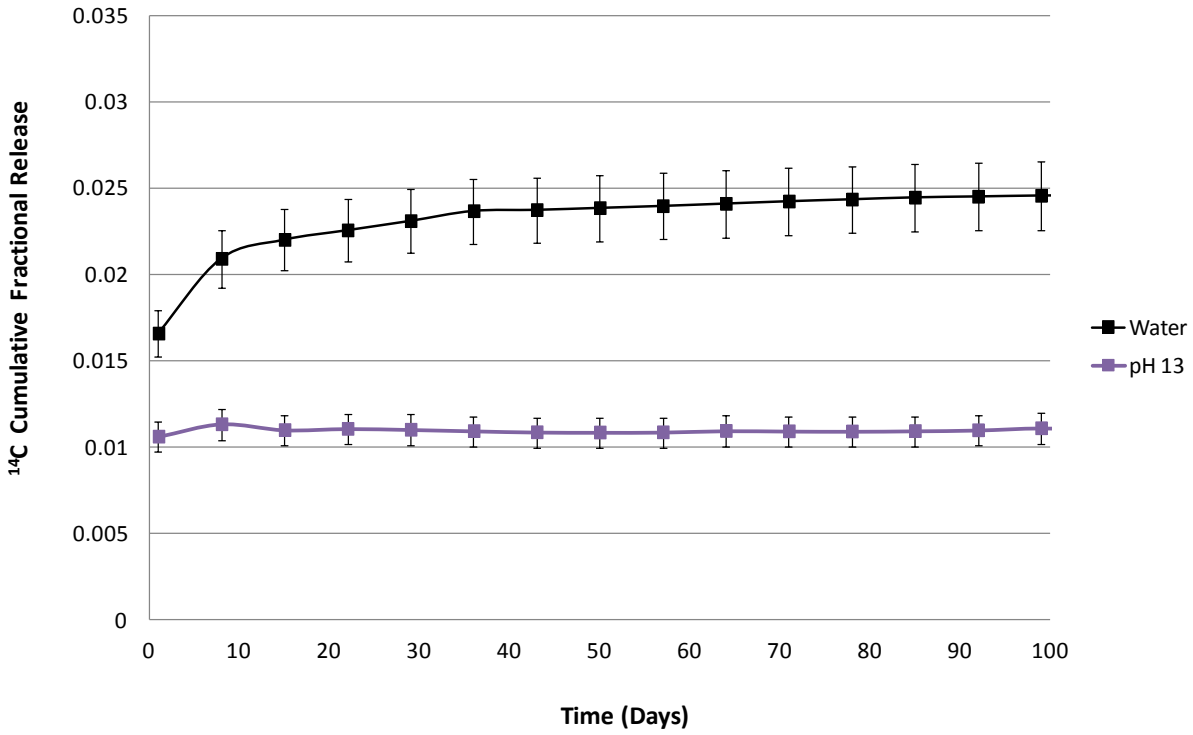


Figure 9 Carbon-14 release under semi-dynamic leaching conditions

Carbon-14 data provided an interesting result with 2.5% of the total carbon-14 inventory being released by 190 days under water conditions and 1.1% released under pH13. This experimental data was collected as part of T-4.3.3-b and other types of i-graphite did not exhibit similar behaviour of reduced release under pH13 conditions, however this is the expected as discussed in literature data. An explanation or mechanism behind pH12 or pH13 isotopic suppression has yet to be determined but whilst there is supporting data research will continue in the field.

As detailed at the start of this section leach rate at ~100 days was determined for these test. Figure 10 shows the results for the wylfa i-graphite as well as the British Experimental Pile Zero (BEPO) i-graphite from the experimental program detailed in report T-4.3.3-b.

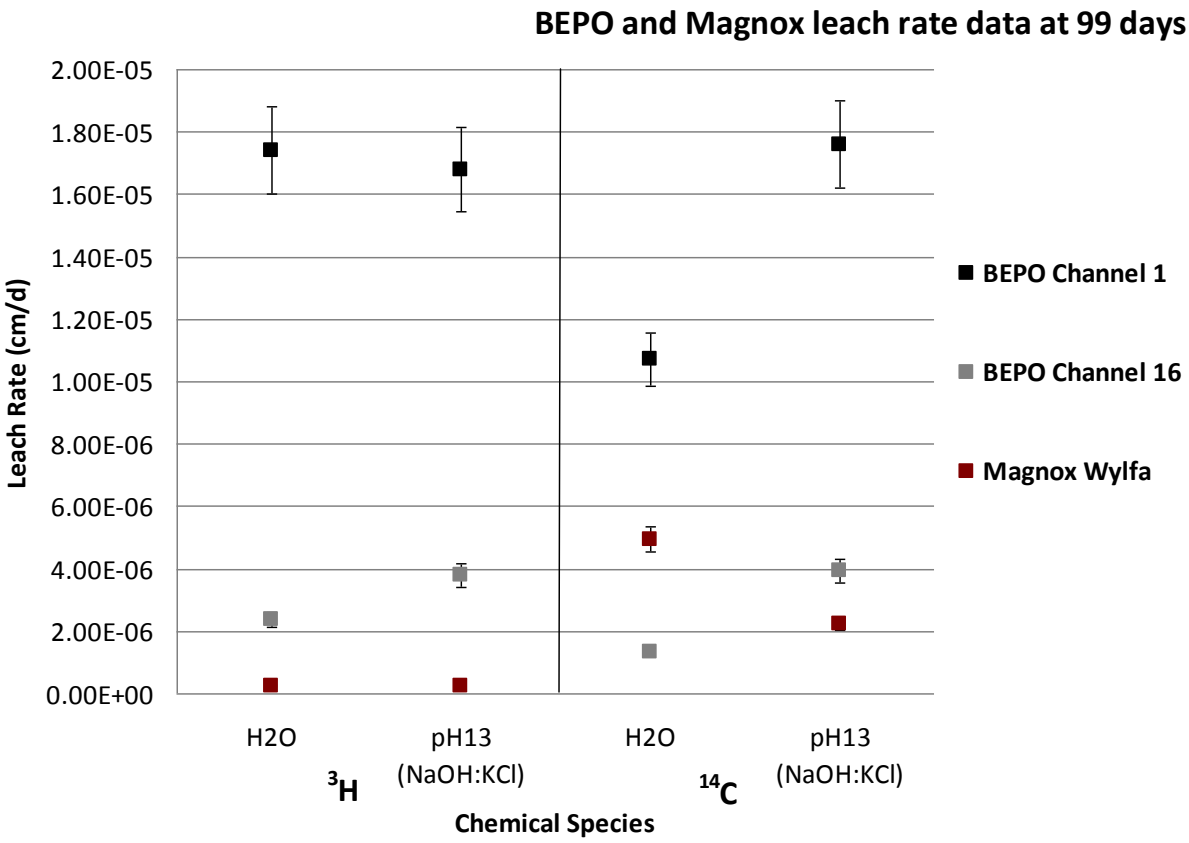
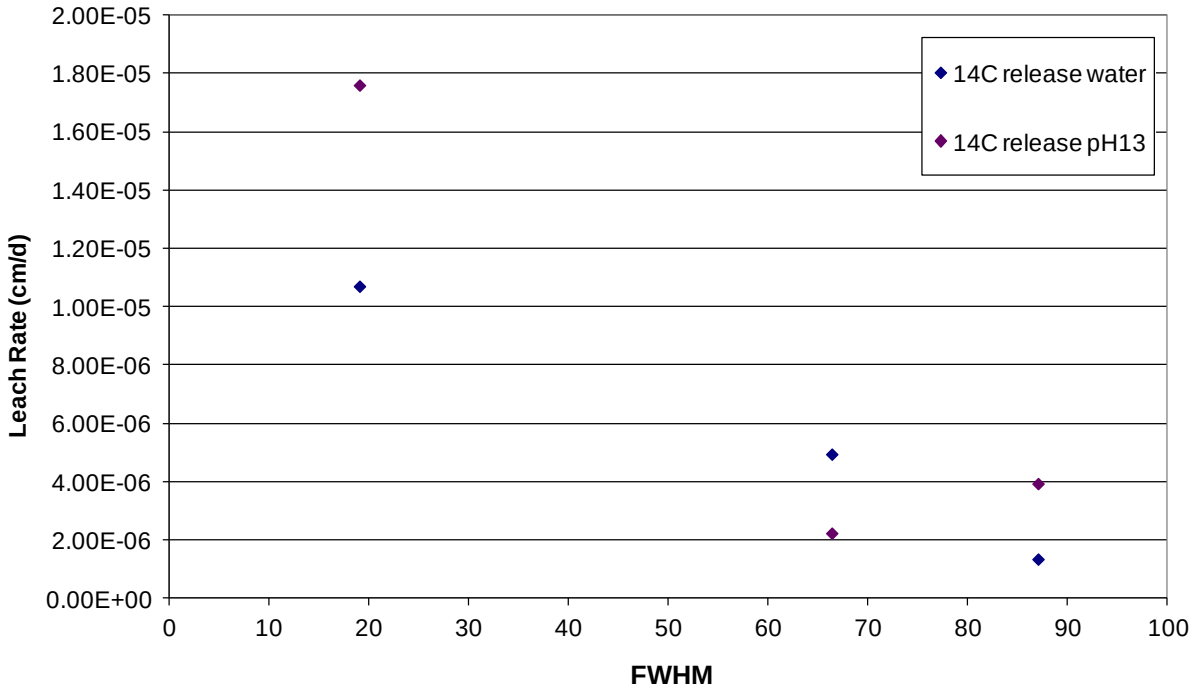


Figure 10 Leach Rates

Leach rate data only really has significance when compared to other i-graphite leach rates. Therefore the data determined for BEPO i-graphite is shown on this graph. Leach rates for moderator i-graphite typically are within $7.5E^{-6}$ to $2.5E^{-7}$ range. The irradiation history and graphite manufacturer/coke source has been considered some of the possible reasons behind the variance observed in leach rate between i-graphite material for BEPO channel 1, 16 and wylfa.

4.2 Future trends in leaching data analysis

Following on from the application of Leach rate comparison Full width half maximum data from Raman spectra has been combined with ^{14}C leach rate. This is the first time this comparison has been made and further supporting data from other sources is greatly needed, figure 11.



4.3 Post leaching thermal analysis

Upon the completion of the leaching experiment the samples were filtered weighted and then thermally analysed for the amount of ^{3}H and ^{14}C that remained. An inhomogeneous distribution of activity was observed between the samples however in most cases the combined thermal analyses with the amount leached out are within the expected quantity of activity present. Figures 12 and 13 show the combined thermal analysis and leaching data for Wylfa graphite analysed as part of T-4.3.3-b. The grey bar was activity determined via thermal analysis, blue bar is activity that was leached out and the red line signifies the total activity thought to be present in the sample determined by an unleached sample undergoing thermal analysis. The data bars are set to 10% error.

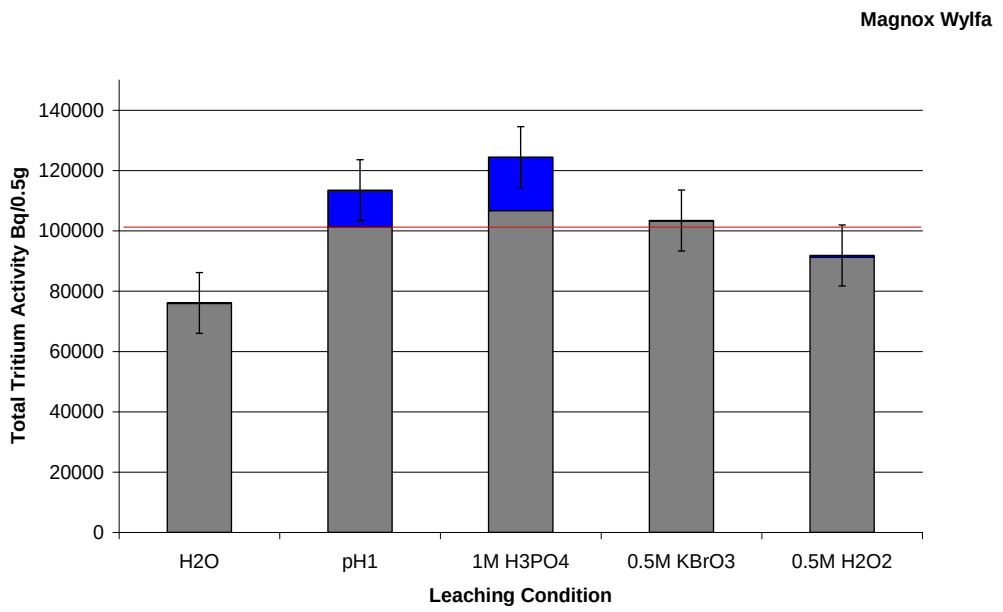


Figure 12 ^{3}H results for Wylfa Magnox thermal and leaching data combined

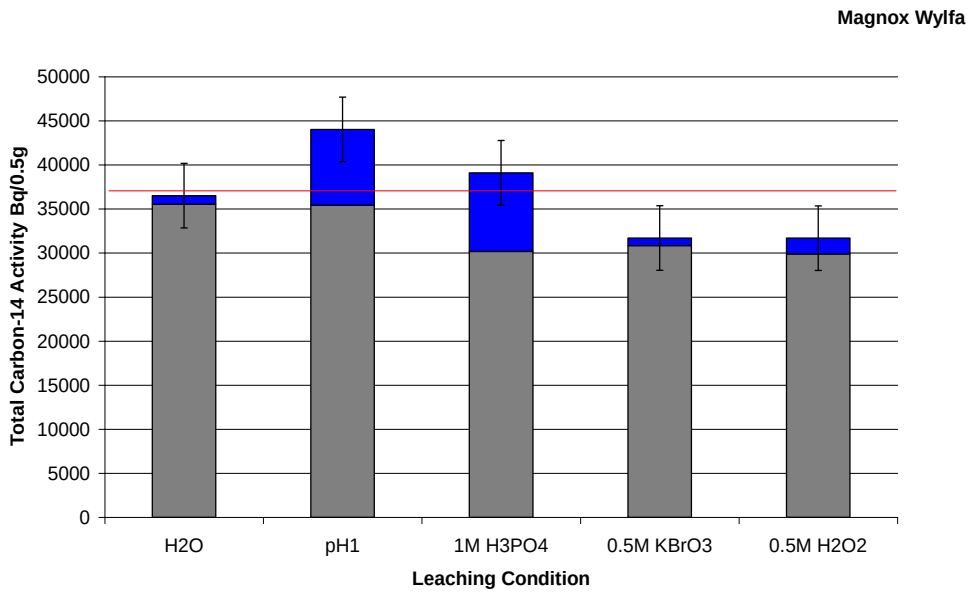


Figure 13 ^{14}C results for Wylfa Magnox thermal and leaching data combined

This methodology of post leaching isotopic analysis has proven significant in proving conclusively that significant amounts of ^{3}H and ^{14}C activity remain within the i-graphite material.

4.4 Data from Oldbury leaching experiments

Powder samples were taken from the oldbury installed sets and leaching under water conditions following the IAEA semi-dynamic approach where carried out. Whilst under review within the CARBOWASTE program fellow researchers asked about the release rate occurring under 24 hours. Therefore for this quick experiment 5 mls of leachant was removed and replaced every hour for 20 hours to determine if solubility or saturation of istopic release was having any impact on the results.

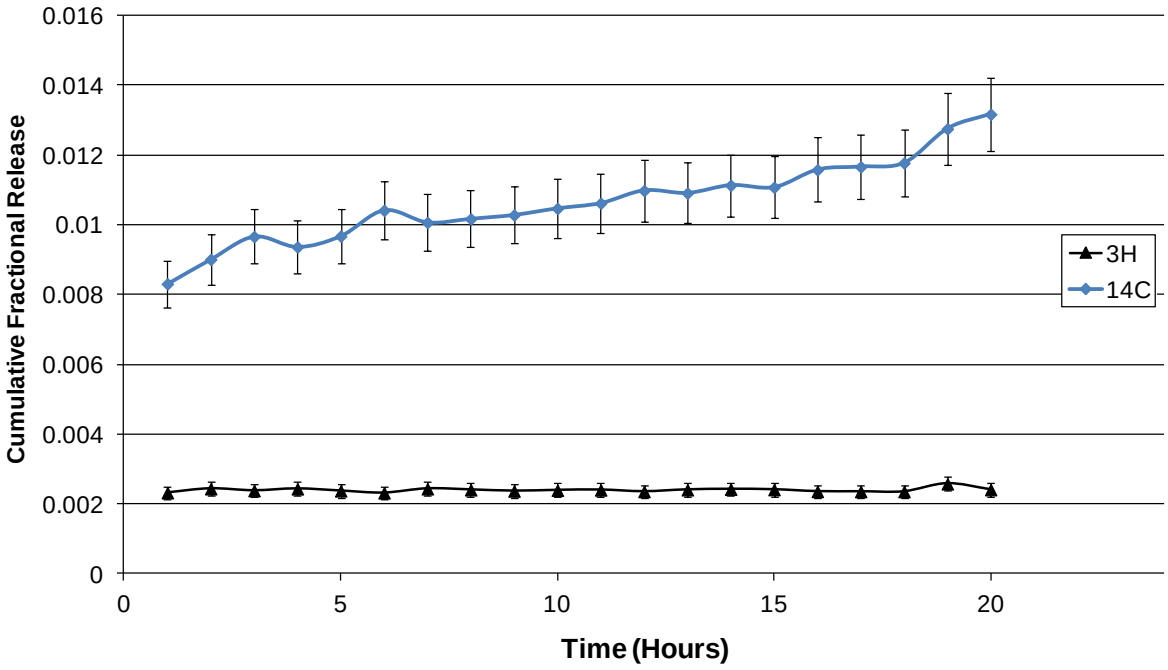


Figure 14 Results from hourly semi-dynamic leach test

As shown in figure 14 results from powdered samples taken from the oldbury installed sets i-graphite had total ^{3}H release of 0.2% and ^{14}C release of 1.5%. This result shows a similar trend to the results from the wylfa samples, the ^{14}C release is greater than the ^{3}H and both release rate are in the same order of magnitude as the previous data. There does appear with the ^{14}C to be a possible water diffusion mechanism behind the continuing increase in release rates, whereas the ^{3}H release appears to have an instantaneous release with little further ^{3}H being released after the first analysis.

4.5 Collaboration work between NNL and UoM

Contribution by Bereket Hagos.

This research work was carried out as part of a research placement at the National Nuclear Laboratory, Sellafield underwritten by the NDA. The work placement carried out by Bereket Hagos was undertaken over for a period of nine months at the National Nuclear Central Laboratory as part of the NNL/UoM Access agreement. The aims of the agreement were to enable this research to perform physical, microstructural and radiochemical analysis in order to determine and understand the isotopic leachability of Magnox graphite under deep repository conditions and to determine critical leaching parameters for further encapsulation tests. The research was performed in Technology Department at NNL over the duration from June 2011 until April 2012.

Irradiated graphite samples from the Oldbury Magnox Reactor 1 core were used throughout this research. A related pair of matching samples, in terms of irradiation history and properties was immersed in solution, representing typical repository conditions as described in Section 2. The composition of the solution simulating ground water, is shown in Table 3. The data collected was used to relate the leachability index to the pH of the solution and the graphite irradiation history.

4.6 i-graphite provenance

Irradiated graphite samples from the Oldbury Magnox Reactor 1 core were used throughout this research. A related pair of matching samples, in terms of irradiation history and properties was immersed in solution, representing typical repository conditions. The data collected was used to relate the leachability index to the pH of the solution and the graphite irradiation history.

Samples from fuel Channel Q09B5 West brick 4, 6 and 8 (L)ower and (U)pper (Upper refers to the top end of the brick and Lower refers to the bottom part of the brick) trepanning positions were chosen. The sample identification (string) Q09B5 describes the location and position of the channel inside the core. The first three characters, Q09 indicates the standpipe position in the reactor and the channel position related to the standpipe indicated by the last two characters, B5. The letter ‘Q’ indicates the channel is located at the North of the core. In the ID the second and third numbers, 09 indicate the channel is positioned at the west. The second character is less than three

then it reveals the channel is in Reactor 1. The fourth character, B specifies one of the eight sections within the standpipe. The last digit in the sample identification characters, '5' shows the position of the channel within this section.

The samples were trepanned using a milling cutter and six samples were cut out from the graphite cores. During operation of the reactor, the samples received fast neutron dose of between 5.6 - 6.8 dpa and have radiolytic weight losses of between 25% and 38%. More sample details are summarised in Table 9.

Table 9 Temperatures and Doses for Oldbury Reactor 1 (2009) Trepanned Samples

Sample ID	Brick	Trepanned Sample Height (m)	Temp. (°C)	DIDO Equivalent Dose (10^{20} n.cm^{-2})	Displacement per atom (dpa)	%wt loss
1/2	4L	2.66	294	45.56	6.0	33
2/2	4U	3.01	302	48.15	6.3	38
5/2	6L	4.26	329	51.49	6.8	33
6/2	6U	4.7	338	50.95	6.7	33
9/2	8L	5.86	356	45.55	6.0	25
10/2	8U	6.22	361	42.86	5.6	27

4.7 Experimental

The six fuel channel i-graphite sample discs approximately 6 mm x 12 mm diameter and mass, 1g were immersed in leachant solution volumes of 50 mls for ten specified time periods as described in Table 10. At periodic intervals, each leachant was renewed and the recovered leachates analysed.

The ANSI 16.1 standard has been modified and was used throughout this leaching trial. The ANSI 16.1 protocol determines the leachability of contaminants from encapsulated low-level radioactive waste samples. This standard provides a uniform procedure to measure and calculate the leachability index of the radioisotopes released from waste forms as a result of leaching in demineralised water for 5 days or

more. The demineralised water was tested out and found to be of pH 6. It is slightly acidic as it absorbs carbon dioxide until it reaches equilibrium with the atmosphere.

Table 10 Leachant renewal schedule

Leach Period	Leaching Interval Time (hours)	Total Time (hours)	Total Time (days)
1	2	2	0.1
2	5	7	0.3
3	17	24	1
4	24	48	2
5	24	72	3
6	24	96	4
7	72	168	7
8	336	504	21
9	672	1176	49
10	1008	2184	91

The standard test procedure was modified for application on solid graphite samples instead of monolithic cement based waste samples, and requires the total quantity of leachate to be removed from the leach container at the end of each leach period and replaced with fresh leachant. According to the procedure the samples should have dimensions of 4.9 cm diameter and 5.8 cm height, hence, a geometric surface area of approximately 127 cm^2. The procedure recommends using deionised water volume of 10 times the volume of the sample equating to 1270ml. During this study the sample size and the volume of the leachate were different from that of the encapsulant, however as the ANSI standard requires a volume/surface area ratio to be at least about 10:1, the leachant volumes used throughout this study were calculated to fulfil this requirement. The surface area of the samples in this investigation was calculated from the physical measurements of the specimens. Moreover, in order to represent typical UK repository conditions based at Sellafield, a simulated ground water was

used instead of demineralised water which is comparable to that of Drigg ground water.

Table 11 Simulated ground water composition

Compound	Deionised Water (g / l)
KCl	0.0066
$MgSO_4.7H_2O$	0.0976
$MgCl_2$	0.0810
$CaCO_3$	0.1672
Na_2SiO_3	0.0829
$NaNO_3$	0.0275
NaCl	0.0094
$NaHCO_3$	0.2424
pH	7.35

4.8 Alpha and beta analysis

The analysis of ^{14}C contained within the leachant solution was investigated by sample digestion, the measurement of total alpha and beta radiation was done by liquid scintillation and investigation of ^{3}H was carried out by separation and analysis. Alpha and beta events may be distinguished from one another in a liquid scintillator by examining the electronic signals that are produced at the photomultiplier tube anode of the detector. The signals produced comprise two components: the prompt component and the delayed component [36-38]. The magnitude of these components in alpha and beta signals are different: the alpha signals are longer than beta signals. The radioactive decay of excited singlet and triplet states of the cocktail molecules produce photons on the cathode of the photomultiplier tube. The fast exponential decay of excited singlet states produces the prompt component. The delayed component of the signal is produced when triplet states interact only with another molecule and emits photons. The collision process takes longer time which causes the delay. The relative scintillation yield from this depends upon specific ionisation potentials. Higher specific ionisation potentials cause a greater fraction of excited molecules to be in triplet states and, hence, causing the alpha signal to have a longer duration. The basis of

alpha/beta separation by signal shape discrimination is the delay of these alpha signals. Most alpha radionuclides emit high-energy particles in the range of 4 - 6MeV and betas have values below 2.5Mev. Separation of alpha from beta is essential because the interaction of alpha particle with the scintillator produces low scintillation or photon yield as compared to betas (approximately it is lower by a factor of 10) shifting their spectra into the beta region.

4.9 Gamma spectroscopy

Gamma spectroscopy was used to quantify the activity of gamma releasing radionuclides. A small volume of solution (5 ml) was extracted from each leachate and used to measure total alpha-gamma and total alpha-gamma without tritium activity using Liquid Scintillation Counter. A blank system and quality control samples were also run in parallel to the system containing graphite to calculate errors on the system and preparation and to determine the accuracy of the method respectively.

The activity of gamma emitting radionuclides was measured using Gamma spectroscopy. The spectrometer uses High-Purity Germanium (HPGe) detector, Model GC10, connected to an Ortec DSPEC jr. digital gamma ray spectrometer and operated using Ortec Gammavision-32 software Version 6. The advantage of using this detector is that it has got Compton Suppression System (CSS) which will always reduce Compton background. It is also called an "active shield." It reduces the cosmic background because cosmic rays produce events (counts) in both detectors.

The geometry of the container was defined by specifying the size of the container from the choice within the software. It also allows materials to be defined from software default entries. All aqueous sources are modelled and defined as water with a density of 1.00 g / cm^3, and all plastic materials were defined by the default plastic option (57% carbon, 9% hydrogen, 34% oxygen, density of 0.94 g / cm^3).

4.10 Results

To measure the total alpha and beta activity released after each specific period of leaching time a small volume of solution (5 ml) was extracted from each leachate and was measured using a Liquid Scintillation Counter. A blank system and quality control samples were also run in parallel to the system containing graphite to calculate errors on the system and preparation and to determine the accuracy of the method respectively. The errors on the measurements were adjusted by subtracting the blank and background measurements from each leachate activity measurement. The efficiency was calculated by placing a known amount of activity (^{241}Am (for alpha) and ^{90}Sr) (for beta) in a designated quality control vial and comparing the input and the output values. The quality of measurement data is directly impacted by the magnitude of the measurement uncertainty associated with it and it this uncertainty was measured to be approximately 6.6%. This value was calculated from the count results using mathematical procedure, i.e., standard deviation (2S).

As it can be seen from Figure 15 the samples which were in the middle of the core and exposed to a high radiation, i.e. 5/2 and 6/2, are the ones with highest amount of leached radioisotopes. These two samples are located at the centre of the core and contribute about 52% of the total activity. When observing the graph there is an initial high release of activity starting to reach a plateau after approximately 21 days. This may be due to the leachate specimen containing many radionuclides that arise from the activation of impurities which were integral with the original graphite components and from other reactor materials which have been activated elsewhere in the core before being carried around the circuit in the coolant gas into the graphite porosity network. So, the activity may have leached out from both the graphite surface and internal porosity surfaces and transported via the complex porosity network.

4.11 Results Beta analysis

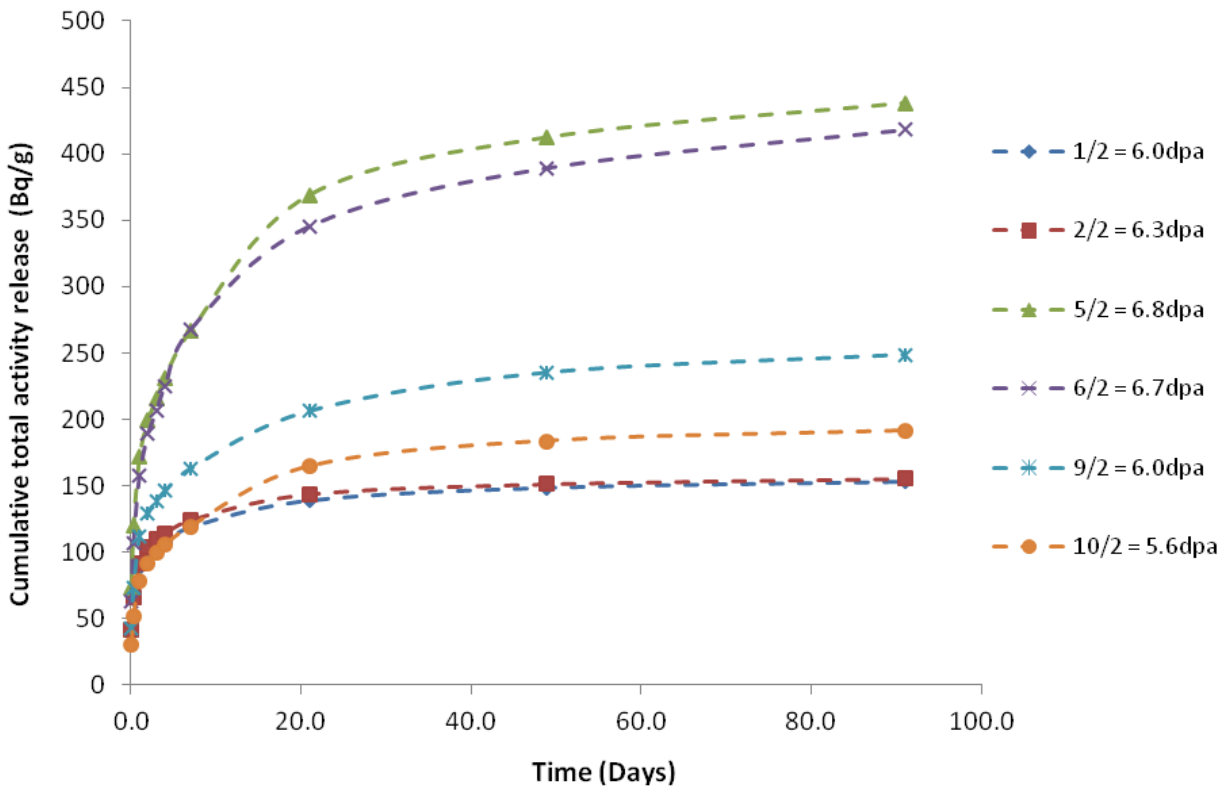


Figure 15 Cumulative total beta activity release measured using liquid scintillation

The total alpha and beta without ^{3}H measurement was achieved by separating the ^{3}H by evaporation. To separate out the ^{3}H from the other isotopes a5 ml volume of sample was extracted from each leachates and then dried at a temperature of 125°C until all the liquid phase evaporated completely. This process eliminates all the ^{3}H leaving only the heavy radionuclides as a solid. These heavy nuclides have higher molecular mass and boiling point than ^{3}H, hence remain inside the vial after the digestion process. 5ml of 0.1 HNO_3 was next added and the resulting solution was mixed with 10ml of scintillation cocktail. Nitric acid is a strong oxidising agent and dissolves the resulting solid particles. If any tritium was left after drying it would have been given off when it reacts with the nitric acid. The ensuing mixture was analysed using a liquid scintillation counter.

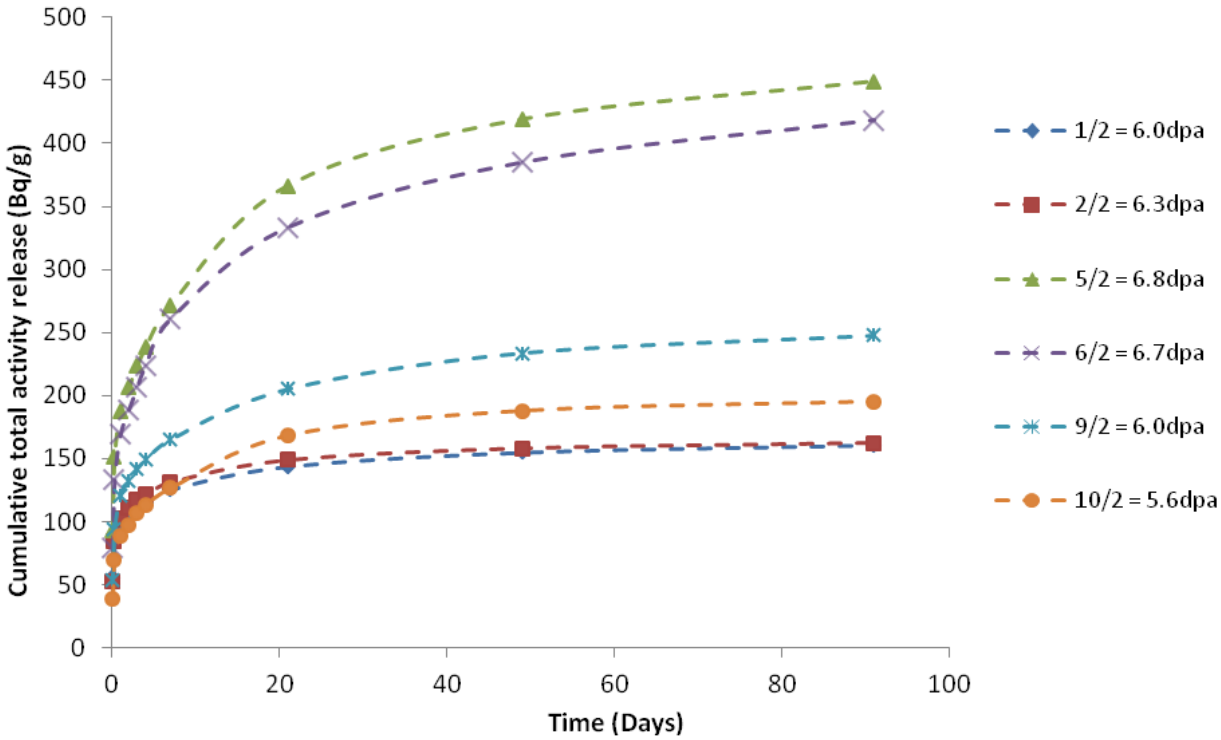


Figure 16 Cumulative total beta without ^{3}H activity release measured using liquid scintillation

The apparatus employs a dry bed absorber system that is designed to separate ^{3}H, ^{14}C and ^{35}S. It uses a series of columns containing either silica gel or soda lime to trap moisture and air from the different species for a specified time. At the end of an experiment the absorbed water is removed from the silica gel column and the ^{3}H content measured by liquid scintillation counting.

For this investigation a simple digestion and distillation technique was used. This method has been chosen because it is inexpensive and easy to perform and the results obtained are fairly accurate. The investigation involves heating 20ml of sample on a hot plate at 60°C for an hour. When digestion of each cycle completed the tritiated water which was distilled off onto the Petri dish cover was collected and transferred to a vial. The process was repeated until 4ml of distillate was collected from each sample. Then, the distillates were mixed with Ultima Gold liquid scintillator for assay. Scintillation cocktail is a mixture of a solvent and a solute and when it

interacts with the emitted radiation from the sample it leads to a count being recorded by the system. Ultima Gold had been chosen because it has an excellent sample holding capacity and it is an ideal choice for aqueous samples. Duplicate samples containing a known amount of tritium standard were processed parallel with the samples and analysed in order to correct any reduction in counting efficiency due to the effect of quenching substances. Quenching occurs when the energy emitted by the radioisotope is not collected completely by the photomultiplier tube of the counting instrument.

The limit of detection is based upon the measurements of replicate blank samples with the activity calculated using the Currie law (Currie 1968) [39]. The MDA (Minimum Detectable Activity) value, as defined in the equation below, determines a lower limit for the detected net activity which corresponds to a specific activity concentration for the sample being analysed. The Currie equation provides a generalised estimate of the MDA which is proportional to the standard deviation of the background counts σ_{bkgrd} at a specific Volume of Interest and 2.71 and 4.65 are constants

$$MDA = 2.71 + 4.65\ \sigma_{bkgrd}$$

$$MDA = \left(\frac{\left(\frac{2.71 + \left(4.65\sqrt{(\text{Blank Average X Count time of Blank})}\right)}{\textit{Count time} \text{ X } 60} \right)}{\textit{Efficiency}} \right) \text{X} \left(\frac{1}{\text{Volume of QC/ Sample}} \right)$$

The cumulative total release of ^{3}H from the irradiated graphite samples is shown in Figure 17. It can be observed that the rate of leaching of ^{3}H increase as the time of leaching increases and starts to plateau after about 7 days. Samples with highest amount of leached radioisotopes are the ones which were trepanned from the middle of the core. The initial rise may possibly indicate the leaching of the contaminant is from the surface of the graphite. The background activity level of ^{3}H in the laboratory was below found to be detection limits (minimum detectable activity is 0.2 Bq.)

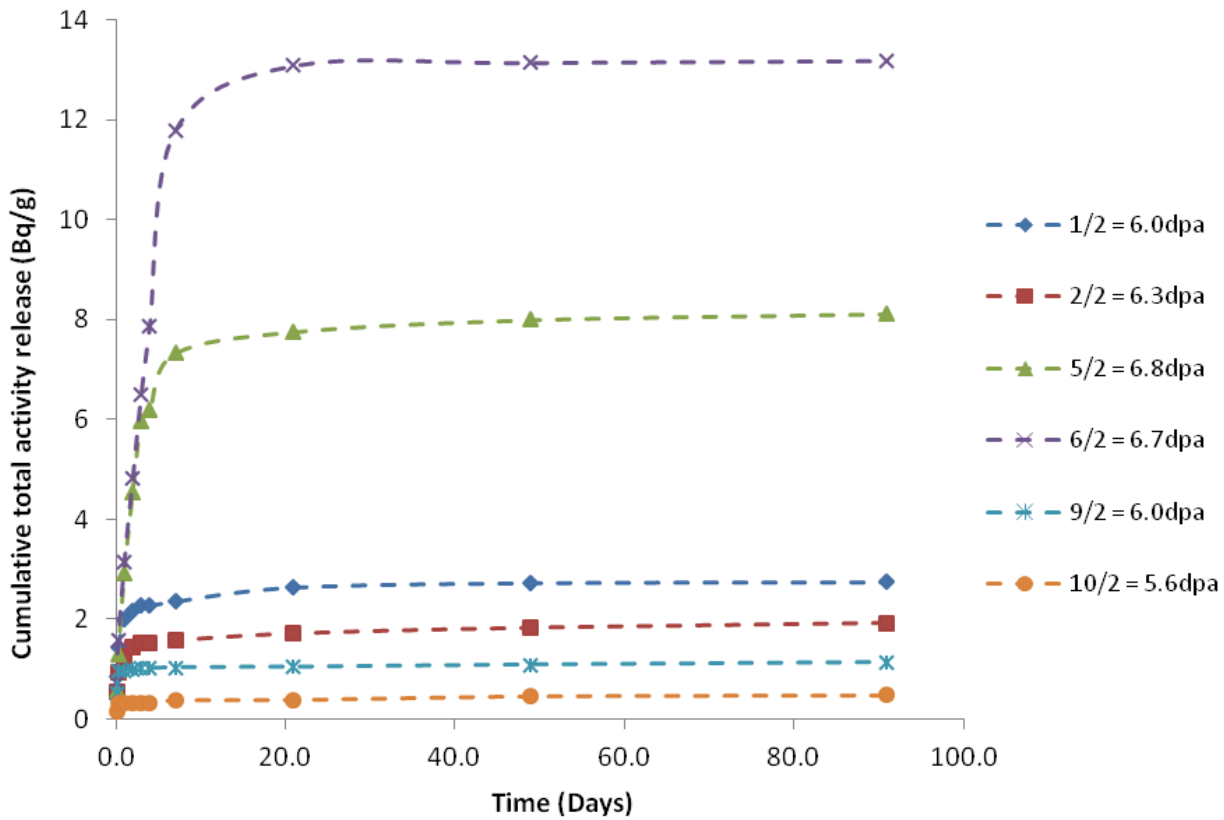


Figure 17 ^{3}H activity release measured using liquid scintillation

Radiochemical separation method was used to determine the ^{14}C inventory data. The separation method used is based on an oxidation technique where carbon is trapped by NaOH. NaOH is highly reactive and forms sodium carbonate when it absorbs the carbon dioxide released. Sodium carbonate is unstable because it is water soluble. Therefore, carbon dioxide trapped in this way needs further treatment. Hence, the resulting sodium carbonate should react with an alkali earth chloride (Calcium, Strontium and Barium) to precipitate out the carbonate. The alkali earth carbonates are stable towards oxidation and heat and insoluble in pure water. The sensitivity of this method is considered sufficient to achieve the required thresholds for the radiological characterisation of the radioactive materials in this study [40].

30ml of deionised water was added onto a round bottom flask and 5g of potassium persulphate added on to it. A citric acid was added to this effluent to act as a ^{14}C carrier. A volume of 5 ml of aliquot was taken from each leachate and added to the

solution, followed by 5ml of 10% silver nitrate. Then, the solution was oxidised for about an hour. Potassium persulphate and silver nitrate catalysts were add to accelerate the reaction. Concentrated sulphuric acid was added to initiate the reaction and the resulting solution was approximately 1M in Sulphuric acid. The solution was heated under reflux to initiate oxidation and liberate carbon dioxide. The released carbon dioxide was trapped in sodium hydroxide. The redox reaction of the process is described by;

$$C_6H_8O_7(aq) + CH_2O(aq) \rightarrow 7CO_2(g) + 4H_2(g) + H_2O(\ell)$$

$$CO_2(g) + 2NaOH \rightarrow Na_2CO_3 + H_2O(\ell)$$

$$Na_2CO_3(aq) + BaCl_2(aq) \rightarrow BaCO_3(aq) + 2NaCl(aq)$$

The carbonate produced precipitated out by adding barium chloride into the solution.

After washing and drying, the precipitate was weighed to calculate the recovery. A mass of 1g ± 20%was measured and was suspended in Insta-Gel scintillation cocktail for counting for ^{14}C beta emission using a Liquid Scintillation Counter. Insta-Gel Plus (1,2,4-Trimethylbenzene) is nearly water-insoluble hydrocarbon liquid based cocktail. It is superior in the incorporation of water and aqueous soluble samples and organic samples due to its resistance to colour quenching and formation of a stable gel. It has very high sample holding capacity and ideal for counting large volumes of water and suspended solids. A blank system and quality control samples were also run in parallel to the system containing graphite to calculate errors on the system and preparation and to determine the accuracy of the method respectively. Any errors from the activity analysis were adjusted by subtracting the blank and background measurements from each leachant activity measurement. The efficiency was calculated by placing a known amount of activity ^{14}C. The quality of measurement is directly related to the measurement uncertainty associated with it and it was measured to be between about 1 - 7%.This value was calculated from the count results using a mathematical procedure, i.e., standard deviation (2S).

The quantities of C-14 obtained in the experiments are shown in figure 18. The background levels of the blank and the laboratory was below detection limits (Minimum detectable activity is 0.2 Bq). The MDA is based upon measurements of replicate blank samples and was calculated based on the Currie law, which was modified as shown below to determine the MDA of ^{14}C analysis, an equation which includes all the parameters used in processing and analysing the samples.

$$MDA = \left(\frac{\left(\frac{2.71 + \left(4.65\sqrt{(\text{Blank Average X Count time of Blank})}\right)}{\textit{Count time} \text{ X } 60} \right)}{\textit{Efficiency}} \right) \text{X} \left(\frac{1}{\text{Recovery}} \right) \text{X} \left(\frac{\text{Mass of ppt produced}}{\text{Mass taken for LSC}} \right) \text{x} \left(\frac{1}{\text{Volume of QC/ Sample}} \right)$$

Over the 91days of the experiment about 106.26 ± 7.01 Bq (in sample size of 50 ml) of ^{14}C was cumulative activity was released from ^{14}C containing carbon dioxide and was captured using a 0.1M sodium hydroxide dreschel bottle from the most active sample. The highest amounts of radioisotope are leached from the samples which were trepanned from the middle brick (i.e. 5/2 and 6/2) inside the core and which were exposed to highest radiation. It can be seen from figure 18 the rate of leaching of ^{14}C increase as the time of leaching increases and plateaus after about 21 days. The leaching period for ^{14}C (21 days) is different from ^{3}H (7 days). ^{3}H which was absorbed at the pore surfaces will be released when in contact with hydrogenous molecules in the leachant. Since it is bound to the surface it leaches out more quickly than ^{14}C radionuclide.

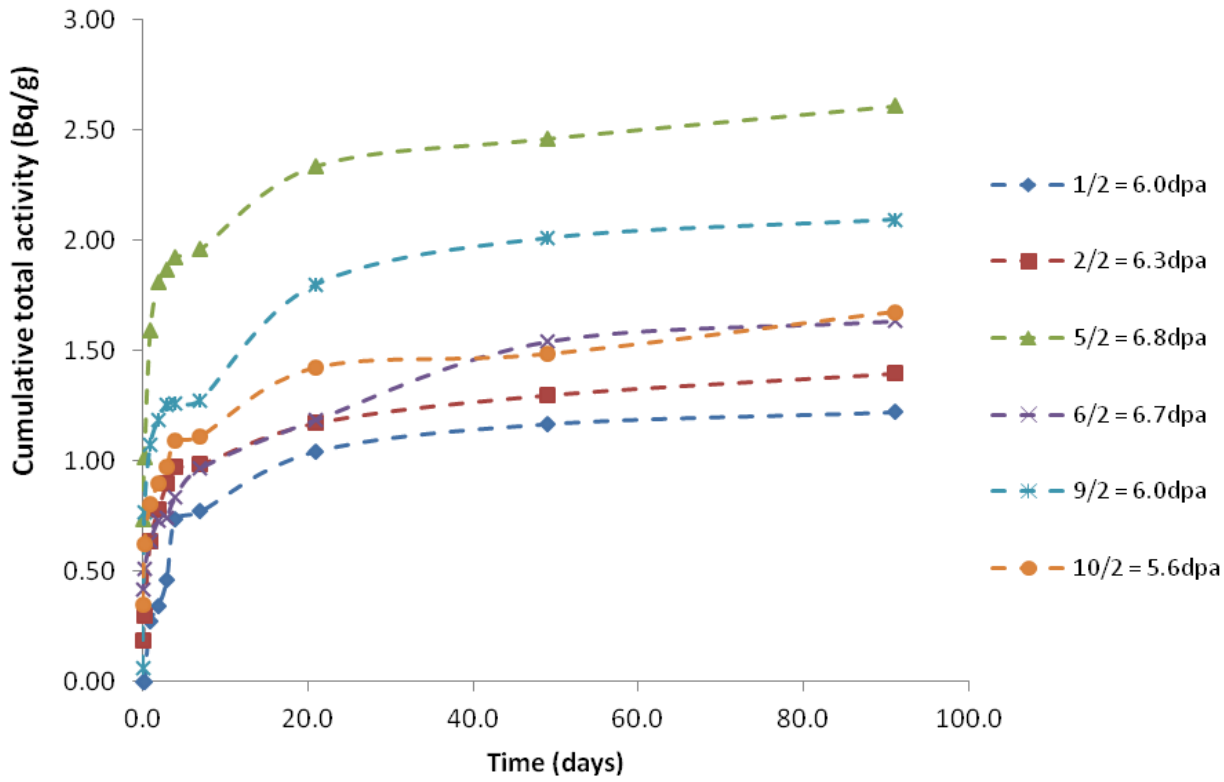


Figure 18 Cumulative total ^{14}C activity release measured using Liquid Scintillation

4.12 Results Gamma Spectroscopy

The cumulative total activity release (sum of activities of each period) of each these species detected is shown in Figures 19 - 24. The release of these activities from each sample was shown to be varied and in general samples which were exposed to a high radiation flux, i.e. located at mid-channel height, show the highest abundance of leached radioisotopes, with over 72% of the total accounted activity.

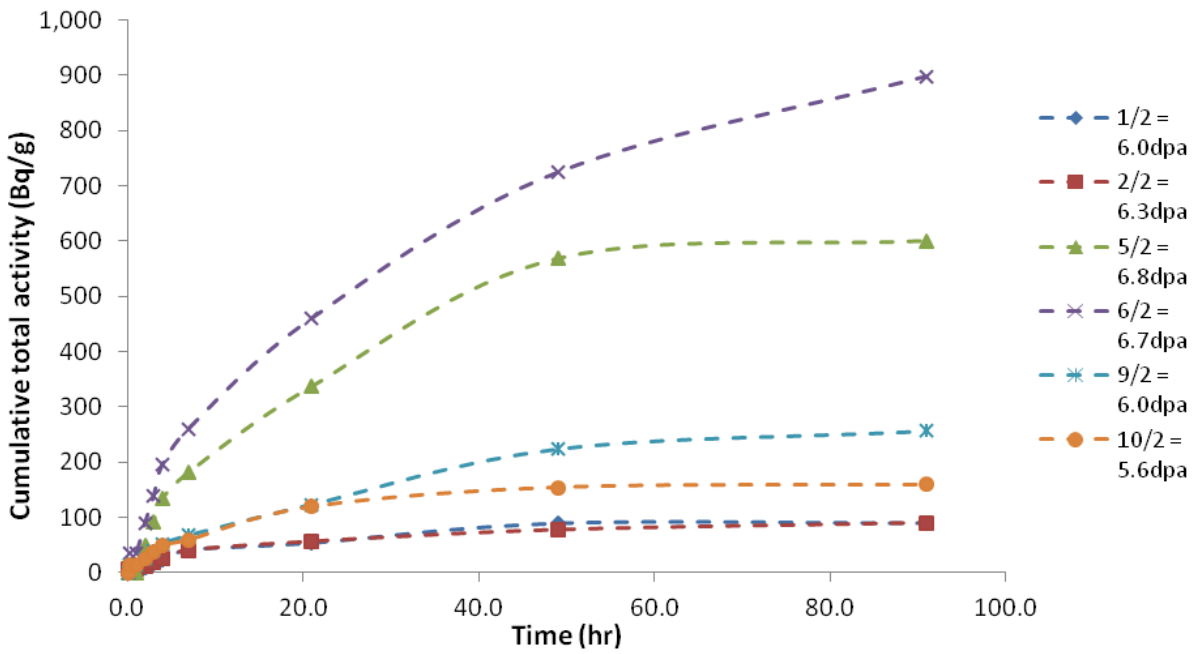


Figure 19 Cumulative total activity release of ^{60}Co measured using gamma spectroscopy

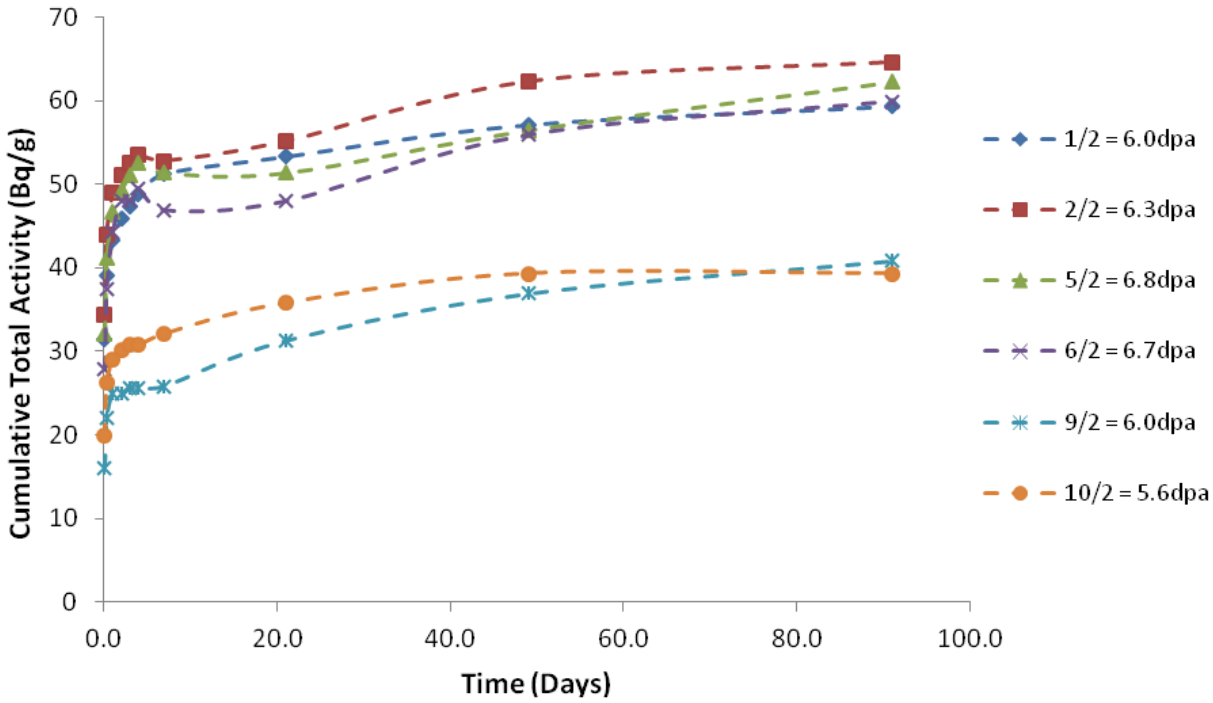


Figure 20 Cumulative total activity release of ^{134}Cs measured using gamma spectroscopy

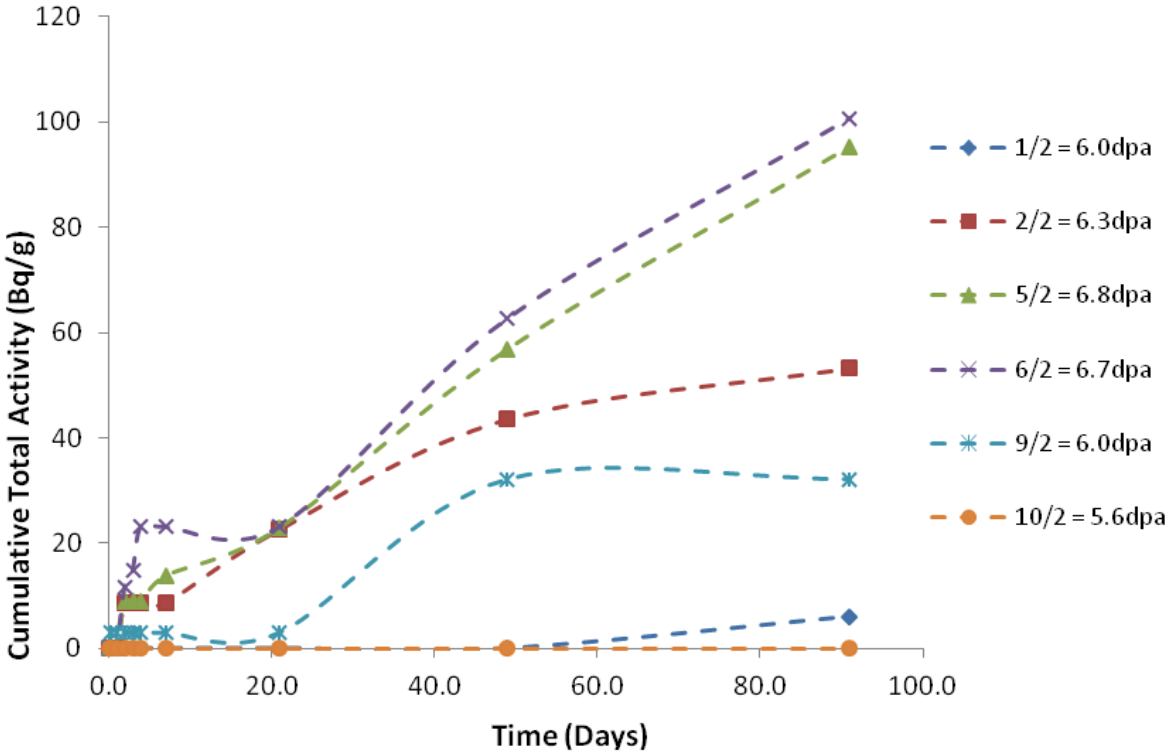


Figure 21 Cumulative total activity release of ^{133}Ba measured using gamma spectroscopy

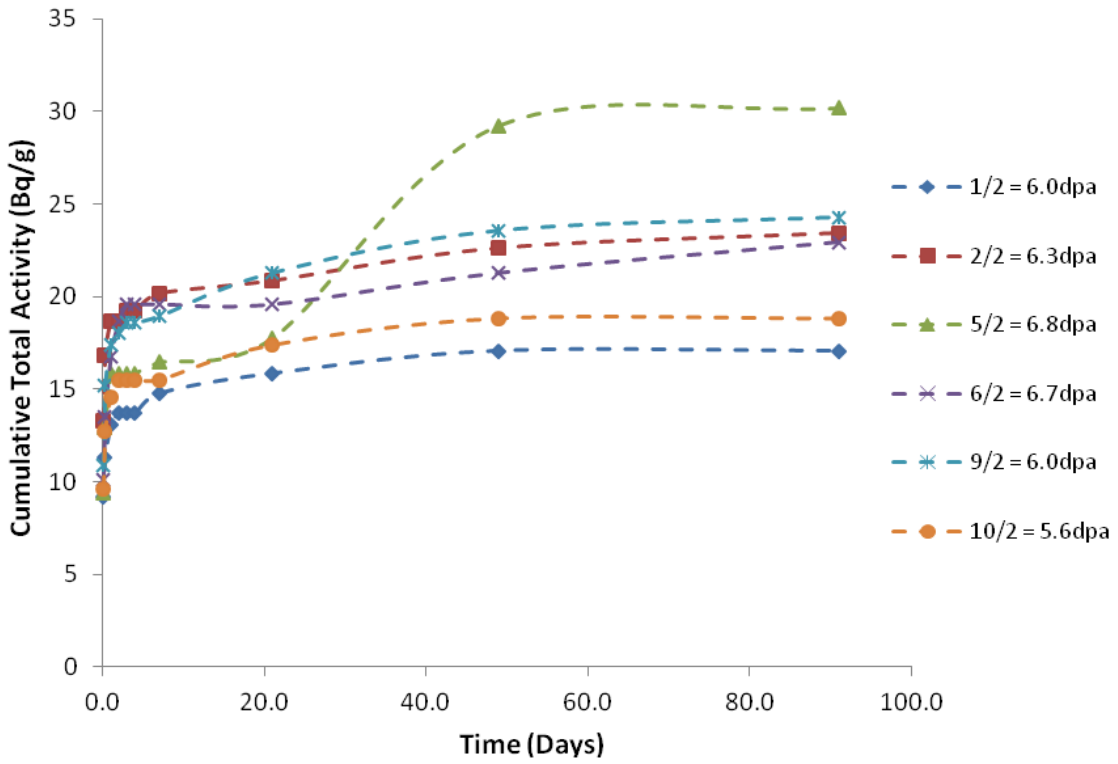


Figure 22 Cumulative total activity release of ^{137}Cs measured using gamma spectroscopy

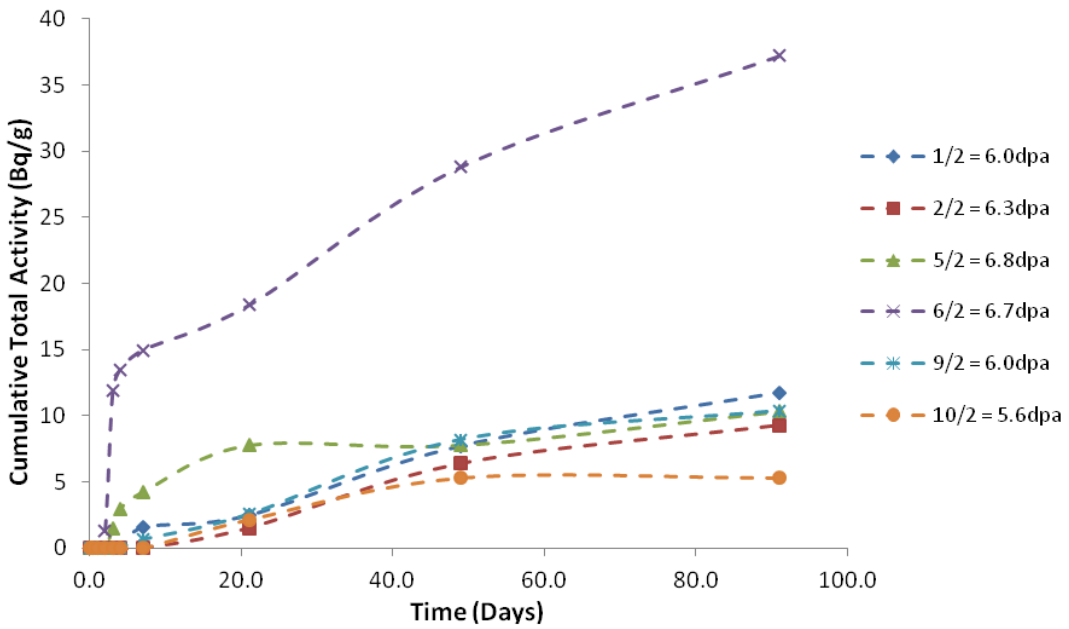


Figure 23 Cumulative total activity release of ^{155}Eu measured using gamma spectroscopy

5 Summary

The aim of this report was to capture and separate baseline experiments carried out as part of work package 4 chemical treatment experiments that where applicable to work package 6 leaching. This transfer of experimental data was also carried out within D-6.1.6.

Standard/baseline experiments have proven in this case highly valuable and transferable, resulting in collaborations between work packages.

5.1 Publications resulting from this work:

- L. McDermott, G. Black, A. N. Jones, A Wickham, B J. Marsden. "Characterisation and Chemical treatment of PGA graphite waste from Wylfa". *CARBON2012, Krakow, Poland June 2012*
- L. McDermott, A. N. Jones, B J. Marsden. "^{3}H and ^{14}C Release in UK Nuclear Graphite by Chemical Treatment". *Modelling and Measuring Reactor Core Graphite Properties and Performance, Birmingham. 31 October – 3 November 2011*
- G. Black, L. McDermott, A. N. Jones, B J. Marsden. "Development of an experimental and simulation process to determine the end of life radionuclide inventory of UK irradiated graphite waste". *Modelling and Measuring Reactor Core Graphite Properties and Performance, Birmingham. 31 October – 3 November 2011*
- G. Black, Dr. A. N. Jones, L. McDermott, Prof. B. J. Marsden. "Modelling the Production of Tritium, Carbon-14 and Cobalt-60 in Irradiated Graphite from a UK Magnox Reactor". *MRS, Argentina, 3-7 October 2011*
- A.N. Jones, L. McDermott, B.J. Marsden, T.J. Marrow, and A.J. Wickham. "Characterisation of Irradiated Graphite Waste in Reactor Decommissioning". *Carbon 2009, Biarritz, France, 14 - 19 June, 2009*
- McDermott L, Jones A N, Marsden B J, Marrow T J. "Characterisation of Irradiated Nuclear Graphite Waste". *Securing the Safe Performance of Graphite Reactor Cores, Nottingham. November 2008*

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