THERMAL TREATMENT OF OLDBURY MAGNOX REACTOR IRRADIATED GRAPHITE

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Abstract

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THERMAL TREATMENT OF OLDBURY MAGNOX REACTOR IRRADIATED GRAPHITE

Approximately 96,000 tonnes of the UK Higher Activity Waste (HAW) inventory consists of irradiated nuclear graphite. The current Nuclear Decommissioning Authority (NDA) baseline strategy for irradiated graphite in England and Wales is isolation in a future Geological Disposal Facility, with Scottish policy endorsing an alternative decision of near surface long-term storage. Irradiated graphite disposal routes in the UK remain under review, however, as there are concerns surrounding timing and whether deep geological disposal is the most appropriate course of action for graphite. An alternative waste management solution is treatment prior to disposal to separate mobile radioactive isotopes such as $^3$H and $^{14}$C from the bulk material, allowing for HAW volume reduction and concentration.

Optimisation of an existing thermal treatment process at the Nuclear Graphite Research Group (NGRG) of the University of Manchester has been effected and a detailed review of the uncertainties associated with quantitative determination of radioisotope releases during thermal treatment of irradiated graphite samples has been conducted. Thermal treatment experiments in both an inert atmosphere and 1% oxygen in argon atmosphere have been conducted for temperatures ranging from 600°C to 800°C, and durations from 4 to 120 hours, to determine the effects of oxidation time and temperature, and the consequent oxidation characteristics on the release rate of prominent radioisotopes, with a focus on the release of $^{14}$C. Lower temperature treatments in an oxidising atmosphere have shown that a preferential release of $^{14}$C-enriched graphite can be achieved from the bulk material of Oldbury Magnox reactor irradiated graphite, with evidence demonstrating that this liberated $^{14}$C-enriched region is located at the graphite surfaces throughout the porous structure. A large proportion of radiocarbon found in this irradiated graphite, however, is uniformly distributed throughout the bulk material and cannot be selectively oxidised. It is found that prominent metallic radioisotopes such as $^{60}$Co are not mobile at these temperatures and remain in the bulk graphite material, inclusive of radioactive caesium which the literature suggests will volatilise.

The preliminary results were undertaken as part of the EU FP7 EURATOM Project: CARBOWASTE, and this studentship has been funded by the Engineering and Physical Sciences Research Council (EPSRC).
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Thesis Structure

This Section provides an outline for the overall format of this thesis. The respective major parts of the thesis can be seen below with a summary statement as to what can be found in each.

1. Introduction:

The introduction gives a broad overview of the context for this work, establishing the global environment in which this programme of research has been conducted and motivations for thermal treatment.

2. Literature Review:

The literature review encompasses analysis of literature surrounding all fields and factors that might significantly affect the thermal treatment of irradiated graphite waste, from the introduction of impurities during the manufacturing process of graphite to production of radioactivity in graphite, thermal oxidation processes and the current worldwide experience with thermal treatment of irradiated graphite waste. The research statement is also included in this Section 2, defining the aims and objectives derived from analysis of the literature.

3. Experimental Methodology:

The third Section begins with the provenance of the irradiated graphite samples utilised for this programme of research, followed by a detailed description of the thermal treatment process and of each characterisation technique used with detailed discussion as to the respective benefits or limitations to the application of these processes and techniques to irradiated graphite material. The final part of the methodology section focuses on data validation, identifying sources of uncertainty in the thermal treatment process and, where possible, quantifying these, to emphasise confidence in the data collected.
4. Results and Discussion: The Effects of Oxygen on Radioisotope Release

The first results section discusses thermal treatment results taken in collaboration at the beginning of this programme of research, which yield a baseline set of data for \(^3\)H and \(^{14}\)C release characteristics from irradiated graphite in an oxidising environment at 700 and 800°C, from which the following experiments are justified.

5. Results and Discussion: The Effects of Time and Temperature

The second chapter of results explore the effects of time and temperature on the release behaviour of \(^{14}\)C from irradiated graphite samples in 1% oxygen, allowing conclusions to be drawn as to their influence by varying the temperature between 600 and 700°C and the treatment duration from 4 to 32 hours.

6. Results and Discussion: The Carbon-14 Release Profile

The next chapter of results investigates the release profile of \(^{14}\)C from a single sample using multiple low temperature treatments at 600°C, from untreated to sample destruction over an accumulated 120 hours of treatment.

7. Results and Discussion: Effects of Thermal Treatment on Tritium and Metallic Radioisotopes

The effects of thermal treatment on all of the remaining prominent radioisotopes such as \(^3\)H and \(^{60}\)Co are explored in this results chapter.

8. Conclusions and Future Work

The major conclusions drawn over this programme of research are highlighted in this Section, along with the future avenues of scientific research that could be explored to either compliment or develop from this programme of experimental research are given in this Section.
1. Introduction

Humankind in the developed world is largely dependent, even if it is often indirectly, on a steady and plentiful electricity supply to provide even the most basic of comforts such as food, heat or light. Traditionally, vast amounts of fossil fuels have been burned, generating heat to boil water, the steam from which turns a turbine and generator, producing electricity. It is becoming noticeably more evident in the scientific community, media and government policy making decisions, however, that this is not a long term solution to the global energy demands, as there is only a finite quantity of this carbonaceous fuel source remaining in the planet’s shrinking natural reserves, coupled with rapidly accelerating global energy demands. Some sources suggest that world oil reserves could be fully depleted over a timescale of the order tens of years\cite{1}. Continued consumption of fossil fuels could also enhance the risk of serious environmental damage by global warming, as a consequence of CO\textsubscript{2} emissions into the atmosphere.

Alternative ‘renewable’ methods of energy production are available, such as harnessing the power of the wind, the sun or the waves, though in today’s energy climate these sources of energy are often unreliably inconsistent, such as wind power, under-invested, expensive to implement, or immature in development, such as tidal energy. Renewable energy methods have a valuable role to play in contributing to the energy mix, though either the modern day levels and consistency of energy consumption must be curbed or the limitations of most renewable energy systems must be understood and accounted for using another energy source capable of providing a consistent baseline to the national grid.

In the first half of the 20\textsuperscript{th} Century a new technology emerged, nuclear power, which has been under development ever since. This technology relies on the chain fission reaction of a suitable high energy density fuel, such as uranium, which similarly to a conventional power station transmits heat energy via heat exchangers to boil water and power turbines. The first man-made reactor to achieve criticality was Chicago Pile 1 in December 1942, since which hundreds of reactor units of various design have been built worldwide. In the UK, there are currently 15 remaining operational reactors\cite{2} of 48 ever constructed including the major test reactors, all of which are graphite-moderated except for one single water-moderated pressurised water reactor (PWR); graphite-moderation was favoured because the capacity for nuclear fuel enrichment in the UK, required to overcome
the neutron absorption properties of water as a moderating material, was not available for civil application at the time\textsuperscript{[3]}. 

Nuclear power is not without its opposition, limitations and disadvantages, a prominent one of which is the issue of nuclear waste; radioactive waste is produced in many forms during a reactor lifetime, through neutron activation and contamination of components such as the containment vessel, control rods, structural steels, or in the case of most UK reactors, the graphite core. Some feel that, in past years, the nuclear waste issue has not been considered with due care, since for a number of decades there was little deliberation towards a long-term solution for the nuclear waste produced, 

“In the decades up to the 1970s no serious thought was given, in the design of either military or civilian facilities, either to decommissioning or to the management of the more highly radioactive wastes that the nuclear enterprise produced.”\textsuperscript{[4]} – Professor Gordon MacKerron

A relatively unique issue for graphite-moderated reactors is the mass-production of carbon-14, a weak beta-emitter with a half-life of \textasciitilde5730 years, and the second most dominant radioisotope found in irradiated graphite behind the relatively short-lived tritium inventory. Carbon-14 is under such scrutiny for a number of reasons:

- Carbon is present in all known life forms, making up approximately 18.5% of a human body\textsuperscript{[5]}. This indicates that the mobility of carbon is high and all organic life forms are susceptible to the intake of radioactive carbon
- Carbon has a low toxicity to humans and so remains in the body for a not insignificant length of time; the biological half-life of carbon-14 is estimated to be 12-40 days, depending on its chemical species\textsuperscript{[6]}
- Carbon-14 has a half-life in the order of thousands of years, meaning that graphite waste management is a long-term issue, in the order of tens of thousands of years; a responsible disposal solution must be found for this isotope because it will take a long time, spanning many generations, to decay to a safe background level

The UK houses more irradiated graphite waste than any other nation on Earth, with an accumulation of approximately 96,000 tonnes\textsuperscript{[7]}, and as of yet there is no confirmed disposal route; plans for a deep geological disposal facility (GDF) have been proposed for all types of intermediate- and high-level radioactive waste in England and Wales, though
finding a suitable site for such a facility is proving to be difficult, largely for socio-political reasons. As a consequence, organisations and universities worldwide are researching alternative means of graphite disposal, such as incineration, as well as treatment of the waste for volume reduction and disposal in currently available sub- or near-surface disposal facilities.

This programme of experimental research aims to investigate factors affecting the thermal treatment of irradiated graphite waste, notably time, temperature and oxygen availability, with the intention of releasing radioisotopes from the bulk material into the gas phase for subsequent capture, whilst also limiting damage to the graphitic structure in a bid to maintain some degree of structural integrity for ease of handling. The use of graphite in the nuclear industry, production of radioactivity within it and exploitation of the thermal oxidation phenomenon for radioisotope removal shall all be described in detail over the course of the literature review portion of this doctoral thesis, followed by detailed analysis of the experimental procedures and results obtained appropriate to thermal treatment of UK irradiated graphite waste.
1.1 Graphite: The Material

Carbon is the fourth most abundant element in the universe\[^8\] of which graphite is the most thermodynamically stable allotrope, even more so than diamond\[^9\]. Hexagonal graphite is composed of arrangements of hexagonal ‘honeycomb’ structure carbon basal planes, or graphene sheets, which layer parallel to each other, as seen in Figure 1, in a formation describable as an alternating ‘ABAB’ structure. The theoretical crystal density, and thus maximum density of perfectly formed graphite neglecting porosity and stacking faults, is 2.266 g/cm\(^3\). The existence of a less common rhombohedral phase graphite should also be acknowledged, in which the stacking follows an ‘ABCABC’ structure\[^9\]. Any natural occurrence of this rhombohedral phase is transformed into hexagonal graphite during graphitisation at high temperatures of the order 3000\(^\circ\)C\[^10\].

![Figure 1: The Carbon Planes Structure of Graphite\[^9\]](image)

Using a conventional Cartesian coordinate system, the planar dimensions along a given graphene layer, equivalent to ‘x’ and ‘y’, are referred to as the ‘a-b’ plane, whereas the dimension through the basal planes is denoted the ‘c’ direction, as seen in Figure 1. Each carbon atom in the ‘a-b’ plane is strongly covalently bonded to three other carbon atoms in the plane, though the planes themselves are only weakly bonded to each other in
the ‘c’ direction, by van der Waals forces. One consequence of this structure is that graphite is used as an industrial lubricant and in pencils, as the basal planes will relatively easily slide over each other. Bulk graphite has anisotropic properties, the extent of which depends on the precise ingredients and manufacturing process leading to alignment of graphite crystallite; by altering the manufacturing conditions and raw materials, near-isotropic material properties of the bulk material can be achieved. It is found that for a graphite crystallite, the structure is electrically conductive along the ‘a-b’ plane, along the graphene layers, and electrically resistant across planes, in the ‘c’ direction. This anisotropic behaviour also applies to a number of other properties, such as thermal conductivity, coefficient of thermal expansion and Young’s modulus. Aside from when the crystal structure becomes damaged, the separation distance between the basal planes should remain largely constant at approximately 3.35Å\textsuperscript{[11]}, as this is the thermodynamically stable energy state. Factors such as neutron irradiation damage or improper manufacture can cause buckling and damage of these planes.

On a larger lengthscale, there are other factors which affect graphite material properties, such as the porosity or the type of filler particles used during manufacture. Porosity is often given as a percentage of the bulk material volume. There are two distinct types of pores in graphite, known as ‘open’ and ‘closed’. Open pores are those which have surfaces exposed to the local environment external to the material, defined as being accessible to gas and often measured using helium pycnometry which relies on helium penetration into the open porosity. This can include surfaces deep within the material connected via a series of open pores. Closed pores, otherwise known as ‘isolated pores’, are those that are independent of the external environment, such that air or vacuum cannot penetrate into or out of them. These are effectively similar to a bubble in the material. This distinction is relevant to the material oxidation behaviour both for treatment and reactor operation because any oxidant, such as the carbon dioxide coolant in a Magnox reactor, will pass through the material via the open pores, and will not be able to penetrate the closed pores. The porosity of graphite is strongly dependent on the manufacturing process. For unirradiated Pile Grade A (PGA) graphite, used widely throughout the UK Magnox reactor fleet and the graphite grade of interest for this research, a typical value might be ~20% porosity by volume, which is inclusive of the order ~10% closed porosity\textsuperscript{[11]}, though these fractions are known to vary considerably between graphite grades and samples.
1.2 Neutron Moderators

Graphite has been used extensively in the UK nuclear industry, most frequently for its neutron moderation and reflection properties. Moderation is necessary to maintain a chain fission reaction in thermal nuclear reactors, since this is the process by which the neutrons emitted from the fission process are slowed, by a series of collisions with moderator material atoms, to reduce their kinetic energy and increase the likelihood of further fission in the fuel. Upon emission from a fuel atom, neutrons have considerable kinetic energy, and so it is necessary to moderate them, by physical intervention of a moderator material, from fast neutrons (~1 MeV or more) towards the energy of thermal neutrons (~0.025 eV). The majority of fissionable fuels have a higher reaction cross section or probability of reaction for slower neutrons in the thermal energy range, and, excluding regions of ‘resonance’, poorer reaction cross section for higher energy neutrons. This is shown in Figure 2, which represents the neutron reaction cross section for uranium-235, a common nuclear fuel.

![U-235 Fission Cross Section](image)

*Figure 2: $^{235}\text{U} \text{ Neutron Absorption Cross Section with Neutron Energy}^{[12]}$, adapted by the author*

As with most engineering applications, the specific material to be used is often a compromise between advantageous and disadvantageous material characteristics or
properties, selecting the one which best satisfies the design brief. Graphite is not an exception to this, since it is an excellent moderator material in some respects, though is not without limitations.

The properties deemed desirable in any candidate moderator material include:

- Small atomic number (A)
- High density (ρ)
- Low cost, or good availability
- Large scattering cross section (σ_s)
- Small absorption cross section (σ_a)

Candidate reactor moderator materials can be seen below in Table 1, for comparative purposes:

Table 1: Candidate Moderator Material Properties. Cross sections are given for incident neutrons of thermal energy 0.025 eV

<table>
<thead>
<tr>
<th>Material</th>
<th>Atomic Weight, A</th>
<th>Scattering Cross Section, σ_s (b)(^{[13]})</th>
<th>Absorption Cross Section, σ_a (mb)(^{[13]})</th>
<th>Density, ρ (g/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen (water)</td>
<td>1</td>
<td>82.0</td>
<td>333</td>
<td>1</td>
</tr>
<tr>
<td>Deuterium (heavy water)</td>
<td>2</td>
<td>7.64</td>
<td>0.519</td>
<td>1.107</td>
</tr>
<tr>
<td>Beryllium</td>
<td>9</td>
<td>7.63</td>
<td>7.6</td>
<td>1.84</td>
</tr>
<tr>
<td>Carbon (graphite)</td>
<td>12</td>
<td>5.55</td>
<td>3.5</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Atomic Weight, A: When a neutron collides with an atom of a moderator material such as graphite, it can transfer some of its energy to that atom by scattering, much like the simplistic model of two billiard balls interacting. The precise amount of energy transferred is dependent on the angle of deflection, if any, and the atomic number of the recipient atom. The maximum fractional energy transferrable by an incident neutron to a target nucleus of atomic number A\(^{[14]}\) is,

\[
E_{\text{max}} = \frac{4A}{(A + 1)^2}
\]  

(1)

It is apparent from Equation (1), that any target material composed of lower atomic number atoms will be a more efficient moderator material, since the energy transferrable per collision is greater. For our candidate moderator materials, the most efficient is hydrogen, as found in light water, which yields a maximum fractional energy transfer of 1,
indicating that theoretically all of the neutron energy can be lost into the hydrogen atom in a single collision. This is comparable to a relatively poor maximum transfer fraction of just 0.284 for carbon, the dominant element in graphite, requiring more collisions to slow the neutrons to the thermal energy range than water.

Density, \( \rho \): As would be expected, a denser material will have more atoms per unit volume, meaning there is an increased chance of neutron interaction with one of its atoms; a greater density material is therefore desirable as a moderator material. The average density of unirradiated synthetic graphite is almost double that of water, which compensates somewhat for the previously established disadvantage of a higher atomic number.

Cost and Availability: The cost of a material and its availability are often directly related. These factors cannot be disregarded as insignificant as they could constitute an appreciable fraction of a reactor’s construction costs. Nuclear graphite can be manufactured from products obtained in the fractional distillation of crude oil, amongst other precursor materials such as the naturally occurring asphalt Gilsonite, which for the coming years at least are readily available, though the manufacture of nuclear grade graphite is lengthy and expensive. Some other materials such as the highly toxic beryllium or Canadian CANDU-design reactor favoured heavy water are also very expensive to produce. ‘Normal’ light water is both cheap and abundantly available, making it the ideal candidate in this category.

Absorption Cross Section, \( \sigma_a \): The neutron absorption cross section of a material, often represented in units of barns (b), equivalent to \( 10^{-28} \) m\(^2\), reflects the likelihood of absorption of a neutron into the incident atom’s nucleus. A high neutron absorption cross section is undesirable in a fission reactor, except in the fuel, control rods and shielding material. The control rods are designed with this property in mind, as their role is to balance the neutronics of the reactor by absorbing neutrons and preventing uncontrollable escalation of the chain-reaction. Similarly, any moderator material with a high absorption cross section will absorb a proportionately large number of neutrons, making a critical chain-reaction difficult to achieve and maintain, and so this property should be considered
with care. Table 1 indicates that water has a much higher neutron absorption cross section than the other materials, with a value almost 100 times larger than the absorption cross section of graphite.

Scattering Cross Section, $\sigma_s$: When a neutron interacts with an atom, one of the possible outcomes is that the neutron will ‘bounce off’ in a different direction. The effectiveness of a material to scatter neutrons in this fashion is determined by its scattering cross section, or likelihood of scatter, and is also represented in units of barns. A high scattering cross section is a desirable property in a moderator material, since a larger amount of scatter suggests a larger number of neutron interactions without absorption occurring, and thus more efficient moderation of the neutrons. Some of the neutrons can be ‘scattered’ back towards the core of the reactor, making a high scattering cross section material a suitable neutron reflector material as well. The scattering cross section of graphite is approximately 5.55 b, whereas the cross section for water is considerable compared to the other moderator material candidates, at 82 b. This property of water is somewhat negated by its undesirable neutron absorption behaviour.

1.3 Graphite as a UK Moderator Material

Following a brief review of the candidate materials and further inspection of Table 1, a definitive conclusion cannot be drawn as to the ideal moderator material. Water is inexpensive yet absorbs a large number of neutrons, heavy water is expensive to produce, beryllium is expensive, highly toxic and difficult to manufacture, and graphite is expensive to manufacture and less efficient at moderating neutrons than other candidates. It comes as no surprise then that there are a variety of designs of water-, heavy water- and graphite-moderated nuclear reactors in current operation around the world.

Globally, water cooled and moderated reactors have largely been favoured, in the form of Boiling Water Reactors (BWRs) and Pressurised Water Reactors (PWRs). A large contributor towards the decision to use graphite as a moderator material for UK reactors was the influence of the moderator neutron absorption cross section property. Historically, the United Kingdom was unable to enrich uranium fuel, which is required to overcome the high neutron absorption cross section of water, and sourcing enriched uranium from overseas was difficult for political reasons\textsuperscript{15}. Consequently, the natural uranium-fuelled,
carbon-dioxide gas-cooled, graphite-moderated Magnox design reactor, a schematic of which can be seen in Figure 3, became the UK’s first fleet of commercial reactors, which with some adaptation was a basic design configuration continued into the UK’s second fleet of power producing Advanced Gas-cooled Reactors (AGRs). Of the UK’s 41 power producing reactors constructed, only one is a PWR with the remainder conforming to graphite moderated designs.

A number of further desirable properties for graphite as a moderator material can be identified:

1) Graphite is a reasonably stable and chemically inert material, with strong covalent bonds. It does not melt, and is known to sublime at approximately 3900 K\(^{[16]}\). The moderator material in question must be suitable for a power producing reactor environment, where temperatures can easily exceed 650K, and thus a high phase-transition temperature is desirable.

2) Graphite also has a relatively high thermal conductivity of between approximately 100 and 200 W/mK (pre-irradiation) depending on graphite grade and direction\(^{[11]}\), attributable partly to its planar structure, compared to approximately 0.6 W/mK for water\(^{[17]}\). As a consequence, the risk of hotspots developing in particular regions of the graphite is low, and the heat generated by the nuclear fission process can be efficiently transferred to the coolant.

3) Manufacturers of graphite are able to produce very pure material, which is almost entirely carbon with impurities measurable in the order of parts per million.

4) Graphite can be utilised for more than one function. In a Magnox- or AGR-design reactor it doubles as both a neutron moderator and a structural component of the core. Graphite can also be used elsewhere for components such as reflectors or fuel assemblies, where its high scatter and low absorption cross sections improve the probability of a neutron fission reaction with a fuel atom.
There are two main disadvantages to using graphite in a reactor environment, namely its reactivity with oxygen and the changes in material properties over a reactor lifetime:

1) In contrast to a previous comment as to the chemical stability of graphite, it is known to readily oxidise in the presence of oxygen or the carbon dioxide coolant used in both Magnox and AGR reactors, by thermal oxidation at elevated temperatures and radiolytic oxidation independent of temperature, which leads to loss of material, less effective moderation and structural integrity issues. UK gas-cooled reactors deliberately operate at temperatures below which thermal oxidation becomes significant, and so radiolytic oxidation is the main source of graphite degradation. Thermal oxidation could become a particularly prominent issue in an accident scenario where reactor core temperatures might be considerably higher or the core could be exposed to air\[^{18}\].

2) The material properties of graphite are heavily influenced by the neutron fluence it has received, with almost all of the properties of graphite changing with increasing radiation\[^{19,20}\]. Under neutron irradiation, the Young’s modulus of graphite increases, making it stronger yet more brittle. The coefficient of thermal expansion, the thermal conductivity and the electrical conductivity also change over a reactor’s lifetime, affecting the efficiency of heat energy removal from the fuel and causing internal stresses in the material. Neutron damage causes irradiated induced dimensional changes in graphite, observable on a bulk scale, the consequent internal stresses of which vary with neutron fluence. In anisotropic Pile Grade A (PGA) graphite, as found in Magnox reactors, opposing irradiation induced dimensional changes occur simultaneously, causing internal stresses within the material. Conversely, poorly understood irradiation induced creep processes relieve internal stresses in the graphite. ‘Wigner energy’, or stored potential energy, can build up in neutron irradiated graphite, particularly in low temperature systems or potentially cooler regions of a graphite reactor core. The rapid release of Wigner energy from graphite is responsible for the Windscale Pile reactor fire in 1957, as a release of self-propagating Wigner energy in the form of heat resulted in the nuclear fuel
catching fire. The contribution of all of these factors makes graphite a notoriously difficult material to predict and model.

![Figure 3: A Schematic of a Typical Magnox Reactor Arrangement](image)

The material used for this research is irradiated graphite from an installed set from Oldbury Magnox Reactor 2, as described in more detail in Section 3.1. A typical graphite-moderated Magnox core consists of multiple components, which can be broadly separated into the graphite core, which acts as both a structural material and neutron moderator, control rods, used for absorbing neutrons and controlling the chain reaction, fuel channels, in which natural uranium fuel rods are placed, the charge face at the top of the reactor from which control rods and fuel are manoeuvred into their respective channels of the graphite core, the heat exchanger, for transfer of heat energy away from the CO₂ coolant for steam generation, and the reactor pressure vessel to contain the coolant. Later Magnox reactors also have a pre-stressed concrete pressure vessel surrounding the reactor.

The two Oldbury Magnox reactors differ from the design seen in Figure 3 as their heat exchangers are housed within the pre-stressed concrete pressure vessel\(^{[22]}\). Their cylindrical graphite cores are 12.8 m across and 8.5 m tall, with 25.6 bar pressure of CO₂ coolant circulating upwards through the core and out through the heat exchangers\(^{[22]}\). Mean coolant inlet and outlet temperatures are 245 and 410°C respectively\(^{[22]}\).
1.4 Current Nuclear Graphite Waste in the UK

1.4.1 UK Classification of Radioactive Waste

Before irradiated graphite waste is explored in more detail, the UK radioactive waste classification structure should be clarified. There are different classes of radioactive waste, ranging from High Level Wastes (HLW), through to Intermediate Level Wastes (ILW) and Low Level Wastes (LLW). The term Very Low Level Waste (VLLW), amongst other specific waste related acronyms, is also sometimes used to describe the waste of least concern. The waste classes are defined by UK legislation as follows:\[23\]:

**High Level (or Heat Generating) Waste (HLW):**
- Wastes in which the temperature may rise significantly as a result of their radioactivity, so this factor has to be taken into account in the design of storage or disposal facilities

**Intermediate Level Waste (ILW):**
- Wastes exceeding the upper boundaries for LLW, but which do not require heating to be taken into account in the design of storage or disposal facilities

**Low Level Waste (LLW):**
- Wastes having a radioactive content not exceeding 4 GBq (gigabecquerels) per tonne of alpha, or 12 GBq per tonne of beta/ gamma activity

Radioactive wastes are also subjected to an alternative categorisation by the NDA, in which they can be designated as Higher Activity Waste (HAW) or Lower Activity Waste (LAW). The entire inventory of HLW and ILW are designated HAW, along with a fraction of the higher specific activity LLW, as seen in Figure 4. Irradiated graphite waste mostly conforms to the HAW classification.
These classifications have consequences for each specific waste streams designated disposal route, as shall be seen.

1.4.2 UK Total Graphite Waste

The Nuclear Decommissioning Authority (NDA) routinely commissions the compilation of a UK radioactive waste inventory every approximately 3 years, in which all of the significant UK sources of radioactive waste are described. More specifically, a thorough summary is given of the current volume of different types of waste in the UK, and where that waste has been produced. The most recent inventory, that of 2013, was assembled by Pöyry Energy and Amec (now Amec Foster Wheeler), which are international consultancies and engineering firms. The inventory is available via the NDA website[23].

There are a variety of sources of radioactive waste in the UK. The most noticeable contribution in terms of activity and volume, arises from civil nuclear power stations, particularly for the manufacture and processing of fuel, and from decommissioning at the end of a reactor’s functioning lifetime. Industry, medicine, research and the military all have application for radioactive material, and so also contribute to a lesser degree towards the UK radioactive waste inventory. The military use a reasonable quantity of radioactive
materials for defence purposes, to produce atomic weaponry, and for naval propulsion in submarines and large military ships such as aircraft carriers.

The dominant producers of irradiated graphite waste in the United Kingdom are the civil nuclear power stations, which frequently utilise graphite as a moderator and reactor core structural component as described previously, leading to an accumulation of large volumes of graphite waste across the entire UK nuclear power industry. Radioactivity is sometimes induced in graphite for research purposes, though these are largely considered to be a negligible amount, such that these contributions are not included in the UK radioactive waste inventory. A brief overview of the reactors contributing to the UK irradiated graphite waste inventory can be found in Appendix A.

Appendix B, compiled directly from the 2010 UK Radioactive Waste Inventory, shows a table of the irradiated graphite waste sources and corresponding volumes of waste. This table indicates that there is an estimated 120,000 m$^3$ of irradiated graphite waste in the UK, 87.4% of which is designated Intermediate Level Waste (ILW). This table also shows that irradiated graphite waste is responsible for over a third of all ILW in the UK, at 36.5% by volume, which only goes to further emphasise the importance of a responsible disposal route. Another source states that, in terms of mass, the UK houses 96,000 tonnes of irradiated graphite waste, over one third of the approximately 260,000 tonnes worldwide$^7$, as seen in Figure 5.

![Figure 5: Irradiated Graphite Worldwide$^7$](image)
1.5 Irradiated Graphite Waste Management in the UK

Technically, irradiated graphite waste is predominantly classed as ILW\(^{[25, 26]}\), with some of the lesser irradiated material designated as LLW, which is largely because of the significant \(^{14}\)C inventory making it unsuitable for disposal at the Low Level Waste Repository (LLWR) near the village of Drigg, as well as the considerable volumes of graphite waste, of the order of 100,000 m\(^3\), requiring substantial space and infrastructure for its containment. Since the half life of \(^{14}\)C is long, at 5730 years, this classification as ILW is unlikely to be reduced by radioactive decay to LLW in the coming years, and as such it is currently assigned for deep geological disposal in a future Geological Disposal Facility (GDF) following a safe storage decay period in their current locations of the order 100 years to allow the activities of shorter lived radioisotopes to diminish\(^{[27]}\). There is some hesitancy to committing graphite to this fate, as suggested by an NDA report on Operational Graphite Management Strategy in which it is written,

“Although it is recognised that the Geological Disposal Facility (GDF) is the planned waste route (for England and Wales) there are perceived issues surrounding timing and whether deep geological disposal of this waste is the Best Available Technique (BAT) approach\(^{[28]}\)

This 2013 report then continues to identify the ‘high-level’ options for graphite waste management, in which two alternatives to disposal in a GDF are presented, as prompt disposal of irradiated graphite waste in a near surface facility or conditioning of the graphite waste to allow a reclassification to LLW, and subsequently disposed of at the LLWR, another readily available facility or released as ‘out of scope’ waste for storage and reuse where possible\(^{[28]}\). This final route of reclassifying waste is subdivided into two potential identified methods, which are by thermal treatment which could have significant benefits in terms of waste volume minimisation as the suggested ratio of graphite to ash produced by incineration is approximately 160:1\(^{[28]}\), and chemical decontamination, whereby radioisotopes are chemically separated from the bulk material to be disposed of separately, also offering potential waste volume minimisation. This demonstrates that although a partial commitment to a baseline of graphite disposal as ILW in a future GDF has been made, there is some flexibility to alter this strategy should evidence arise of a more appropriate course of action\(^{[25]}\).

Further motivation for adopting an alternative solution to disposal in a GDF is found when the European Parliament waste hierarchy methodology\(^{[29]}\) is considered, which is
applicable to management of all waste products and designed to reduce the environmental impacts inherent in waste production\textsuperscript{[30]}. Treatment, which could incorporate reduction, preparing for re-use and recycling of irradiated graphite waste, is a preferred option to landfill or GDF disposal as can be seen in Figure 6\textsuperscript{[31]}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{waste_hierarchy.png}
\caption{Waste Hierarchy Methodology\textsuperscript{[31]}, adapted by the author}
\end{figure}

1.6 International Irradiated Graphite Waste Research

There is a global initiative to investigate alternative solutions for irradiated graphite waste disposal because of the large volumes encountered around the globe, as seen in Figure 5, and evidenced by an International Atomic Energy Agency (IAEA) Coordinated Research Project (CRP) for ‘Treatment of Irradiated Graphite to Meet Acceptance Criteria for Disposal’ involving international contributions from China, France, Germany, Lithuania, Russia, Spain, Switzerland, Ukraine, United Kingdom and the United States of America\textsuperscript{[32]}. This CRP was heavily involved with another European consortium project launched under the 7\textsuperscript{th} EURATOM Framework Programme, known as ‘CARBOWASTE’, from which this programme of thermal treatment research has effectively stemmed, involving collaboration between research groups in the majority of the European countries outlined above. The intention of CARBOWASTE was to “develop an integrated waste management concept as well as innovative processes for treatment and recycling of purified material”, which applies directly to the reclassification of UK irradiated graphite waste disposal option identified by the NDA, as described in Section 1.5. A portion of the results presented in this thesis, which will be later identified in detail, were collected in collaboration and contributed directly to the CARBOWASTE project deliverable D-4.3.6 report\textsuperscript{[33]}. 
Despite the graphite waste related IAEA CRP and CARBOWASTE projects coming to a successful closure, a sequel project for CARBOWASTE, CARBOSolutions, has been proposed\[34], and there remains an active international community for further irradiated graphite research as there are many technicalities of irradiated graphite waste that are as of yet unanswered. This research aims to contribute to the global knowledge base for radioisotope behaviour, particularly $^{14}$C, during thermal treatment of UK-derived irradiated graphite waste.

1.7 Summary of Section 1

The main findings of this introductory section are:

- A basic overview of the structure and properties of graphite, such as the ABAB stacking sequence of graphene layers and on a larger lengthscale the existence of open and closed porosity, have been described
- The desirable properties and candidate materials for a neutron moderator material have been discussed, and the reasons why, for UK constructed reactors to date, graphite has almost exclusively been selected for the moderator
- Graphite specific advantages and disadvantages as a moderator material are explored
- The UK radioactive waste classification structure has been defined, describing the distinctions between LLW, ILW, HLW, LAW and HAW
- The quantity of irradiated graphite waste in the UK and how this compares to the international inventory of irradiated graphite waste is reviewed, showing that the UK is housing over one third of the global total
- An investigation into the sources and quantities of UK irradiated graphite waste from graphite moderated and test reactors is made
- A review of radioactive waste management in the UK is provided, demonstrating that in the early years of nuclear power little thought was given to future wastes arising
- In latter years, many organisations have sought to resolve the UK irradiated waste issues, arriving at the conclusion that a deep geological repository is a suitable solution with the Scottish Government opting for an alternative
route of near site, near surface repositories. As of yet, an appropriate site for a UK Geological Disposal Facility (GDF) is proving to be difficult to select

- Although the NDA baseline strategy is for graphite disposal in a future GDF, questions have been raised as to the suitability of disposing of irradiated graphite waste by this route, and so alternative irradiated graphite management solutions, such as thermal treatment and chemical decontamination, are being explored

- International research collaborations for irradiated graphite waste, such as an IAEA CRP and the CARBOWASTE project, have been previously successfully implemented, and an active research community for irradiated graphite waste remains

- This research aims to contribute to the global knowledge base for radioisotope behaviour during thermal treatment of UK-derived irradiated graphite waste
2. Literature Review

The literature will now be consulted to identify the global level of knowledge surrounding this topic of thermal treatment and the multitude of factors that may bear an influence on a thermal decontamination process. This review will include detailed insights into:

- The manufacturing process of graphite
- Production of radioactivity in graphite during reactor operation, excluding $^{14}\text{C}$
- Production and location of $^{14}\text{C}$ in irradiated graphite
- Thermal oxidation, including mechanisms and influencing factors
- Thermal treatment experience with irradiated graphite across the globe

2.1 The Manufacturing Process of Graphite

The manufacturing process of graphite is a lengthy and expensive process. Natural graphite can be mined, though the impurity content is high and variable. Graphite can also be manufactured by graphitisation of carbonaceous raw materials such as coke, pitch or natural asphalts, which can produce incredibly pure nuclear grade graphite with carbon purities that may exceed 99.999%; it is essential for both reactor performance and decommissioning purposes to remove as many impurities as possible that might deplete the neutron economy required for sustained fission chain reaction or contribute to undesirable activation products, such as $^{14}\text{C}$ or $^{60}\text{Co}$, whilst in a nuclear reactor environment. Many properties of graphite change under neutron irradiation, the effects of which can be somewhat compensated for by using manufacturing techniques specific to producing desirable semi-isotropic graphite, such as Gilsocarbon, as opposed to the anisotropic Pile Grade A (PGA) graphite used in Magnox reactors. This manipulation of the graphite prior to irradiation cannot directly inhibit the effects of irradiation damage, though can produce graphite that will behave more predictably and uniformly under irradiation.

Unirradiated nuclear grade graphite is a polygranular crystalline material that has an initial density of approximately 1.6-1.8 g/cm$^3$, depending on the raw materials and manufacturing process utilised, comparable to a theoretical 2.266g/cm$^3$ for perfect graphite crystals$^{[35]}$. The drop in density is a consequence of internal porosity and other artefacts such as crystal imperfections in the manufactured product.
2.1.1 The Process

A flow chart of an entire graphite manufacturing process is seen in Figure 7. There are a number of necessary processes throughout the manufacture of artificial graphite, each of which will contribute either favourably or adversely to the impurity content in the final product. It should be noted that there is some sensitivity surrounding the manufacturing process, for commercial or military reasons\(^{[9]}\), and as such there may be some variation between manufacturers and grades of graphite so far unavailable in the open literature. The basic manufacturing method, outlined in Figure 7, should remain similar irrespective of the source of the graphite, with variations in, for example, the raw materials or forming methods. The methods outlined here by Nightingale, in 1962, will be reflective of the manufacturing process for Pile Grade A (PGA) graphite, the grade of interest for this programme of research and used in Magnox reactors during the same era, and are mostly reflective of the later manufacture of semi-isotropic Gilsocarbon utilised in the current fleet of UK Advanced Gas-cooled Reactors (AGRs).

![Flow Chart of the Graphite Manufacturing Process](image)

*Figure 7: A Flow Chart of the Graphite Manufacturing Process\(^{[9]}\)*
The manufacturing process of nuclear grade graphite will now be discussed with particular attention paid to the influence of each stage of the manufacture on the impurity content, which will have ramifications for the final radioactive inventory in the irradiated graphite waste, as shall be explored in Section 2.2.

Artificial graphite can be divided into two phases, known as the filler phase and binder phase. The filler phase consists of carbonaceous particles and the binder phase is usually a carbonaceous high viscosity fluid to bind the filler particles together, in suspension, prior to baking into a solid article. It is the activation of the impurities in irradiated graphite by neutron absorption that cause it to become radioactive, and so they are of some interest to this thermal treatment research, with particular interest to be paid to the nitrogen content, a known precursor of $^{14}\text{C}$.

The process begins with selection of the raw materials for the filler particles; this will vary depending on the manufacturer and desired properties of the resultant graphite product. Petroleum coke, a by-product in the refining of crude oil, has been used for the manufacture of some nuclear grade graphites, such as Pile Grade A (PGA) graphite used in UK Magnox reactors$^{[11]}$. Raw materials with high degrees of crystallinity are desirable for nuclear application because this gives the resulting graphite desirable levels of thermal conductivity and small basal plane spacing, increasing the density of carbon atoms for neutron moderation.

Impurity content of the raw petroleum coke ingredient is significant before any processing occurs, as given by Nightingale$^{[9]}$ and seen in Table 2.

**Table 2: Impurities in Raw Petroleum Coke$^{[9]}$, adapted by the author**

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Range</th>
<th>Typical Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total ash impurity, %</td>
<td>0.05 to 0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>Sulphur, %</td>
<td>0.1 to 2.0</td>
<td>0.8</td>
</tr>
<tr>
<td>Vanadium, ppm</td>
<td>3 to 500</td>
<td>15</td>
</tr>
<tr>
<td>Boron, ppm</td>
<td>0.1 to 0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>Nitrogen, %</td>
<td>0.1 to 1.4</td>
<td>1.0</td>
</tr>
<tr>
<td>Hydrogen, %</td>
<td>3 to 4.5</td>
<td>4.0</td>
</tr>
</tbody>
</table>
Table 2 indicates that there is typically a 1% nitrogen impurity in raw petroleum coke, which is of significant interest for the production of radioactivity in irradiated graphite, as $^{14}$N is one of the precursor impurity isotopes activated to form $^{14}$C.

The next stage of the manufacturing process is ‘calcination’ whereby higher temperatures are utilised, up to 1400°C, the primary functions of which are to remove the more volatile hydrocarbons and cause shrinkage of the filler particles before they are incorporated into the graphite article. One method of calcination is by using an inclined steel tube lined with brick, which is fired internally at the low end by oil or gas, and rotated slowly so that the mixture, which is placed in the top end, is allowed to slowly traverse the length of the pipe. As the mixture gets closer to the bottom it becomes hotter and the more volatile, lighter hydrocarbons evaporate and then ignite due to the high temperatures, causing further rises in temperature, further evaporation, and further ignition, so the process becomes slightly self-supportive.

According to Ragan, ‘green’ coke, which is yet to be calcined, contains approximately 5 to 15% volatile matter, by weight, and as per Nightingale, approximately 25% of the weight of the raw coke is lost during this process, which includes the volatile matter and water from the raw materials. This leads to appreciable volume reduction during calcination, removing a significant proportion of the impurities. Nightingale has collated values for the typical metallic impurities found in calcined petroleum coke, as seen in Table 3.

**Table 3: Metallic Impurities in Calcined Petroleum Coke**, adapted by the author

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Usual Range</th>
<th>Typical Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total ash impurity, %</td>
<td>0.1 to 0.5</td>
<td>0.15</td>
</tr>
<tr>
<td>Silicon, ppm</td>
<td>30 to 300</td>
<td>50</td>
</tr>
<tr>
<td>Iron, ppm</td>
<td>30 to 1500</td>
<td>40</td>
</tr>
<tr>
<td>Vanadium, ppm</td>
<td>3 to 500</td>
<td>15</td>
</tr>
<tr>
<td>Titanium, ppm</td>
<td>1 to 20</td>
<td>10</td>
</tr>
<tr>
<td>Aluminium, ppm</td>
<td>15 to 300</td>
<td>30</td>
</tr>
<tr>
<td>Manganese, ppm</td>
<td>5 to 50</td>
<td>10</td>
</tr>
<tr>
<td>Nickel, ppm</td>
<td>25 to 100</td>
<td>40</td>
</tr>
<tr>
<td>Calcium, ppm</td>
<td>15 to 250</td>
<td>20</td>
</tr>
<tr>
<td>Magnesium, ppm</td>
<td>5 to 50</td>
<td>10</td>
</tr>
<tr>
<td>Boron, ppm</td>
<td>0.1 to 0.3</td>
<td>0.1</td>
</tr>
</tbody>
</table>
These impurities are of interest, for both neutron economy and activation reasons, with elements such as boron having a relatively large neutron absorption cross section, and isotopes of iron and nickel eventually activating to radioactive cobalt-60. It can be noted at this stage that the impurities are no longer regarded in percentages, but in parts-per-million, demonstrating that the calcined coke is significantly more pure than the raw petroleum coke it is derived from. There is no indication here of the nitrogen impurity in the calcined material, which is of interest for carbon-14 production.

Milling and pulverising of the calcined coke is required to reduce the particle sizes\textsuperscript{36}; any oversize particles are crushed, and any particles finer than approximately 0.5mm are taken to a mill and turned into a very fine ‘flour’\textsuperscript{9}. Ragan\textsuperscript{36} notes that a compromise between graphite density and practical particle size must be reached, because if the filler particles are too small then there is not space for volatile gases to escape the bulk during baking, causing internal stresses and potentially fracture of the article.

This crushing process will increase the surface area of the coke particles and expose them to air, a large proportion of which is \textsuperscript{14}N, thus likely increasing the amount of nitrogen impurity associated with them, adsorbed or otherwise. This might have consequences for \textsuperscript{14}C production.

The basic process for producing filler particles has been outlined above, though it should be emphasised that there are different types of filler for differing applications. Coking of feedstocks with high concentrations of aromatic carbon produces a high quality needle coke, as found in PGA graphite used for UK Magnox reactors. The resultant filler particles are needle-shaped, as seen in Figure 8, leading them to align with each other during the extrusion process described later in the manufacturing process. This leads to a degree of preferential alignment of graphite crystals and basal planes at an atomic scale, which propagates through to produce anisotropic material behaviour on the bulk scale, whereby properties such as thermal conductivity change depending on the direction through the graphite.
Other filler materials than those sourced from petroleum coke have also been used for nuclear application, such as Gilsoarbon, which is produced from naturally occurring asphalt cokes mined from Gilsonite veins found between Colorado and Utah. These particles were used to make graphite for AGRs because their ‘onion-skin’ type structure, seen in Figure 9, coupled with a moulding manufacturing process gives the resulting graphite a higher density and strength, and semi-isotropic properties\[11\].

After a suitable filler material has been produced, a ‘binder’ phase material must now be applied to the coke to plasticise the filler powder so that it can be formed into...
blocks. A commonly used binder material is coal-tar pitch, a relatively inexpensive by-product from destructive distillation of bituminous coal in coke ovens, employed in the manufacture of steel, which graphitises more readily than other commercially available binder materials. Further advantages of using coal-tar pitch are that it is already approximately 93% carbon (a large proportion of the impurities of which are removed during the baking process), and it has a higher density than other available binder materials, which is an important consideration for an effective moderator material. Marrow notes, however, that many variations of coal tar binder have been used by graphite manufacturers, and as such it is difficult to predict the precise composition of the PGA graphite binder phase.

The binder phase of artificial graphite could be considered a considerable source of impurities. The typical impurity content in a coal-tar pitch can be seen in Table 4, as per Nightingale.

Table 4: Chemical Constituents in Coal-Tar-Pitch Binders, adapted by the author

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total ash impurity, %</td>
<td>0.03 to 0.3</td>
</tr>
<tr>
<td>Carbon, %</td>
<td>92 to 93</td>
</tr>
<tr>
<td>Hydrogen, %</td>
<td>4.2 to 4.5</td>
</tr>
<tr>
<td>Sulphur, %</td>
<td>0.6</td>
</tr>
<tr>
<td>Nitrogen, %</td>
<td>1.1</td>
</tr>
<tr>
<td>Oxygen, %</td>
<td>1.0 to 2.0</td>
</tr>
</tbody>
</table>

It should be highlighted that the impurities are now given as percentages, as opposed to parts-per-millions, demonstrating that the raw coal-tar pitch is significantly less pure than the filler particles that it binds. The nitrogen content, of 1.1%, is of particular interest for production of $^{14}$C, and is approximately consistent with that found in the petroleum coke prior to purification by calcination. Thermal treatment of the pitch prior to use as a binder material can be employed, yielding advantages to the pitch properties during the manufacturing process, though this increases the number of quinoline insolubles (QIs) in the pitch. The QI particles are described by Ferrito as “consisting primarily of solid particles, ... are mostly complex hydrocarbons of high molecular weight ... [or] any insoluble ‘dirt’ such as coal or coke dust.” It is possible that some of these chemically stable QI particles will not be removable during purification processes, and contain nitrogen.
in their composition, potentially contributing to the total nitrogen inventory found in the final graphite product, and thus in the reactor environment.

The carbonaceous mixture of the filler and binder phase can now be formed, increasing the density of the mix by compressing the article into a suitable shape for baking. PGA graphite has been formed by use of an extrusion press\textsuperscript{19}, whereby the mixture is forced through a circular opening, forming a large cylinder.

Although impurities could be introduced from the local environment and any cooling water used following extrusion, the green article is one piece of carbon with limited open porosity, and as such the active surface area available for impurity permeation, from water or air, is now significantly reduced.

The initial baking of the ‘green article’ is a delicate process, since this is the stage at which the pitch is converted from a thermoplastic material to an infusible solid by raising the temperature of the artefact to between 800 and 1000°C\textsuperscript{36}. At approximately 800 to 1000°C volumes of hydrogen gas, an impurity, are produced and released, which lead to a significant shrinkage and the carbon becomes simultaneously more brittle. A typical baking process takes 3 weeks, with a cooling time sufficiently slow that the bricks do not begin cracking\textsuperscript{9}.

The porosity of this baked article is approximately 26\%\textsuperscript{9}, which is rather high for modern nuclear application, a significant fraction of which will be open porosity. This exposes significant surface areas to nitrogen adsorption from the air and is a potential source of nitrogen impurities in the finished product.

Since dense graphite is desirable for nuclear moderator application, and due to the high porosity found in the baked article, an ‘impregnation’ process is introduced to decrease the volume of the pores and increase the density of the final product. This is done by using pressure to pass a carbonaceous fluid through the graphite that will deposit further carbon on the surface of the pores before undergoing further baking processes. The impregnant is often a low melting point petroleum or coal-tar pitch, as seen utilised previously for the binder phase, although the impregnation pitch often differs slightly from the binder pitch because it has some of the heavier hydrocarbons removed before application\textsuperscript{9}. A single brick of graphite can undergo impregnation multiple times, though the relative benefit reduces with each iteration\textsuperscript{36} and so a practical compromise must be reached.
As seen in Table 4, the purity of the raw coal-tar pitch is questionable, and so impregnation could be introducing a region of localised impure graphite throughout the surfaces of the internal porosity. It should be noted that this could include a relatively high 1.1% nitrogen content seen in Table 4, which will likely be predominantly the naturally abundant $^{14}\text{N}$ and consequently a precursor isotope for formation of $^{14}\text{C}$. It is plausible that a large proportion of any nitrogen introduction in the impregnant will escape the graphite by volatilisation during the following graphitisation stage.

The graphitising process can now begin, which is sometimes undertaken using an Acheson furnace; the graphite is placed in a large brick lined furnace with electrodes at each end and layers of finely ground silicon carbide coke and sand, to provide both a defence against thermal oxidation and an electrical resistance to raise the temperature of the furnace. Electricity is supplied to the furnace at rates from 600 to 4000 kW, which is sufficient to raise the temperature of the article to approximately 3000°C\cite{9, 36}. The temperature is raised over a number of days before a slow cooling process is begun; it can take up to 2 weeks to cool the stock sufficiently that it can be exposed to air. The elevated temperatures encountered cause the carbon to develop into an ordered crystallographic structure, which is graphite.

The high temperatures utilised for graphitisation also cause many impurities to diffuse out of the bulk structure, allowing nuclear grade graphite to be manufactured to purities that may exceed 99.999% carbon\cite{9}. It will be seen, however, that impurities at a ppm level are sufficient to cause significant activation concerns following irradiation with neutrons in a reactor environment.

For a nuclear reactor application, it may be necessary to purify the graphite such that the neutron economy is not hindered by impurities in the moderator graphite absorbing neutrons from the reactor core. There are three generalised methods for purifying graphite. The first is to use purer raw materials, as exemplified by using petroleum pitch in the manufacture of PGA graphite\cite{9}. The second is to perform thermal purification by graphitising at a sufficiently high temperature that the impurities diffuse out of the graphite, though this only incompletely removes the impurities\cite{9}. The third and most effective method is to perform chemical purification, whereby halogens are used to penetrate the bulk graphite, react with impurities and remove them as volatile halide salts\cite{9} and other compounds. At the time of manufacture, the resultant irradiated waste in years to come was not under so much scrutiny, and so this method removes the largest
proportion of impurities, yet is known to leave behind minute residues of undesirable impurity isotopes, such as those of chlorine, which themselves can become activated and problematic for final irradiated graphite waste disposal.

The manufacturing process is complete, and the carbon purity and density of this finished product are appropriate for effective moderation in a nuclear reactor. There appears to be agreement that the impurity content in manufactured nuclear grade graphite is low, measurable in parts-per-million.

2.1.2 Summary of Section 2.1

The main findings of this section of the literature review about the manufacturing process of nuclear grade graphite, appropriate to thermal treatment of irradiated graphite, are:

- The manufacturing process for artificially produced nuclear grade graphite has been described, allowing greater insight to its macro- and microstructure, with features such as porosity bearing a direct influence on $^{14}$C production and its treatability
- An appreciation as to the purification stages and the final sources of impurities which will undergo neutron activation into radioisotopes within artificially produced nuclear grade graphite has been developed, inclusive of metallic radioisotopes and the $^{14}$C precursor nitrogen content
- The quality of the raw ingredients and impurity content of the finished product will likely influence the final radionuclide inventory in irradiated graphite, and potentially the location of $^{14}$C, affecting its treatability
- One of the final stages of the manufacturing process, impregnation, could be introducing a relatively impure layer to the surfaces of the internal porosity of the graphite
2.2 Production of Radioactivity in Graphite

The reason that irradiated graphite waste is of any concern for disposal is solely because of the radioactive inventory it contains. Graphite is predominantly carbon-12, which in its graphitic form poses very little hazard to life, and so it is the possibility of widespread release of the radioactive elements produced in neutron irradiated graphite, such as $^3$H or $^{14}$C, into the bio- and geo-sphere which necessitate special considerations towards the disposal of irradiated graphite waste. This section of the literature review describes how radioactivity arises in the graphite, and provides an overview of the prominent radioisotopes requiring disposal.

2.2.1 Activation

In the nuclear context, ‘activation’ is the process whereby previously stable atoms become radioactive, most often through impact and absorption of a nucleon, a neutron or proton, resulting in a heavier unstable isotope of that element. This process occurs frequently in a nuclear reactor environment, such as the core of a Magnox reactor, where a considerable neutron fluence is passing through the core each second.

The neutron capture cross section gives the likelihood that an incoming neutron is captured and retained in the nucleus, producing an isotope of that element with +1 atomic mass. An example of this would be a neutron absorption reaction with carbon-12 to form an atom of carbon-13, with an extra neutron in its nucleus. Depending on the interaction type, another form of energy must be ejected from the atom during this reaction, often in the form of a gamma ray or alpha particle, to compensate for the lost additional kinetic energy of the incoming neutron.

An example absorption cross section plot for boron-10, commonly used for control rods in a reactor, can be seen in Figure 10, including three example types of absorption reaction. Nuclear reactions of this type are written in the form:

“parent isotope (incident radiation, resultant radiation) daughter isotope”

so that a neutron absorption reaction by boron-10 resulting in ejection of an alpha particle and transmutation to lithium-7 would be written $^{10}$B$(n,\alpha)^7$Li. The resultant radiation terms ‘γ’ and ‘p’ represent gamma radiation and a proton respectively.
Figure 10: Neutron Absorption Cross Sections for Boron-10 Depending on Reaction Type, data from the JANIS software

Figure 10, which gives the cross section across the broad spectrum of neutron energies that could be encountered in a thermal fission reactor such as a Magnox reactor, the magnitude of the cross section is highly dependent on the incident neutron energy, with the probability of reaction between a boron-10 atom and a neutron for these reaction types falling as the neutron energy increases. In this instance and across most of the neutron flux spectrum the $^{10}\text{B}(n,\alpha)^{7}\text{Li}$ reaction would be the dominant and most likely interaction of these three by a significant margin of approximately four orders of magnitude over the next most likely reaction, $^{10}\text{B}(n,\gamma)^{11}\text{B}$. Boron is used as a control isotope in a reactor because of the considerable absorption cross section, which makes this isotope of boron able to absorb large numbers of neutrons in the reactor system, disrupting the critical chain reaction and allowing control of the reactor to be maintained.

2.2.2 Radioactivity in Graphite

The radioactivity associated with irradiated graphite waste is predominantly sourced from activation of impurities present in the graphite upon installation in the reactor and any additional radioactive contamination arising from the coolant.
Therefore, activation in graphite in a typical graphite-moderated reactor can be affected by the operating environment and neutron fluence of the core, the elemental composition of the graphite, contamination in the reactor coolant circuit and, for some radioisotopes, the rate of graphite weight loss by radiolytic oxidation\textsuperscript{[42]}. Given its importance in the activation process, the impurity content of UK reactor graphites, some of the prominent radioisotope production routes and their properties will be discussed in this section.

As seen in Section 2.1, the impurity content of artificially manufactured nuclear grade graphite is low, measurable in ppm, yet this can still have a significant influence on the final radionuclide inventory found in irradiated graphite waste following its operational exposure to a fast and thermal neutron flux in a nuclear reactor environment because of neutron absorption and activation. Black\textsuperscript{[42]} notes that most impurities in irradiated graphite have until recently been considered in terms of the reactor neutron economy rather than the end-of-life waste. This is evident when the literature is consulted, as the historic authors who have published on this topic of impurities in graphite for nuclear reactor application, such as Nightingale\textsuperscript{[9]}, provide little or no mention as to the activation products or the consequences for end of life irradiated graphite waste disposal. More recently, a detailed graphite specification has been published as an ASTM International document, indicating the maximum levels of impurities given in ‘Equivalent Boron Content’ appropriate to modern graphite for suitability for nuclear application\textsuperscript{[43]}. An appendix in this ASTM International specification describes some of the prominent radioisotopes that can arise in irradiated graphite, demonstrating that forward thinking as to the radioactive composition of the resultant waste is now being considered.

There is some ambiguity as to the impurity content of unirradiated UK PGA graphite. White et al. recognised that the graphite supplied to different UK nuclear power stations would vary somewhat in composition due to the different dates of manufacture\textsuperscript{[44]}. Black\textsuperscript{[42]} has compiled a comprehensive review of the available impurity data for unirradiated PGA graphite as seen in Table 5.
Table 5: Compilation of Available Impurity Data for Unirradiated PGA Graphite\cite{42}, adapted by the author

<table>
<thead>
<tr>
<th>Element</th>
<th>White et al.\cite{44}</th>
<th>NNL\cite{42}</th>
<th>AERE Report\cite{42}</th>
<th>NDA Characterisation Study\cite{42}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Max</td>
<td>Average</td>
<td>Max</td>
</tr>
<tr>
<td>Ag</td>
<td>0.001</td>
<td>&lt;0.05</td>
<td>1.2</td>
<td>20.0</td>
</tr>
<tr>
<td>Al</td>
<td>1.0</td>
<td>7.0</td>
<td>0.08</td>
<td>0.22</td>
</tr>
<tr>
<td>B</td>
<td>0.1</td>
<td>0.016</td>
<td>1.9</td>
<td>15.0</td>
</tr>
<tr>
<td>Ba</td>
<td>1.5</td>
<td>10.0</td>
<td>&lt;0.02</td>
<td>&lt;0.06</td>
</tr>
<tr>
<td>Be</td>
<td>0.02</td>
<td>&lt;0.05</td>
<td>&lt;0.1</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>Bi</td>
<td>0.08</td>
<td>&lt;0.5</td>
<td>0.08</td>
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<td>&lt;0.04</td>
<td>0.04</td>
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<td>&lt;2.0</td>
<td>4.0</td>
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<td>&lt;0.03</td>
<td>&lt;0.02</td>
<td>0.06</td>
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<td>2.5</td>
<td>0.42</td>
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</tr>
<tr>
<td>Cs</td>
<td>0.05</td>
<td>0.05</td>
<td>&lt;0.06</td>
<td>&lt;0.20</td>
</tr>
<tr>
<td>K</td>
<td>0.24</td>
<td>0.36</td>
<td>0.24</td>
<td>0.43</td>
</tr>
<tr>
<td>Li</td>
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<td>0.36</td>
<td>0.06</td>
<td>0.2</td>
</tr>
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<td>Mg</td>
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<td>3.0</td>
<td>0.13</td>
<td>0.6</td>
</tr>
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<td>Mn</td>
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<td>0.2</td>
<td>0.04</td>
<td>0.5</td>
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<td>Mo</td>
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<td>N</td>
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<td>10.0</td>
<td>11.13</td>
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<td>Ni</td>
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<td>6.0</td>
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<td>Pb</td>
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<td>3.0</td>
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<td>S</td>
<td>50.0</td>
<td>&lt;50.0</td>
<td>&lt;50.0</td>
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<td>Si</td>
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<td>Sm</td>
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<td>&lt;0.04</td>
<td>&lt;0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Sn</td>
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<td>&lt;0.15</td>
<td>&lt;0.04</td>
<td>0.4</td>
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<td>Sr</td>
<td>0.4</td>
<td>1.0</td>
<td>0.4</td>
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<tr>
<td>Te</td>
<td>0.2</td>
<td>2.0</td>
<td>0.2</td>
<td>0.2</td>
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<tr>
<td>Th</td>
<td>3.0</td>
<td>8.0</td>
<td>4.0</td>
<td>20.0</td>
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<td>Ti</td>
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<td>60.0</td>
</tr>
<tr>
<td>U</td>
<td>0.12</td>
<td>&lt;0.04</td>
<td>&lt;0.15</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>Zn</td>
<td>0.13</td>
<td>&lt;0.4</td>
<td>&lt;0.15</td>
<td>&lt;0.4</td>
</tr>
</tbody>
</table>

This comprehensive table demonstrates that there are large variations in impurities both between data sources and in some cases locally in the graphite, and also hints at the
complexity of whole core activation modelling, with a number of variables such as impurity level, corresponding absorption cross sections, local neutron flux profiles and extensive multi-stage radioisotope production pathways requiring complex activation codes to predict the final radioisotope inventory.

Some of these source impurity isotopes are of greater interest than others in the context of irradiated graphite waste management. Given the large variety of impurities found in irradiated graphite, it is sensible to assume that a wide array of resultant radioisotopes will be present following neutron activation of these. It should be emphasised that variations in the radioactive inventory exist locally within a reactor, and between reactors and reactor types. Many radioisotopes produced are short-lived and decay quickly following reactor shutdown, or are isotopes with radioactive half lives so long that the resultant number of decays per second, or activity, is small and so they do not present a radiological hazard. Thus, it is most often the medium-term radioisotopes, with half lives between approximately 5 and 30 years that pose a concern for dismantling UK graphite reactor cores. There are some exceptions to this, such as carbon-14 with a half life of 5730 years\[45\], which poses a radiological risk because of both its mobility in the biosphere and the large quantity of radiocarbon produced over a reactor’s lifetime, meaning that despite the long half life there are so many atoms of carbon-14 that there is still overall a significant number of radioactive decays per unit time.

Graphite reactor core activation models often impose a significant duration of neutron irradiation, which reflects the operational lifetime of the graphite core, followed by a cool-down period to reflect the time that will likely pass before the core is dismantled\[25\]. Many of the very short half life radioisotopes will decay in this period, and as such are a lesser concern for graphite waste management. Figure 11 shows the relative activity of some prominent radioisotopes found in irradiated graphite over 40 years reactor operation and then a 100 years cool down period following reactor shutdown, the transition between which is indicated by the dashed black line. The medium-term problematic isotopes such as $^3$H and $^{60}$Co will decay to relatively low levels, whereas isotopes with much longer half lives such as $^{14}$C and $^{36}$Cl will remain.
Figure 11: Relative Activity of $^3$H, $^{14}$C, $^{36}$Cl and $^{60}$Co after 40 years operation followed by 100 years decay$^{[42]}$

A model produced by White et al.$^{[44]}$ using the impurity data provided in the ‘White’ column of Table 5 simulates the expected final radioisotope inventory in a ‘typical’ Magnox reactor fleet, totalling 50,000 tonnes of graphite, following 40 years of reactor operation and a 10 year cool-down period. The results for the highest activity radioisotopes in the system can be seen in Table 6. Although the absolute values given are questionable because this is a simplified model$^{[42]}$, assuming equivalent conditions in all Magnox reactors, an order of magnitude study demonstrates that the highest activity radioisotopes following a 40 year operational period and a 10 year cool-down period are $^3$H, $^{14}$C and $^{60}$Co, in that order. The ASTM specification mentioned previously specifically notes that cobalt-60 is a problem isotope$^{[43]}$. Other prominent isotopes in this table that might be expected in Magnox irradiated graphite waste include $^{36}$Cl, $^{41}$Ca, $^{55}$Fe, $^{63}$Ni, $^{133}$Ba and $^{155}$Eu. After consulting the IAEA NuDat2.6 nuclear data database$^{[45]}$, it is apparent that despite their high activities $^{41}$Ca, $^{55}$Fe and $^{63}$Ni each produce relatively low energy radioactive emissions, and so contribute a small amount to the local radiation field and the hazard associated with the irradiated product. Equipment limitations mean that quantification of these isotopes will not be possible, as these isotopes are almost entirely beta-particle emitters, and have no gamma portion to be analysed for using gamma spectrometry$^{[45]}$. As such, they will be discarded for the remainder of this study. Chlorine-36 and $^{90}$Sr/$^{90}$Y also remain undetected using the experimental techniques utilised for this programme of research, though will remain as radioisotopes of interest in the remainder of this literature review because of the
international concern regarding the specific hazard these radioisotopes pose, largely due to their mobility and retention in organic life. More detail of the hazards posed by these radioisotopes can be found in Appendix C.

Table 6: Activation Inventory for UK Magnox Programme (9 Twin Reactor Stations plus 2 Quadruple Reactor Stations)\textsuperscript{[44]}

<table>
<thead>
<tr>
<th>Radioisotope</th>
<th>Activity (Bq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3$H</td>
<td>$2.6 \times 10^{15}$</td>
</tr>
<tr>
<td>$^{10}$Be</td>
<td>$1.6 \times 10^{12}$</td>
</tr>
<tr>
<td>$^{14}$C</td>
<td>$1.9 \times 10^{15}$</td>
</tr>
<tr>
<td>$^{36}$Cl</td>
<td>$2.1 \times 10^{13}$</td>
</tr>
<tr>
<td>$^{41}$Ca</td>
<td>$1.6 \times 10^{13}$</td>
</tr>
<tr>
<td>$^{54}$Mn</td>
<td>$6.0 \times 10^{9}$</td>
</tr>
<tr>
<td>$^{55}$Fe</td>
<td>$3.5 \times 10^{14}$</td>
</tr>
<tr>
<td>$^{59}$Ni</td>
<td>$2.1 \times 10^{12}$</td>
</tr>
<tr>
<td>$^{60}$Co</td>
<td>$5.9 \times 10^{14}$</td>
</tr>
<tr>
<td>$^{63}$Ni</td>
<td>$2.9 \times 10^{14}$</td>
</tr>
<tr>
<td>$^{65}$Zn</td>
<td>$4.8 \times 10^{9}$</td>
</tr>
<tr>
<td>$^{93}$Mo</td>
<td>$1.9 \times 10^{10}$</td>
</tr>
<tr>
<td>$^{93m}$Nb</td>
<td>$1.2 \times 10^{10}$</td>
</tr>
<tr>
<td>$^{94}$Nb</td>
<td>$2.2 \times 10^{6}$</td>
</tr>
<tr>
<td>$^{99}$Tc</td>
<td>$3.9 \times 10^{9}$</td>
</tr>
<tr>
<td>$^{108m}$Ag</td>
<td>$5.3 \times 10^{11}$</td>
</tr>
<tr>
<td>$^{113m}$Cd</td>
<td>$2.2 \times 10^{11}$</td>
</tr>
<tr>
<td>$^{121m}$Sn</td>
<td>$1.0 \times 10^{12}$</td>
</tr>
<tr>
<td>$^{133}$Ba</td>
<td>$1.3 \times 10^{13}$</td>
</tr>
<tr>
<td>$^{152}$Eu</td>
<td>$4.9 \times 10^{12}$</td>
</tr>
<tr>
<td>$^{154}$Eu</td>
<td>$1.1 \times 10^{14}$</td>
</tr>
<tr>
<td>$^{155}$Eu</td>
<td>$3.5 \times 10^{13}$</td>
</tr>
</tbody>
</table>

Fission products may also be present in irradiated graphite. White\textsuperscript{[44]} presents results of fission products and their respective activities that might be produced if 0.1 ppm natural uranium impurity were to be irradiated in a Magnox reactor using the same 40 year operation and 10 year cool down model. This value of 0.1 ppm is not so far removed from

- 54 -
the measured 0.07ppm uranium content found in the NDA characterisation study in Table 5\cite{42}. The most prominent isotopes produced from fission of uranium impurities, in terms of their final activities, include $^{90}\text{Sr}/^{90}\text{Y}$, $^{134}\text{Cs}$, $^{137}\text{Cs}$, $^{147}\text{Pm}$, $^{154}\text{Eu}$, $^{238}\text{Pu}$, $^{241}\text{Pu}$, $^{241}\text{Am}$ and $^{244}\text{Cm}$\cite{44}. Of these, apparatus limitations mean that characterisation of $^{147}\text{Pm}$, $^{238}\text{Pu}$, $^{241}\text{Pu}$ and $^{244}\text{Cm}$ are out of the scope of the project and will not be possible for reasons that will be explained in greater detail in Section 3.2; similarly to $^{41}\text{Ca}$, $^{55}\text{Fe}$ and $^{63}\text{Ni}$ above, these isotopes are either solely alpha- or beta-particle emitters, and have no gamma portion to be analysed using gamma spectrometry\cite{45}.

To summarise, the radioisotopes of interest for this programme of research are, in atomic number order:

$^3\text{H}$, $^{14}\text{C}$, $^{36}\text{Cl}$, $^{60}\text{Co}$, $^{90}\text{Sr}/^{90}\text{Y}$, $^{133}\text{Ba}$, $^{134}\text{Cs}$, $^{137}\text{Cs}$, $^{152}\text{Eu}$, $^{154}\text{Eu}$, $^{155}\text{Eu}$ and $^{241}\text{Am}$

Detailed analyses of each of these radioisotopes including their decay schemes, production routes in a nuclear reactor environment and their associated hazards to life are included in Appendix C. The hazards associated with these radioisotopes vary, with radioisotopes such as $^3\text{H}$, $^{14}\text{C}$ and $^{36}\text{Cl}$ amongst others being inherently mobile in the bioand geosphere, and radioisotopes such as $^{90}\text{Sr}$ having ‘bone seeking’ properties, such that it can accumulate in bone and bone marrow tissue.
2.2.4 Summary of Section 2.2

The main findings of this section of the literature review, appropriate to thermal treatment of irradiated graphite, are:

- Radioactivity associated with irradiated graphite waste predominantly arises from neutron interaction with impurities within the manufactured graphite product
- There is some ambiguity as to the precise impurity content of the unirradiated graphite, which varies between reactors, batches and locally within the graphite
- There are a number of prominent radioisotopes of concern that can be found in irradiated graphite waste of varying half lives, which have been identified
- Shorter-lived prominent radioisotopes will decay to low levels within a proposed reactor cool down period, though long-lived radioisotopes such as $^{14}$C and $^{36}$Cl will remain for much longer timeframes

The production pathways associated with $^{14}$C and its location in irradiated graphite waste have not been discussed, as this comparably complex topic will be explored in the upcoming Section 2.3.
2.3 Production and Location of Carbon-14 in Irradiated Graphite

In the previous section it was seen that the radioactivity associated with irradiated graphite predominantly arises from neutron interaction with impurities inherent in the graphite and the reactor circuit. Carbon-14 is no exception to this, though the production route and consequent location have been a topic of debate, with suggestion that carbon-14 derived from a nitrogen-14 precursor atom will likely be found near a graphite geometric or pore surface. This section will analyse the wide variety of sources that have studied this phenomenon of $^{14}$C production in irradiated graphite and try to draw some conclusions as to the expected location of $^{14}$C within the graphitic matrix for the samples encountered in this programme of research, of Oldbury Magnox reactor irradiated graphite. Demonstration of either a concentration or random distribution of $^{14}$C could prove ultimately vital to the optimisation and effectiveness of any designed thermal treatment process.

The activation processes and the precursor isotopes for carbon-14 production are well-known$^{[41, 46]}$. There are three dominant production routes in irradiated graphite, which are through neutron activation of isotopes $^{13}$C, $^{14}$N and $^{17}$O, as given in Table 7 along with their natural isotopic abundance and neutron absorption cross section for thermal neutrons of 0.025 eV energy.

Table 7: The Dominant Production Routes of $^{14}$C in Neutron Irradiated Graphite. Cross sections are given for incident neutrons of thermal energy 0.025 eV.

<table>
<thead>
<tr>
<th>Production Route</th>
<th>Isotopic Abundance (%)$^{[47]}$</th>
<th>Reaction Cross Section (b)$^{[40]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{13}$C(n,γ)$^{14}$C</td>
<td>1.07</td>
<td>0.001378</td>
</tr>
<tr>
<td>$^{14}$N(n,p)$^{14}$C</td>
<td>99.632</td>
<td>1.83981</td>
</tr>
<tr>
<td>$^{17}$O(n,α)$^{14}$C</td>
<td>0.038</td>
<td>0.236406</td>
</tr>
</tbody>
</table>

There is general agreement that for production of carbon-14 within the graphite itself, the oxygen-derived $^{14}$C production route seen in Table 7 is negligible compared to the other two as a consequence of the relatively low oxygen impurity content in graphite, the low natural abundance of $^{17}$O in oxygen, at a mere 0.038%, and the comparably small neutron absorption cross section as compared to other isotopes in the reactor$^{[41, 48]}$, seen in Figure 12. The dilemma as to which of the remaining production routes dominates the $^{14}$C production arises because of the discrepancy in their neutron absorption cross sections and the relative amounts to be found in a graphite moderated reactor system; the neutron absorption cross section for nitrogen-14 is approximately three orders of magnitude higher than that of carbon-13, as seen in Figure 12, yet the relative atomic composition is much
lower for nitrogen because carbon-13 is 1.07% abundant in carbon, equivalent to 10,700 ppm randomly distributed throughout the carbon in the entire graphite core versus tens or hundreds of ppm nitrogen in the reactor. A further difficulty is that the precise quantity of nitrogen in a reactor core during irradiation, which will likely affect the production of $^{14}\text{C}$, is largely unknown and thought to vary over a reactor’s lifetime depending on factors such as reactor outages, as shall be seen in Section 2.3.2.

![Figure 12: Comparison of $^{14}\text{C}$ Precursor Isotope Neutron Absorption Cross Sections](image)

With time, it is plausible that neutron absorption of $^{12}\text{C}$ to form $^{13}\text{C}$ and then a second reaction to $^{14}\text{C}$ will become a significant contributor to the radiocarbon, or $^{14}\text{C}$, inventory. The neutron absorption cross section for $^{12}\text{C}$ is higher than that of $^{13}\text{C}$ over the majority of the neutron energy spectrum, suggesting that given the high isotopic abundance of $^{12}\text{C}$ in graphite, under irradiation it will become $^{13}\text{C}$ more quickly than the $^{13}\text{C}$ isotope can ‘burnup’ potentially leading to an overall acceleration of $^{14}\text{C}$ production by this route over a reactor’s lifetime. The timescales over which this might noticeably occur are unknown to this author, and may well significantly exceed the operational lifetime of a graphite moderated reactor.
2.3.1 Sensitivity to Nitrogen

Since the neutron absorption cross section for nitrogen-14 is so much higher than that of carbon-13, the possibility exists that the nitrogen-14 production route could dominate despite there being orders of magnitude more carbon-13 in the system. This relationship has been investigated previously in a sensitivity study conducted by Black\cite{42}, the results of which are presented in Figure 13.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure13.png}
\caption{\textit{14C Production Pathways as the Nitrogen Impurity in the System is Altered}\cite{42}}
\end{figure}

This plot has been produced using FISPACT, an activation modelling code, whereby the nitrogen concentration in the system, simulating a Wylfa Magnox reactor core, has been varied from 0 to 100 ppm, exploring either side of the predicted impurity levels seen in Table 5, and the resultant production route of the $^{14}$C\cite{42}. It was found using this model that impurities of only approximately 10 ppm nitrogen are sufficient to make this nitrogen route the dominant production route in a graphite moderated reactor environment, demonstrating just how sensitive this system is to the nitrogen content. The author notes that this is a simplified model and as such losses of precursor isotopes, graphite mass and $^{14}$C loss through radiolytic oxidation have not been captured in the model.

Similar models have been constructed in the literature by various individuals and groups, and many similar values for this nitrogen concentration required for a change in
production route dominance have been deduced. Doyle and Hammond’s\textsuperscript{[49]} model arrived at a production route equilibrium value of 7 ppm nitrogen in the reactor system, whilst Metcalfe\textsuperscript{[46]} calculates it to be 8.8 ± 0.3 ppm, noting that this prediction does not include the full spectrum of neutrons involved.

An alternative model presented in a Serco Assurance report for a UK Advanced Gas-Cooled Reactor (AGR) model, which is graphite moderated and carbon dioxide cooled similarly to a Magnox reactor, demonstrates that, neglecting radiolytic weight loss or products of decomposition from the coolant gas phase, a concentration of 50 ppm nitrogen and 100 ppm oxygen in the system lead to a $^{14}\text{N}:^{13}\text{C}:^{17}\text{O}$ precursor $^{14}\text{C}$ production ratio of 305:33:1, highlighting that the ratio is extremely sensitive to the actual nitrogen content\textsuperscript{[50]}.

The initial nitrogen impurity in a graphite moderated reactor environment, and that introduced during operational procedures, could have significant impact on the final $^{14}\text{C}$ activity produced and the proportion of $^{14}\text{C}$ produced from the respective production routes, which in turn could have consequences for the radioisotope’s location in the graphite structure. The question arises: how much nitrogen is actually in Magnox reactor graphite?

\subsection*{2.3.2 Nitrogen Impurity Levels}

This uncertainty in the actual nitrogen impurity is of notable interest not only for determining the potential location of any formed $^{14}\text{C}$, but for determining the total inventory of $^{14}\text{C}$ requiring disposal following a reactor closure, as the $^{14}\text{C}$ total activity rises quickly with increasing nitrogen impurity in the graphite, seen in Figure 13. Doyle and Hammond noted that predictions were critically dependent upon nitrogen impurity levels\textsuperscript{[49]}, whilst the Serco Assurance report referred to earlier agrees that the precursor production ratio is ‘extremely sensitive to the actual nitrogen content’\textsuperscript{[50]}. It is important to note that nitrogen depletion is not expected over a 30 year reactor operating lifetime\textsuperscript{[46]}.

From Section 2.1 exploring the manufacturing process of graphite, it is known that nitrogen exists in graphite as a notable impurity, thought to be largely sourced from impurities in the raw materials. Although purification of the graphite components occurs throughout the manufacturing process through stages such as calcination and baking there is the possibility that a significant amount of the nitrogen impurity associated with graphite is introduced at a late stage of the manufacture, in the impregnant fluid\textsuperscript{[9]}, which will be
solidified throughout the pore surfaces of the finished graphite article. It is unclear how much of this nitrogen in the impregnant will escape from the graphite article during the graphitisation process. Podruzhina\cite{51} states that the nitrogen in graphite is ‘in the bound state, substituting for carbon atoms in the nodes of crystal lattice, or in gaseous form filling pores in graphite’, though it is unclear whether this refers to the open or closed porosity. Exploring this idea of nitrogen at the pore surfaces, Walker’s review paper\cite{52} suggests that a proportion of gases will chemisorb to a relatively small fraction of the surface of graphite, with nitrogen covering approximately 0.4% of the graphite surface, though chemisorption experiments have shown the surface to be heterogeneous, and so this value will likely vary.

The quoted nitrogen levels in graphite vary widely, with one source stating discrepancies of between 10 and 100 ppm\cite{52}. Another Russian source gives between 0.5 and 70 ppm for ‘typical’ Reaktor Bolshoy Moshchnosti Kanalnyy (RBMK) graphite moderated and water cooled reactor graphite\cite{53}, which may not be entirely representative of UK graphite, though the range of values is indicative that this inconsistency in the amount of nitrogen, an important precursor for $^{14}$C production, is an issue across all graphite types. The nitrogen impurity in a reactor system will also vary with time, as even though nitrogen burnup is not expected to occur over a reactor lifetime, introduction of nitrogen to the reactor through exposure to atmosphere during maintenance outages\cite{50} or air leaks in the reactor coolant circuit\cite{54} can occur. Table 5 shows that for those data sets the nitrogen impurity values range from approximately 10 ppm to 13 ppm\cite{42}, a significantly narrower range suggesting that this might be closer to an ‘average’ value. Bush et al. state that for their Magnox reactor activation model, 61% of the $^{14}$C produced was derived from the $^{14}$N precursor production route with a 10 ppm nitrogen impurity in the system\cite{55}, which is the same proportion quoted in an IAEA technical document for an example calculation using “the averaged nitrogen impurity in a typical Magnox-reactor coolant, taken together with the initial impurity level within the graphite structure itself”\cite{41} strongly suggesting that the nitrogen impurity used for this ‘averaged nitrogen impurity’ is around 10 ppm. Poncet and Petit find that the value of 10 ppm nitrogen is not representative for French UNGG reactor graphites, and overestimates the $^{14}$C inventory compared to measured values, suggesting that a typical value of 4 ppm is more appropriate for their graphites\cite{56}. Metcalfe notes that calculations using values around 0 ppm align with measurements of $^{14}$C in Wylfa Magnox reactor graphite conducted by the UK National Nuclear Laboratory (NNL), but also notes that calculations using a 10 ppm nitrogen impurity would be more representative of the broader Wylfa database for $^{14}$C inventory\cite{46}. It is well recognised, however, and should
not be underestimated that graphite is largely a heterogeneous material\textsuperscript{[52, 56]} and that the nitrogen content may vary from position to position and batch to batch of material, and across different types of graphite found in the UK\textsuperscript{[56]} affecting the resultant local and total $^{14}$C inventory.

Part of the issue of determining the nitrogen content in graphite lies in its variability, the high abundance of nitrogen in air and the difficulty of measuring it. The latter is alluded to by Ancius et al.\textsuperscript{[53]} in their paper studying the broad range of impurities in RBMK graphite, in which they have not been able to experimentally determine the nitrogen impurity in their graphite samples using their method of Glow Discharge Mass Spectrometry (GDMS), and have used ‘typical’ values from the literature. A Japanese group have attempted to measure the total amount of nitrogen in unirradiated graphite, supplied by the Japan Atomic Power Company, by ‘melting’ a sample and measuring the thermal conductivity of the resultant gas\textsuperscript{[57]}. The first stage of this experiment is to raise the temperature of the graphite to 400°C and measure the thermal conductivity of the off gas to determine the amount of nitrogen adsorbed to the surface, though Walker’s\textsuperscript{[52]} paper suggests that there will be other impurity elements bound to the graphite that could contribute to the measurement, and it is unclear whether this technique can discriminate between elements in the off gas. This stage is followed by ‘melting’ of the sample at 2800°C with additions of a 0.5g piece of tin and a nickel capsule in a helium environment, and the thermal conductivity technique used to quantify the total nitrogen content in the released gas. The purpose of the additional tin and nickel remain unclear. The recorded nitrogen values are seen to increase in proportion to the specific surface area of the samples used as might be expected, and are between 40 and 160 µg g\textsuperscript{-1} nitrogen impurity, equivalent to ppm, which is somewhat higher than that determined elsewhere. The results also suggest that the nitrogen content measured is independent of the test temperatures utilised, meaning that either the nitrogen is sufficiently stably adsorbed that it does not become liberated from the graphite at 400°C, or that only a negligibly small proportion, if any, is actually adsorbed, as opposed to bound within the graphitic structure. The high proposed nitrogen impurity levels and the lack of detailed description of the experimental procedure throw this data into suspicion, though this paper does highlight the difficulty associated with determining the nitrogen content in graphite.

Given the variability in the data for the amount of nitrogen proposed to be in unirradiated graphite in a reactor environment, and the known sensitivity of this nitrogen
to the \(^{14}\text{C}\) production, can reasonable estimates be drawn as to the proportion of \(^{14}\text{C}\) produced from each of the precursor isotopes?

### 2.3.3 Carbon-14 Production Pathway Analysis

The proportion of \(^{14}\text{C}\) produced from each precursor isotope could have ramifications on the location and potentially the ease of removal of this formed \(^{14}\text{C}\) within the graphitic structure, and as such the prominence of each pathway is of as much, if not more, importance to any applicable treatment process than the total \(^{14}\text{C}\) inventory irrespective of production route.

There is general agreement amongst the scientific community that the two prominent production pathways for \(^{14}\text{C}\) in irradiated graphite are through \(^{13}\text{C}\) and \(^{14}\text{N}\) precursors, with recognition that there is a lesser contributing \(^{17}\text{O}\) precursor route\[^{46, 54}\]. A number of sources\[^{51, 57, 58}\], however, make the assumption that \(^{14}\text{C}\) in gas-cooled graphite moderated reactors is produced predominantly through the neutron absorption and activation of \(^{14}\text{N}\), because of its larger cross section and high isotopic abundance in natural nitrogen\[^{51}\], yet as we have seen the dominance of either the \(^{13}\text{C}\) or \(^{14}\text{N}\) route in graphite is remarkably sensitive to the nitrogen impurity level, and it is seen in Section 2.3.2 that this impurity level is not well known and varies considerably between graphites. Metcalfe\[^{46}\] states that “a generally held misconception concerning C-14 in irradiated graphite is that generic statements can be made about its precursors and their location. C-14 location and activities will depend upon the composition of the original manufactured graphite (raw materials, impurities), graphite mass loss due to radiolytic oxidation, the chemical environment of the graphite during service and the irradiation history of the graphite”, introducing a number of further variables that could affect the \(^{14}\text{C}\) inventory.

Models for \(^{14}\text{C}\) activation in UK specific reactors have been produced in Black’s doctoral thesis, including representative models for both Oldbury and Wylfa Magnox reactors\[^{42}\], using the appropriate neutron flux spectra, irradiation history and impurity data. Black found that the dominant production pathway differed depending on which impurity source data was input into the model, from Table 5, which is unsurprising given the known sensitivity to the nitrogen content. The model suggests that the contribution of the \(^{14}\text{N}\) precursor production route to the whole core \(^{14}\text{C}\) inventory in Oldbury Magnox reactor graphite varies from 48.6% to 55.1% depending on the nitrogen impurity input,
though the suggested nitrogen impurities only vary from 10 to 13 ppm. The production pathway proportion for Wylfa Magnox reactor graphite, using the same impurity data with corrected flux and operational history, is similar to the Oldbury result, differing between 48.4% and 54.9%. It should be noted that the results for these early models did not include variables such as external sources of contamination, fuel burnup or graphite density loss with time, which were included in later models. As noted previously, Bush et al.\cite{55} found that approximately 61% of the resultant $^{14}$C inventory was attributable to the $^{14}$N precursor isotope in their Magnox reactor system model, which is the same value published in an IAEA technical document\cite{41}, though the precise nature and source of this model are not discussed. Conversely, Metcalfe\cite{46} finds that their mass balance calculations for the Wylfa Magnox reactor system imply that the $^{13}$C precursor makes more of a contribution to the total $^{14}$C inventory, at a $^{13}$C : $^{14}$N production precursor ratio of 7.21 : 2.34 using a 10 ppm nitrogen impurity content. Metcalfe’s sensitivity study indicates that a nitrogen impurity of over 30 ppm would be required in this system for it to become the dominant precursor isotope in this model based on reactor discharge data.

Some insight into the $^{14}$C production routes could be gleaned from analysis of alternative reactor types, since ‘there may be some similarities across reactors/types’\cite{46}. Much of the discussion surrounding $^{14}$C production by the $^{14}$N route in the literature revolves around soviet RBMK reactors, the graphite for which is usually irradiated in an inert helium and nitrogen mixture\cite{59}. This has two major consequences for carbon-14 production in RBMKs, which differ from the UK Magnox and AGR experience. Firstly, there is a much larger abundance of the $^{14}$N precursor isotope in the system than found in UK reactors, which it has been suggested will contribute to $^{14}$C associated with the graphite even though it is a surrounding gas\cite{41,50}, and so this will likely be the dominant production route\cite{41}. Secondly, there are no radiolytic oxidation processes occurring, conversely to graphite moderated carbon dioxide cooled reactors, and so any carbon-14 arising from the nitrogen at the surface of the graphite will not be removed by a later oxidation process\cite{50}. These two factors will contribute to the apparent large specific activity of $^{14}$C produced in RBMK graphite compared to other graphite moderated reactor designs\cite{50}. LaBrier et al.\cite{60} note that the majority (60-70%) of $^{14}$C produced in helium cooled graphite moderated High Temperature Gas Reactors (HTGRs) is thought to arise from neutron activation of $^{14}$N that has adsorbed to the outer geometric or pore surfaces.

As is briefly discussed above, the relative fraction of $^{14}$C produced in irradiated graphite through the $^{17}$O precursor route is thought to be negligible, ‘due to the small
quantity of $^{17}$O present and its low neutron absorption cross section\cite{41, 48}, though it is not neglected entirely because of its expected contribution to $^{14}$C production in the reactor carbon dioxide coolant\cite{50}, as will be discussed in greater detail later in this section.

In summary, there is general agreement that nitrogen is a significant source of $^{14}$C in neutron irradiated graphite, with many sources, particularly for the inert gas cooled HTGR- and RBMK-design reactors, confidently describing the $^{14}$N precursor route as the dominant production pathway. The picture is less clear for UK reactor graphites, where the process is arguably more complex due to radiolytic oxidation. There is little agreement as to the contribution of each precursor to the overall $^{14}$C yield, with Black's\cite{42} models based on available impurity data suggesting an approximately equal production rate between $^{13}$C and $^{14}$N precursors, and Metcalfe’s\cite{46} data signifying that in the Wylfa Magnox reactors $^{13}$C could be the dominant precursor isotope.

### 2.3.4 Consequent Location of Produced Carbon-14

The proportion of carbon-14 produced from each contributing precursor isotope production pathway may be of significance to the resultant location of a noticeable proportion of the radioactivity associated with irradiated graphite.

Carbon-13, one precursor of $^{14}$C which is approximately 1.07% abundant in all carbon, will likely be randomly distributed through the graphitic structure, occupying the lattice position exactly as a $^{12}$C atom might. Chemically, these isotopes of carbon will behave identically, and so the only means of identifying this isotope is through its higher atomic mass because of the additional neutron in its nucleus. Dunzik-Gougar notes that $^{13}$C is a considerable source of $^{14}$C which is likely to be homogeneously distributed throughout a graphite component\cite{54}, which strongly suggests that any $^{14}$C derived from this precursor will, at the time of formation at least, also be randomly distributed throughout the bulk material\cite{50}. At the instant that neutron absorption occurs in a $^{13}$C atom, the recoil energy is sufficient to break the chemical bonds to surrounding carbon atoms and dislocate the resultant $^{14}$C from its position in the lattice. It is thought that this $^{14}$C atom will either recombine with vacancies and other defects in the graphite structure, or remain and migrate as an interstitial between the graphene layers\cite{61}. Metcalfe presents data for $^{14}$C measurements across an entire Wylfa Magnox reactor core, seen in Figure 14, two analyses and a prediction from the National Nuclear Lab (NNL), along with an illustrative ‘axial form
factor' giving the neutron flux profile showing a correlation between neutron flux or position in the reactor and resultant carbon-14\textsuperscript{14}. It is noted by the author that some correlation between the measured data and neutron flux profiles is to be expected, evidenced by those regions receiving a lesser neutron fluence at the edges of the core yielding lower specific activities of carbon-14. The large scatter in the data could be reflective of unpredictable localised variations in the nitrogen impurity. Figure 14 shows that the radioactive inventory can vary considerably with position in the reactor.

\textit{Figure 14: Axial Variation in C-14 Activity in the Wylfa Cores Compared with Activation Modelling Prediction\textsuperscript{46}}

The ability of nitrogen to adsorb to a graphite surface is a familiar phenomenon, which is utilised during application of the Brunauer-Emmett-Teller (BET) technique for determining surface area to graphite samples, whereby known concentrations of nitrogen gas are deliberately adsorbed to the entire surface of a sample at low temperatures\textsuperscript{62}. Studies of nitrogen adsorption on graphite in various forms, of dust, powder and rod, have indicated that for a given determined surface area the same concentration of nitrogen is adsorbed\textsuperscript{50}, which is supported by similar data produced by Takahashi\textsuperscript{57}. These works demonstrate the importance of surface area available at the time when nitrogen is likely to be absorbed, such as during the manufacture or reactor operation\textsuperscript{50}. This phenomenon of
a consistent quantity of nitrogen adsorbed per unit surface area suggests that with time in a reactor environment, and increasing irradiation damage and radiolytic oxidation, the irradiated graphite could become more prone to adsorption of nitrogen to its surfaces during maintenance outages and exposure to atmosphere because of an increasing surface area. A Serco Assurance report notes that some of the adsorbed nitrogen derived from exposure of the reactor to atmosphere will be driven off when the reactor returns to power, though any remaining nitrogen would be available for production of $^{14}$C in subsequent operation$^{[50]}$. This could have consequences for the location and final inventory of $^{14}$C for disposal in UK irradiated graphite waste.

Experiments conducted by Takahashi$^{[57]}$ using Secondary Ion Mass Spectrometry (SIMS) indicate that the nitrogen content in an unknown Japanese grade of unirradiated graphite is largest on the surface, and decreases in concentration with depth into the sample. By analysing the CN$^-$ signal intensity over 1nm depth steps and relating this to the nitrogen impurity, it was determined that the concentration of nitrogen decreases over approximately 30nm, as seen in Figure 15, at which point an equilibrium nitrogen impurity value around 40 ppm is reached. Takahashi suggests that external “nitrogen molecules cannot penetrate [the] interior of nuclear-grade graphite”, which is presumably referring to a diffusion process from the surface. The precise method used to obtain the quantitative nitrogen profile seen in Figure 15 from the SIMS spectrum is not described, and this value for the nitrogen impurity of the bulk is a little higher than those expected in Table 5 for UK graphites, though it is not unreasonably high given the large variations in nitrogen impurity found in graphite in the literature, explored in Section 2.3.2.
Takahashi\cite{57} also suggests that the $^{14}$C atom formed by neutron interaction with a $^{14}$N atom will remain in the same position as the original atom, which is a theory supported by a single source\cite{51} though contradicted by much of the rest of the literature. Vulpius and von Lensa state that the recoil energy of a formed carbon-14 atom is 40 keV, which is “considerably higher than any chemical bond... [and as such the newly formed] $^{14}$C atom will be substantially displaced from its origin to form a new chemical compound in the graphite lattice”\cite{58}. A Serco Assurance report agrees that the recoil energy of the $^{14}$C production reaction will result in a distribution of these atoms, though it is noted further in this report that a more significant translation of $^{14}$C atoms may occur as a consequence of higher energy fast neutron damage to the graphite during subsequent reactor operation\cite{50}.

A study of nitrogen location in ion irradiated RBMK reactor graphite is described by Vulpius and von Lensa, where 40 keV $^{14}$N atoms are implanted into previously unirradiated graphite to mimic the effect of recoil energies during $^{14}$C production\cite{58}. A Time of Flight Secondary Ion Mass Spectrometer (ToF-SIMS) is then used to analyse the CN signal, and consequently depth profile of nitrogen in the implanted graphite, the results of which are shown in Figure 16.

![Figure 15: Distribution of Nitrogen Concentration with Depth from the Sample Surface\cite{57}](image)
Figure 16: Depth Profile of $^{14}$N-implanted RBMK Graphite$^{[58]}$

Figure 16 shows a ‘clearly recognisable implantation profile’$^{[58]}$ with a large CN peak at approximately 300 nm depth. It is noted that these nitrogen atoms have been implanted perpendicularly to the sample, and as such this precise profile is unlikely to occur in a reactor environment$^{[58]}$ where atom recoil will occur in all directions, though it is feasible that a concentration gradient of formed $^{14}$C or recoiled $^{14}$N in reactor irradiated graphite could exist in a thin layer, from the surface inwards. This is supported by a Serco report$^{[50]}$ which states that “$^{14}$C atoms formed from $^{14}$N may have a more complex distribution [compared to $^{13}$C derived $^{14}$C], depending on the initial location of the nitrogen impurities which may be enhanced adjacent to pore surfaces”.

LaBrier and Dunzik-Gougar$^{[48]}$ investigate the location of nitrogen in test reactor neutron irradiated NBG-25 graphite, an alternative nuclear grade graphite, using a number of techniques. Their analysis of the surface of the sample using Energy Dispersive X-ray Spectroscopy (EDX) revealed little nitrogen at the surface of the sample, but a significant presence of nitrogen, up to 10% atomic composition compared to 1% in unirradiated samples, is found deeper into the sample. According to LaBrier$^{[48]}$, the working distance of their EDX system is 1 to 3 µm, and so it is proposed that there may be a substantial presence of nitrogen deeper within the sample. Scanning Electron Microscopy (SEM) reveals that there may be ‘clusters’ of nitrogen forming in irradiated graphite, as shown in Figure 17, seen here at a depth of approximately 1 µm below the graphite surface. It is
proposed by LaBrier and Dunzik-Gougar that these clusters of nitrogen bind to the graphite due to sample neutron irradiation; nitrogen atoms initially bound to the graphite are liberated from their bonds and migrate into the graphite, which after multiple iterations could cause the migrating nitrogen atoms to form into clusters. This theory is partially supported by mass spectroscopy analysis performed by Vulpius and von Lensa\cite{58}, as seen in Figure 18, where a comparison is drawn between nitrogen implanted RBMK graphite and both irradiated and unirradiated fuel pebble graphite from a German prototype pebble bed reactor (AVR).

\textit{Figure 17: Nitrogen Clusters Located in Closed Pore of Irradiated NBG-25, 3500x (left) and 65,000x (right)\cite{48}
Vulpius and von Lensa’s\cite{58} mass spectrometry analysis shows that the nitrogen implanted and neutron irradiated graphites exhibit a significantly large $^{12}$C$^{14}$N peak compared to the unirradiated, indicating that, following irradiation, at least some of the nitrogen impurity has reacted with the graphite. Vulpius and von Lensa explain that this phenomenon could be because of “generation of highly reactive nitrogen atoms by splitting of the chemical bonds”. These highly reactive nitrogen atoms can then easily form chemical bonds to carbon atoms abundant in the graphite. The clusters of nitrogen, as observed by LaBrier and Dunzik-Gougar, could be prime candidates for activation to $^{14}$C\cite{48}. A number of surface characterisation techniques have also been applied to test reactor irradiated NBG-25 graphite, by LaBrier and Dunzik-Gougar, including SIMS, X-ray Photoelectron Spectroscopy (XPS) and Raman Spectroscopy. The SIMS results, seen in Figure 19, where mass spectrometry was performed at the surface and at a depth of 5 nm into the graphite by sputtering, indicate that almost the entire signal corresponding to mass 14, which could be indicative of either $^{14}$N or $^{14}$C as they have very similar atomic masses, is lost with increasing depth. The authors conclude that this signal is likely to correspond to $^{14}$C at the surface rather than nitrogen because of the alternative characterisation techniques utilised showing no nitrogen content at the surface of the sample. This may be a difficult point to argue because of the similarity in masses between nitrogen-14 and carbon-14, the risk of
minute amounts of surface contamination by air, and the small depth through which this study is conducted (5 nm) compared to other sources suggesting nitrogen profiles in hundreds of nanometers\textsuperscript{[58]}, though it remains a compelling argument with multiple characterisation techniques providing supportive evidence.

Figure 19: Surface (top) and 5 nm (bottom) Negative Ion Spectra for Irradiated NBG-25, m/z 14\textsuperscript{(48)}

Given that the literature suggests that a concentration gradient of nitrogen exists near a graphite surface, and that this could be indicative of where a proportion of the $^{14}$C may form, it is important to consider sources that have analysed irradiated graphite for $^{14}$C content to confirm or negate this theory. Podruzhina\textsuperscript{[51]} and Fachinger\textsuperscript{[63]}, both of Research Centre Julich FZJ, have separately published evidence from characterisation of irradiated graphite, from a pool type test reactor column and graphite sourced from a pebble bed design test reactor, to show existence of a concentration of $^{14}$C on the surfaces of graphite blocks, with Fachinger suggesting that the greatest concentration of radiological contamination in irradiated graphite exists near graphite surfaces. This is supported by an IAEA technical document\textsuperscript{[41]} discussing decontamination of graphite blocks from the graphite moderated British experimental reactor GLEEP, whereby around 63% of the $^{14}$C existing in the graphite was liberated into the gas phase following calcination of the blocks at 1150°C for approximately 3 hours in an unknown cover gas. The authors state that
because atomic solid-state diffusion is not thought to become significant in graphite until 1800°C that this gas phase release must be attributable to $^{14}$C located near the geometric and pore surfaces. Contrary to this, Metcalfe$^{[46]}$ states that radiochemical analysis of two Wylfa Magnox reactor samples have shown no evidence for $^{14}$C enrichment at the surfaces, with further complementary modelling analysis suggesting that the amount of $^{14}$C found in the samples is reflective of $^{13}$C being the only precursor isotope, though it is noted by the author that “it is unwise to attach too much significance to two measurements.”

One source also gives an indication as to $^{14}$C production in a helium cooled High Temperature Gas Reactor (HTGR), where it was found that the surface 1mm layer of graphite was surprisingly rich in $^{14}$C$^{[64]}$. It has been suggested that the discrepancy between the estimated and measured $^{14}$C could be because air ingress during maintenance periods was not considered in the predictions$^{[50]}$, reinforcing that air ingress could also be an important source of the $^{14}$N precursor isotope for other reactor systems, such as Magnox reactors. It should be noted that because HTGRs are helium cooled, there will be little in the way of oxidation processes (thermal or radiolytic) to remove any carbon-14 formed at the graphite surface from this source, and as such a larger concentration may be evident on HTGR graphite than in graphite from carbon dioxide cooled reactor systems.

There are a number of sources agreeing that an accumulation of $^{14}$C exists near the surface of neutron irradiated graphite, from differing types of test and power producing reactors, with a single UK analysis from the Wylfa Magnox power station suggesting the alternative that this phenomenon may not be applicable to UK Magnox reactor graphites$^{[46]}$, though a larger number of samples require analysing before any conclusions could be drawn. It is thought that this $^{14}$C enriched layer of graphite arises as a consequence of neutron absorption of nitrogen, which is predominantly found near geometric and pore surfaces of graphite, though the source atom will likely be significantly displaced from its initial location by reaction recoil and fast neutron damage, leading to a potential concentration gradient of $^{14}$C from the surface of the graphite. There is some ambiguity as to the lengthscale over which this phenomenon of a $^{14}$C concentration gradient occurs, with most sources suggesting a scale of tens or hundreds of nanometres from the surface into the graphite bulk.
2.3.5 Alternative Sources of Carbon-14 in Irradiated Graphite

Although $^{14}$C production in irradiated graphite occurs predominantly in the bulk moderator material,$^{55}$ it is thought that some of the $^{14}$C inventory found in irradiated graphite will arise from the carbon dioxide coolant phase, either from $^{14}$C containing particles,$^{65}$ a carbonaceous deposit thought to arise from a number of processes, generally involving carbon monoxide in the coolant,$^{50, 66}$ or impurities and residual air,$^{50}$ in the coolant circuit.

The typical impurity composition of the carbon dioxide coolant in a Magnox reactor, given in parts per million by volume, can be seen in Table 8.

Table 8: Typical Composition of CO$_2$ Coolant in Magnox Stations$^{42}$

<table>
<thead>
<tr>
<th>Element/Compound</th>
<th>Concentration (ppmv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon monoxide</td>
<td>&lt; 15,000</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>25 - 45</td>
</tr>
<tr>
<td>Methane</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Water</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Argon</td>
<td>5</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>500</td>
</tr>
</tbody>
</table>

Black$^{42}$ describes that a number of these impurities affect the reactor chemistry, in both a beneficial and detrimental way. It is known that carbon monoxide and methane act as inhibitors to radiolytic oxidation, and have been manually added to some Magnox and AGR reactors for this purpose.$^{41}$ Table 8 shows that, amongst other impurities, there is a comparatively large amount of nitrogen present in the reactor coolant circuit, a known significant precursor element for $^{14}$C. Previous sections of this literature review suggest that nitrogen from the gas phase can interact with the solid graphite, potentially contributing to the nitrogen impurity and consequent $^{14}$C at the surface of the graphite.$^{54, 59}$

It should be noted that $^{17}$O has not been discarded from previous production pathway analyses because it could become a significant contributor to $^{14}$C production in the coolant phase, existing as a component of carbon monoxide, water and any small amounts of air that could exist in the coolant.$^{50}$ Metcalfe’s analysis of activation in the coolant phase suggests that the contribution to the total $^{14}$C inventory in the reactor system from the coolant is of the order 20%$^{46}$, and only a fraction of this $^{14}$C will likely interact with the graphite itself. Vulpius and von Lensa’s paper$^{65}$ indicates that the coolant gas of carbon dioxide cooled graphite moderated reactors could contain $^{14}$C compounds or $^{14}$C-containing
particles which are deposited onto the surfaces of the reactor internals, as a “thin film with a high concentration of $^{14}$C”. A Serco Assurance report\textsuperscript{[50]} refers to Canadian CANDU reactor experience where irradiation of a nitrogen annulus gas resulted in the formation of a solid compound paracyanogen ($C_2N_2$)$_n$, in which each carbon atom was $^{14}$C because they were derived from activation of $^{14}$N. These sources together suggest that although $^{14}$C production in the coolant is low compared to in the graphite, it could contribute to a relatively high concentration of $^{14}$C at the graphite surfaces. Metcalfe\textsuperscript{[67]} poses the question as to whether the carbonaceous deposits found in UK Magnox and AGR reactors are rich in $^{14}$C, suggesting that there must be some data alluding to this. This is supported further by work from Payne et al.\textsuperscript{[68]} where SIMS has been used to investigate the distribution of $^{14}$C in Magnox reactor core graphite. They conclude, by comparison of mass spectra and visual analysis using scanning electron microscopy (SEM), that there is an apparent enrichment of $^{14}$C in the carbonaceous deposit found on the channel wall surface of a trepanned irradiated graphite sample taken from an Oldbury Magnox reactor core, which is closely comparable to the graphite used for this programme of research. The level of $^{14}$C enrichment is not quantified.

Another source of $^{14}$C, which is arguably both part of the graphite structure and not, is from activation of gases trapped in the closed porosity of the structure as a consequence of the manufacturing process\textsuperscript{[50]}. It is presumed that any gases trapped within the closed porosity at the time of starting reactor operation will either diffuse out, form compounds of carbon, nitrogen and oxygen following irradiation, or in the case of any present nitrogen become activated to carbon-$^{14}$ by neutron absorption\textsuperscript{[50]}. This hypothesis leads to the potential of ‘pockets’ of $^{14}$C trapped throughout the graphite structure within closed porosity, which could become exposed by oxidation processes, radiolytic or otherwise. In support of this, the work by LaBrier and Dunzik-Gougar\textsuperscript{[48]} analysing nitrogen below the surface of liquid nitrogen immersed graphite, seen in Figure 17, shows an accumulation of nitrogen into ‘clusters’ in a closed pore in neutron irradiated NGB-25 grade nuclear graphite.
2.3.6 Summary of Section 2.3

The main findings of this $^{14}\text{C}$ production section of the literature review, appropriate to thermal treatment of irradiated graphite, are:

- Carbon-14 is produced by three different neutron absorption reactions in neutron irradiated graphite, the source isotopes for which are $^{13}\text{C}$, $^{14}\text{N}$ and $^{17}\text{O}$.
- The dominance of either the carbon- or nitrogen-derived $^{14}\text{C}$ production route is extremely sensitive to the nitrogen impurity content in the graphite, with an equilibrium in production from $^{13}\text{C}$ and $^{14}\text{N}$ source isotopes occurring at a mere approximately 10 ppm nitrogen impurity.
- There are many discrepancies in the literature as to the actual amount of nitrogen in a graphite moderated reactor system, as it is difficult to measure and seems to vary heavily between batches of graphite, reactor type, operational history and locally within the graphite. Values range from 0.5 to 100 ppm nitrogen impurity in the graphite, with a ‘typical’ value for UK Magnox reactors suggested as just over 10 ppm.
- It is generally agreed that $^{17}\text{O}$ does not greatly contribute to the $^{14}\text{C}$ in the graphite itself, yet there is some dispute in the literature as to which of the other production routes of $^{14}\text{C}$ dominate in irradiated graphite. For UK Magnox reactors, suggestions vary from an approximately 50:50 relationship between $^{13}\text{C}$- and $^{14}\text{N}$-derived $^{14}\text{C}$ to the $^{14}\text{C}$ being wholly formed from $^{13}\text{C}$.
- Carbon-14 derived from $^{13}\text{C}$ will likely be randomly distributed throughout the bulk material in the graphite. There is evidence in the literature that a decreasing nitrogen concentration profile exists from the surface of the graphite inwards, over a lengthscale of typically hundreds of nanometers, which following activation by neutron irradiation and subsequent fast neutron interactions will likely result in an elevated concentration and distribution of nitrogen-derived $^{14}\text{C}$ near the surface of the graphite.
- A $^{14}\text{C}$ rich surface has been experimentally identified on the surface of irradiated graphite by multiple sources using multiple techniques, with a single UK source suggesting that there was no evidence of $^{14}\text{C}$ enrichment on the surface of their Wylfa Magnox reactor samples and an alternative
UK source suggesting $^{14}$C enrichment on the surface of Oldbury Magnox reactor samples

- The UK experience of $^{14}$C enrichment on the surface of irradiated graphite differs somewhat from reactors of many other nations, such as the Russian RBMK reactors, because of the carbon dioxide coolant utilised in the Magnox reactors and AGRs, and consequent radiolytic oxidation corrosion processes removing surface carbon.

- Some of the $^{14}$C attributable to the graphite could also arise from the carbon dioxide coolant, either as a source of nitrogen and oxygen impurities, or through accumulation of potentially radioactive carbonaceous deposits that form on the geometric surfaces of the graphite following complex interactions in the gas phase, evidenced by one source looking at the radiocarbon content of the deposit on graphite from the UK Oldbury Magnox reactors.

- The possibility exists that ‘pockets’ of $^{14}$C could be found inside closed porosity throughout the graphite structure, where nitrogen has become trapped during the manufacturing process or accumulated by other fast neutron irradiation damage processes.
2.4 Thermal Oxidation

2.4.1 Introduction to Thermal Oxidation

Oxidation is a phenomenon of particular concern to the UK fleet of electricity generating nuclear reactors, the cores of which, excluding a single PWR, are constructed from graphite. Carbon is known to oxidise by two methods in a nuclear reactor environment, namely radiolytic and thermal oxidation. Radiolytic oxidation occurs by radiation-induced energy deposition in the carbon dioxide coolant producing excited chemical species in the open pore volume which oxidise the carbon at the geometric and pore surfaces[69]. Following a reactor closure and defuelling, the local radiation field and environment are no longer suitable for inducing any noticeable radiolytic oxidation, and as such this process is not applicable to any thermal treatment of waste and will not be discussed in any further detail. Thermal oxidation is a largely temperature dependent chemical reaction between carbon and oxygen, carbon dioxide, steam or hydrogen, which occurs measurably, though negligibly, down to approximately 300°C in air[70]. It is this phenomenon of thermal oxidation coupled with using carbon-dioxide as a coolant, which is less oxidising than air as shall be seen, which has restricted reactor efficiency in the UK, as the reactors cannot be operated at higher temperatures than they have without significant and relatively rapid weight loss to the graphite structure; in current generation AGRs a ‘re-entrant’ flow system is used to maintain reactor core graphite temperatures below 450°C[71].

The basic concept of thermal treatment utilised for this research should be outlined, for context, before the literature is consulted; an irradiated graphite sample is placed into a tube furnace, at an elevated temperature, with a suitable cover gas flowing past the sample. If an oxidant is present then the phenomenon of thermal oxidation could be exploited for thermal treatment of irradiated graphite waste, whereby oxidation can release radioisotopes such as ³H or ¹⁴C into the gas phase, allowing extraction from the bulk material. One hypothesis already explored in the literature is that a significant proportion of the ¹⁴C inventory in irradiated graphite is concentrated near to pore and geometric surfaces. This section of the literature review will discuss the factors affecting oxidation behaviour in graphite, which will lead to optimisation and investigation of experimental parameters and variables relevant to the efficient release of radioactivity from a solid irradiated graphite sample.
2.4.2 Carbon Oxidation Reactions

There are a number of relevant primary and secondary reactions that can cause carbon gasification, as described by Walker et al. in a 1959 review paper\textsuperscript{[52]}. These include reaction of carbon with oxygen, steam, carbon dioxide and hydrogen and are shown below with their corresponding heats of reaction at 18°C and 1 atmosphere pressure.

<table>
<thead>
<tr>
<th>Carbon-Oxygen Reactions</th>
<th>Heat of Formation (ΔH, kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C(s) + \frac{1}{2}O_2(g) = CO(g)$</td>
<td>$\Delta H = -111.4$ (3)</td>
</tr>
<tr>
<td>$CO(g) + \frac{1}{2}O_2(g) = CO_2(g)$</td>
<td>$\Delta H = -282.0$ (4)</td>
</tr>
</tbody>
</table>

The term ‘s’ represents a solid phase material, and the term ‘g’ represents atoms in the gaseous phase. Reactions (2) and (3) are the reactions induced at the graphite surface during treatment in a limited oxygen environment at elevated temperatures, whilst reaction (4) is a potential secondary reaction in the gas phase. The negative heats of formation indicate that these are all exothermic reactions. The reaction between air, containing approximately 21% oxygen, and graphite only becomes significant at temperatures of the order 400°C\textsuperscript{[19]}.

<table>
<thead>
<tr>
<th>Carbon-Carbon Dioxide Reaction</th>
<th>Heat of Formation (ΔH, kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C(s) + CO_2(g) = 2CO(g)$</td>
<td>$\Delta H = +170.7$ (5)</td>
</tr>
</tbody>
</table>

The oxidation of graphite by reaction with produced carbon dioxide is of minor concern for thermal treatment, as an undesirable secondary reaction in the gas phase. The quantity of carbon dioxide relative to oxygen in the system is likely to be small, and the rate of reaction is of the order $10^{-5}$ smaller than that of oxygen, as seen in Table 9. An alternative source of carbon dioxide for this reaction could be as an impurity in the cover gas, though this will likely be negligible. It should be noted that this reaction has a positive heat of formation, or is endothermic, such that it will remove heat from the system rather than contribute to the local energy field.
Table 9: Approximate Relative Rates of the Gas-Carbon Reactions at 800°C and 0.1 Atm. Pressure[52], adapted by the author

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Relative rates</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-O₂</td>
<td>1 x 10⁵</td>
</tr>
<tr>
<td>C-H₂O</td>
<td>3</td>
</tr>
<tr>
<td>C-CO₂</td>
<td>1</td>
</tr>
<tr>
<td>C-H₂</td>
<td>3 x 10³</td>
</tr>
</tbody>
</table>

The reactions of carbon with water, or steam, can be seen in Equations (6) and (7) below.

Carbon-Water Reaction                      Heat of Formation

\[ C(s) + H₂O(g) = CO(g) + H₂(g) \quad \Delta H = -393.4 \]  \quad (6)

\[ CO(g) + H₂O(g) = CO₂(g) + H₂(g) \quad \Delta H = -111.4 \]  \quad (7)

Reactions (6) and (7), those of carbon with water, are relevant because there are multiple potential sources of moisture, such as adsorbed moisture on the sample, sample boat and furnace internals, or oxidation of the tritium content in irradiated graphite. Since radioisotopes are indistinguishable chemically, they will behave the same as their stable isotope variants, and thus tritium undergoes oxidation into water vapour similarly to hydrogen. This reaction is given in Equation (8)[72].

\[ 2H₂ + O₂ = 2H₂O \]  \quad (8)

For thermal treatment of irradiated graphite samples, there is the possibility that the hydrogen-oxygen reaction product could be in the form of H₂O, HTO or T₂O, where ‘T’ represents tritium. Probability suggests that T₂O will be the least frequent product, as this requires two tritium atoms to be within close proximity of each other during the reaction. It is unlikely, however, that this moisture will react with a graphite sample in any noticeable fashion because of the elevated temperatures required for this reaction to occur. Nandi[73]
writes that “the steam-carbon reaction ... is endothermic and its rate does not become significant below about 750°C” indicating that the small amount of moisture inevitable in a laboratory treatment system should not affect oxidation behaviour except when above this temperature region. This is supported by an Oak Ridge National Laboratory study[74] of graphite-steam reactions, as seen in Figure 20, whereby the reaction rate between steam and a large graphite specimen was analysed between 1200 and 1600°F (which corresponds to approximately 650 and 870°C respectively) at over 10 bar pressure. The rate of reaction with steam can be observed to drop sharply with temperature. Table 9 also indicates that any oxygen present will have a markedly more pronounced oxidation effect than any moisture.

Figure 20: Steam-Graphite Reaction Rate for EGCR Fuel Element Graphite Sleeve[74]

The authors note that pressure appears to have little practical effect on the reaction rate, and so this data is thought to be applicable to a laboratory tube furnace;
Walker\textsuperscript{[52]} shows that for a C-CO\textsubscript{2} reaction, increasing the oxidant pressure by increasing the cover gas flow increases the reaction rate, which is to be expected because the density of oxidant atoms at the carbon surface will increase, and as such this data for reaction of steam with graphite at 10 bar pressure will overestimate the effect of moisture in a laboratory scale experiment at approximately atmospheric pressure, further supporting that the influence of oxidation by steam for this research programme is negligible.

<table>
<thead>
<tr>
<th>Carbon-Hydrogen Reaction</th>
<th>Heat of Formation $(\Delta H, \text{kJ/mol})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C(s) + 2H_2(g) = CH_4(g)$</td>
<td>$\Delta H = -74.8$</td>
</tr>
</tbody>
</table>

Any carbon-hydrogen reaction in this experimental arrangement will likely be sourced from hydrogen impurities in the cover gas. Another potential source of hydrogen for this reaction could be tritium, known to be found in irradiated graphite, though impurities in nuclear grade graphite are present in parts-per-million quantities, and as such it may seem credible that any contribution of this hydrogen impurity to the gas phase will be small. As seen in Table 9, hydrogen is of the order $10^{-8}$ less reactive with carbon than oxygen, and so coupled with the small amounts of hydrogen expected in a laboratory tube furnace environment, it is thought that reaction (9), from carbon to methane, will likely play a negligible role in the total reaction chemistry.

### 2.4.3 Oxidation Mechanisms and Influencing Factors

An IAEA technical document\textsuperscript{[19]} details the mechanisms and controlling factors influencing oxidation of graphite. There are a number of chronological steps incorporated into the oxidation reaction of carbon, which are given as:

(i) Transport of oxidant to the graphite surface
(ii) Adsorption of oxidant onto the graphite surface (physisorption)
(iii) Formation of carbon-oxygen bonds (chemisorption)
(iv) Formation of carbon-hydrogen bonds, where applicable (reduction)
(v) Breaking of the carbon-carbon bonds
(vi) Desorption of carbon monoxide, or other product
(vii) Transport of reaction product from the graphite surface
Any of these fundamental steps will be directly or indirectly influenced by a number of external factors, limiting or enhancing the reaction rate. These are listed below, separated into controllable and uncontrollable, along with a brief description of each factor and how these might be controlled during thermal treatment in a laboratory environment:

**Controllable Factors:**

- **The rate at which the oxidant is supplied to the surface** – this can be adjusted by altering the composition and flow rate of the cover gas
- **The partial pressure of the oxidant** – this will be affected by the cover gas temperature and flow rate
- **The temperature** – controllable using a tube furnace
- **The rate at which reaction products are removed** – this will be dependent on many factors such as temperature, cover gas flow rate, and the microstructure of the graphite

**Uncontrollable Factors:**

- **The reactive surface area available to the oxidant at the surface** – the reactive surface area is inherent in the material and will be dependent on the microstructure of the graphite in question and any processes which may have altered this microstructure, such as annealing or fast neutron damage
- **The amount and distribution of catalytic impurities in the graphite** – despite a lengthy manufacturing process with purification stages, trace quantities of impurities remain in nuclear grade graphite, some of which catalyse the thermal oxidation reaction
- **The fast neutron damage to the graphite** – the neutron damage will be dependent on the neutron fluence received during its functional life in a reactor
- **The amount of pre-oxidation (radiolytic or thermal)** – the amount of oxidation already subjected to the sample depends on the reactor conditions under which the graphite operated
• **The quantity of in-pore deposits** – some reactors are known to cause more carbonaceous ‘sooty’ deposits in the reactor core during operation than others. This will vary across a core

• **The effective diffusion coefficient** – the diffusion coefficient will be heavily dependent on the microstructure of the graphite, with porosity having a large influence

There are a large number of factors that affect thermal oxidation of irradiated graphite; this indicates that control of as many of these factors as feasible should be sought for any thermal oxidation experiments, such that there are as few unknown or unmanageable influences on the experiment as possible. The influence of these variables on the oxidation behaviour of graphite will be discussed in greater detail below.

### 2.4.4 Regimes of Oxidation

As a further complication to the thermal oxidation process, there are three known oxidation regimes, the chemical, in-pore diffusion, and surface boundary layer controlled regimes. A graphical representation of how these differ in terms of reaction rate and oxygen concentration into the graphite bulk, as seen in Figure 21.

Figure 21 is not dissimilar to that presented by Walker[52], demonstrating common acceptance of this model. It should be noted that in the upper diagram the y-axis is logarithmic and the x-axis represents ‘1/T’, the reciprocal of temperature, and so the graph decreases in temperature from left to right.
Regime I – Chemical Regime: The first regime is the lowest temperature regime in which the reaction rate is essentially determined by the rate of the chemical reaction, or the intrinsic reactivity of the graphite, whereby the distribution of oxygen throughout the open porosity can be considered as constant, and so reaction occurs at all ‘open’ surfaces throughout the bulk of the body. The graphite geometry remains largely unaffected in this regime as the majority of surface area is found in internal porosity. At these lower temperatures, the transport of oxidant into the structure and reaction products out of the structure is relatively unimpeded\textsuperscript{[50]}, and so do not affect the reaction rate. The rate of reaction may still differ through the structure as a consequence of “gas composition [varying] in non-transport pores and ... the effect of a given gas composition [varying] with pore shape”\textsuperscript{[19]}, due to gas phase reactions. It can be noted that other features of the microstructure of graphite also affect oxidation, though these will be covered later in the thesis.
Regime II – In-pore Diffusion Regime: The second regime can be considered an intermediate regime between I and III whereby in-pore diffusion becomes more restrictive with increasing temperature. This occurs because at elevated temperatures the chemical reaction occurs more quickly than in Regime I, such that the rate at which oxygen can be transported to the internal pore surface and the rate at which the products can diffuse back out of the graphite are slow enough to inhibit the natural intrinsic rate of reaction. This can also occur in a material with a particularly restrictive structure\textsuperscript{[19]}.

One of the consequences of this is the development of a concentration gradient of reacting gases through the bulk of the graphite, which can be seen in the lower diagram of Figure 21. The outer surfaces, those closer to the external gas flow, are now undergoing preferential oxidation, as less oxidant is able to reach the internal surfaces farthest from the gas flow.

Regime III – Surface Boundary Layer Controlled Regime: The third regime applies to all temperatures above those applicable for Regime II. In this regime, which can be otherwise known as the ‘mass transfer’ regime, the temperatures are elevated high enough, and the reactivity of the graphite increased so much, that the majority of the oxidant is consumed at the surface of the graphite without any penetration to the internal porosity\textsuperscript{[19]}. A boundary layer forms at the surface of the graphite, and it is the mass diffusion through this layer that limits the oxidation process; oxidants are restricted from accessing the graphite surface, and to some extent reaction products restricted from leaving, and so it is in this regime that the external geometry of the graphite will be most affected.

For a sample undergoing oxidation in this regime, the structure of the graphite in question has little influence on the oxidation reaction, supported by Moormann and Hinssen\textsuperscript{[76]} in their modelling paper where it is given that in the third regime “mass transfer rules are usually applied... meaning that kinetics are not influenced by the properties of the solid”.
The transition from one regime to another is considered to be progressive with temperature, though the approximate temperatures at which this transition between regimes occurs in graphite remain somewhat undefined. A PhD student at Idaho State University has compiled a table demonstrating the apparent variation in data defining the transition between oxidation regimes for graphite, an adapted copy of which is found in Table 10.

Table 10: Temperature Regions of Graphite Oxidation According to Various Sources, compiled by James Cleaver, Idaho State University. Adapted by the author

<table>
<thead>
<tr>
<th>Reference</th>
<th>Regime I</th>
<th>Regime II</th>
<th>Regime III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propp, 1998[75]</td>
<td>&lt; 700 – 825°C</td>
<td>Between I and III</td>
<td>&gt;1371°C</td>
</tr>
<tr>
<td>IAEA, 2000[49]</td>
<td>Less than II</td>
<td>600-900°C</td>
<td>Greater than II</td>
</tr>
<tr>
<td>Snead and Burchell, 2002[78]</td>
<td>&lt; 500°C</td>
<td>Between I and III</td>
<td>&gt;900°C</td>
</tr>
<tr>
<td></td>
<td>Steam: &lt; 850°C</td>
<td>Steam: 850-1350°C</td>
<td>Steam: &gt; 1250 –</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1400°C</td>
</tr>
<tr>
<td>EPRI, 2005[79]</td>
<td>Starts at 350 – 400°C</td>
<td>- -</td>
<td>- -</td>
</tr>
</tbody>
</table>

As can be seen in Table 10, the oxidant affects the temperature boundaries between oxidation regimes, with steam transitioning between regimes at higher temperatures than that of oxygen. It has been suggested that factors other than temperature, such as graphite density, microstructure and impurity content can influence the temperature of transition between regimes[80], which could assist in explaining the variability in data.

In summary, the important conclusion to draw from this section about oxidation regimes is that the location of mass loss to an irradiated graphite sample during treatment in an oxidising atmosphere will likely vary depending on the temperatures utilised, with high temperature oxidation corroding the outer geometric surfaces of the sample, low temperatures allowing for oxygen ingress into the sample before reaction and consequently corroding all surfaces throughout the internal porosity, and temperatures appropriate to the second in-pore diffusion regime exhibiting corrosion somewhere between these two extremes, with a decreasing concentration gradient of oxidation occurring from the outer geometric surfaces inwards. This distinction between oxidation regimes is important when considering the likely location of any formed ¹⁴C intended for chemical removal, as seen in Section 2.3.4.
2.4.5 Effect of Pressure

When considering the controllable and uncontrollable variables listed in Section 2.4.3, it is important to note that these are largely intertwined. The rate at which an oxidant is supplied to the surface of the sample will, in this instance using a tube furnace, be largely dependent on the flow rate of the cover gas, though this will have consequences for the partial pressure of the gas phase which in turn might cause an acceleration or adverse effect on the oxidation rate. Walker\textsuperscript{[52]} finds that for a constant flow rate, oxidising in the second oxidation regime using carbon dioxide as an oxidant and nitrogen as an inert balance gas, the oxidation characteristics of a graphite rod at varying temperatures and pressures are as shown in Figure 22.

![Graph showing oxidation characteristics of a graphite rod with varying oxidant pressure and temperature.]

Figure 22: Oxidation Characteristics of a Graphite Rod with Varying Oxidant Pressure and Temperature\textsuperscript{[52]}

Walker’s results show that for a four-fold increase in cover gas pressure, under these oxidation conditions, the rate of reaction approximately doubles irrespective of the temperature, suggesting that on a bulk scale significant changes to the flow rate would
have to be effected to noticeably alter the oxidation rate of a graphite sample, though this effect could be more pronounced when oxygen is present.

### 2.4.6 Single Layer Oxidation

Some work has been conducted to try and understand the fundamental mechanisms of oxidation in graphite by observing the reaction at a very small, approaching atomistic scale. It is plausible that bulk oxidation rates could also be affected by graphite properties at a nano-scale, particularly when considering oxidation of irradiated graphite which has considerable fast neutron damage to the structure, and so a basic awareness of these mechanisms will likely be beneficial.

There is evidence from as far back as the 1950s suggesting that oxidation occurs more easily, approximately 17 times faster, along a basal plane edge than perpendicular to them\[^{81}\]. This has been investigated by Grisdale et al., who were passing an electrical current through carbon crystallite samples. It is known that carbon is more electrically conductive along the basal planes than perpendicular to them, and so the voltage could be monitored to determine when carbon oxidation, due to elevated temperatures from the resistivity of the samples, was occurring. This phenomenon therefore suggests that the reactivity of carbon will be at a maximum when its surface contains the largest fraction of crystallites with their basal plane perpendicular to the surface, demonstrating that crystal orientation and alignment on a microscopic scale could affect bulk oxidation behaviour. This is particularly applicable to highly ordered nuclear grade graphites.

Smith and Polley confirmed this idea that edge sites oxidise more easily in their paper\[^{82}\]. The sample types used for comparison were both carbon blacks, except that some had been graphitised at temperatures up to 2700°C, which will significantly reorder the material into structured planes. Their interpretation of how the crystallites might be arranged, adapted for use by Walker in his review, is presented in Figure 23.
It was indeed found that the graphitised samples in this configuration were far more resistant to oxidation than the ‘original’ samples. A much lesser increase in surface area is observed for a given weight loss, investigated using the BET adsorption isotherms of nitrogen method, for the graphitised samples. This suggests that the development of further active sites for oxidation, by oxidation along basal planes, was hindered in the relatively well ordered graphitised samples. It should be noted that this is particularly applicable to these carbon black samples, which form polyhedral shaped particles. Although the same could occur in graphite planes if the oxidation occurred perpendicular to the basal planes, the crystal orientation in graphite is less likely to provide as much of a ‘defensive’ closed structure as seen in carbon black. This is supported by an experiment conducted by Babout et al.\cite{83}, where the effects of controlled oxidation in a CO-CO$_2$ mix atmosphere at 900°C on the structure of PGA graphite samples were observed using X-ray tomography. The CO-CO$_2$ mix allowed for slow, controlled degradation of the sample, yielding a consistent ~3% weight loss a day up to ~35% weight loss. Although difficult to determine due to similar densities between the carbon material phases, it was seen using this 3-dimensional X-ray imaging technique that preferential oxidation of the binder phase had occurred, with more filler particles exposed in higher weight loss samples. The graphitised needle-shaped filler particles, as seen in Section 2.1.1 Figure 8, have a more defined, less random structure than the surrounding binder phase, and as such could have a more ‘closed’ structure, smaller surface area and a greater resistance to oxidation.
Further to this preferential oxidation along basal planes, work by Thomas\textsuperscript{84} explores the variation in oxidation rate depending on which ‘type’ of basal edge is reacting. Thomas demonstrates that there are two different types of basal edge that can occur, aptly known as the ‘armchair’ and ‘zig-zag’ configurations, as seen in Figure 24 below.

\textbf{Figure 24: A Graphite Basal Plane Demonstrating the Armchair and Zig-Zag Configuration Edge Sites}\textsuperscript{85}, original image adapted by the author

It has been found that these configuration edges behave slightly differently, and at an oxidation temperature of 846°C the reaction rate of the zig-zag face is approximately 1.20 times faster than that of the arm-chair face. This indicates that the oxidation behaviour of any graphite will be somewhat anisotropic and reflective of the relative fraction of edge sites. Jiang et al.\textsuperscript{86}, in reviewing Thomas’ paper, go on to explain that one means of determining this relative fraction of edge or defect sites on carbon, at which the oxidation process will occur, is to measure the amount of oxygen chemisorption at ‘active’ sites. Radovic et al.\textsuperscript{87}, amongst others, have studied the importance of carbon active sites in the oxidation process, stating that the ‘active surface area’ at which the reaction takes place is not equivalent to the ‘total surface area’. The ratio between these two surface areas will vary considerably depending on which form of carbon is analysed, and appears to be at least partially dependent on how ordered the carbon structure is, as demonstrated by Welham and Williams\textsuperscript{88} in their 1998 paper, looking at the effects of milling graphite and activated carbon on their oxidation behaviours. They found that the reactivity of both graphite and activated carbon with oxygen increased with milling time, and “the greatest increase was concomitant with a decrease in graphite crystallinity”, which is reasonable given that basal plane sites, as found in abundance in undamaged graphite, are thought to be less reactive than edge sites. As will be seen, this is particularly relevant, to the reactivity
of irradiated graphite, which will inevitably be less ordered and thus potentially more reactive than virgin graphite, as a consequence of fast neutron damage.

The work conducted by Jiang et al.\textsuperscript{[86]} demonstrates the influence of the relative fraction of edge sites on the oxidation behaviour of natural graphite, used for its predictable prismatic structure. They studied natural graphite samples with differing average particle sizes, from 2 to 40 µm, and were able to use Thermal Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) to demonstrate that with increasing average particle size came a reduction in specific surface area, and consequently higher ‘ignition’ temperature in flowing air, consistent with other literature. This, however, does not truly indicate the concentration of ‘active’ edge sites, and so the authors use a simple geometric model to estimate the fraction of edge sites; this is not a simple derivation, and is dependent on several physical parameters, such as the basal plane length, the thickness of edge planes, the size of the layer planes, the crystallite parameter and the distance between the layer planes. Using these factors, coupled with simultaneous TGA and DTA, the authors were able to demonstrate that the graphite samples with the highest calculated fraction of edge sites had the lowest temperature of ignition. It should be emphasised that this was a calculated fraction of edge sites, rather than an experimentally determined fraction, though the results coincide well with the literature indicating that perhaps the theory is correct.

2.4.7 Oxidation of Irradiated Graphite

In the 1950s, when graphite moderated reactors were being constructed in the UK, Walker et al.\textsuperscript{[52]} were aware that concerns had been raised over “the effects of irradiation on the rate of reaction of the graphite with gases”. Though the fundamental reactions and theories are the same, irradiated graphite cannot be said to behave in precisely the same manner as virgin material.

Kosiba and Dienes\textsuperscript{[89]} examined the influence of both neutron damage and gamma-radiation on the rate of oxidation of graphite in 1957. They found that graphite exposed to a neutron dose of approximately $4 \times 10^{20}$ neutrons/cm$^2$, which is a similar order of magnitude to that experienced by UK reactor graphites over their operational lifetime\textsuperscript{[90]}, irradiated at room temperature, which is not typical of UK power production reactor conditions, would have a reactivity around a factor of 6 times higher than that of virgin material between 250 and 450°C in air. This disparity in oxidation rates between irradiated...
and unirradiated material is observed to decrease with increasing temperature, as seen in Figure 25\textsuperscript{[89]}.

Figure 25: Arrhenius Plots for the Rate of Oxidation in Air of both Unirradiated and Previously Irradiated Spectroscopic Graphite, as presented by Walker\textsuperscript{[52]}

It was concluded from this that displaced atoms, a feature of neutron damage, exert a significant influence on the rate of oxidation. The authors decided that since this elevated reaction rate in irradiated graphite persists into high weight losses, the displaced atoms themselves are not undergoing preferential oxidation but are somehow increasing the overall reactivity of the graphite. The conclusions reached by Kosiba and Dienes do align somewhat with later literature, such as the previously discussed work by Welham and Williams\textsuperscript{[88]} who concluded that oxidation rates rise with increasing disorder of the carbon structure; neutron damage is known to cause disorder and displace atoms in graphitic planes, which will facilitate a faster rate of reaction with an oxidant.

Lang et al.\textsuperscript{[91]} investigated the effects of pre-irradiation on the thermal oxidation rate of purified graphite in air, published in 1967. They found that a sample previously irradiated with fast neutrons to doses of a comparable magnitude to reactor conditions, in
a vacuum at room temperature, exhibited a large increase in the initial corrosion rate when oxidising in air at 438°C, up to a factor 60 larger than expected. This effect appears short-lived, and after around 0.04% weight loss to the sample the oxidation rate settles at approximately four times that found for non-irradiated graphite. A similarly irradiated sample oxidised at 620°C in dry air, a temperature more appropriate to those likely required for treatment of graphite samples, showed a relative oxidation rate approximately twice that of unirradiated reference graphite. These results correlate with the data presented in Figure 25, as the difference in oxidation rates has reduced with increasing temperature. The authors also induce radiolytic oxidation to 16% weight loss in a sample of purified graphite by irradiation in CO₂ at 200°C, which is more reflective of conditions in a Magnox reactor, and find that the oxidation rate has increased compared to those samples irradiated in a vacuum, indicating that both prior radiolytic oxidation and fast neutron damage will influence the final oxidation rate of the graphite.

In support of these, a more recent 2012 conference paper considering thermal treatment of liquid nitrogen immersed irradiated graphites demonstrates that at 900°C in an argon cover gas the carbon gasification rates for unirradiated and irradiated were 1.72 and 2.49 x10⁻⁴ g/hr respectively, whilst at an elevated temperature of 1400°C the rates for unirradiated and irradiated were 4.49 and 4.27 x10⁻⁴ g/hr⁹². It should be noted that for inert treatment, any small amounts of oxidation will likely source from oxygen adsorbed to the surface of the sample, residual air from installation of the sample into the furnace, impurities in the cover gas or minor leaks in the system. This data does demonstrate however that, consistent to the work by Kosiba and Dienes⁸⁹, there do appear to be more active oxidation sites in the irradiated graphite and the discrepancy between the unirradiated and irradiated oxidation rates does reduce with increasing temperature.

Conversely, a similar paper looking at treatment of liquid nitrogen immersed irradiated graphitic foams and NBG-18, a nuclear grade graphite, suggests that ‘most unirradiated graphites oxidised at a slightly higher rate than their irradiated counterparts’⁵⁴, which directly contradicts the previous sources discussed. All of the experiments presented in this paper involve oxidation at relatively high temperatures, ranging from 700 to 1400°C and as such it is possible that the discrepancy between irradiated and unirradiated oxidation rates has been negated by the oxidation temperatures utilised, as per Figure 25, and any observations of a trend in oxidation rates could in this instance be statistical noise. It is noted in the paper that most studies in the literature have not been performed on graphitic foam, which may behave differently,
although it is unclear whether the NBG-18 is also observed to behave similarly. The author goes on to suggest that this phenomenon is likely a result of a change in the surface’s chemical environment.

For graphite material irradiated in a Magnox- or AGR-design reactor which utilise a carbon dioxide coolant, there are two further competing processes which might influence oxidation behaviour, namely the evolution of porosity and surface area due to gamma irradiation-induced radiolytic oxidation[^69] and the closure of porosity due to neutron irradiation-induced dimensional change[^20]. The respective effects of these processes will vary with position and degree of irradiation in the core.

It is difficult to draw conclusions from the small amount of literature available surrounding this topic as to whether irradiation damage could augment or inhibit oxidation of graphite specimens. Aside from a single source, the literature appears to suggest that a damaged, disordered graphitic structure which has been radiolytically oxidised could enhance the reactivity, with buckled basal planes, vacancies and interstitials presenting basal edges, which are known from Section 2.4.6 to oxidise more quickly, and so it is reasonable to expect that irradiated PGA graphite samples may oxidise more readily than their unirradiated equals.
2.4.8 Oxidation of Carbonaceous Deposits

As seen in Section 2.3.5, it is known that ‘sooty’ carbonaceous deposits occur in graphite due to complex reactions including polymerisation of carbon monoxide or methane in the gas phase, induced by the intense radiation field\textsuperscript{[56, 67]}. This carbonaceous deposit can act as a useful sacrificial layer preventing radiolytic oxidation damage to graphite surfaces, though also as an undesirable thermal insulator when it deposits onto components such as the fuel cladding, where obstruction of the transfer of heat energy away from the fuel can cause local hotspots and changes in ceramic structure\textsuperscript{[93]}.

The levels of carbonaceous deposition in UK graphite moderated reactors are routinely monitored during graphite trepanning campaigns, whereby the deposit is defined as “material that oxidises at a higher rate than substrate graphite”\textsuperscript{[50]}. A Serco Assurance report\textsuperscript{[50]} notes that this could also refer to material that has a higher rate of oxidation due to catalytic contamination, since making a distinction between this material and any equally reactive sooty deposit will be difficult. This effect of catalytic oxidation will be discussed further in Section 2.4.9.

2.4.9 Graphite Oxidation by Impurity Catalysis

It is well known and documented that metal impurities or additives can affect the oxidation of graphite, some of which will even remain in nuclear grade graphite after the relatively intensive manufacturing process. Walker\textsuperscript{[52]} states that although some metals such as iron, cobalt or copper are known to accelerate the rate of oxidation along a basal plane, other metals such as boron, titanium or tungsten inhibit the reactivity. The precise mechanism by which catalysis occurs in graphite is largely dependent on the temperature, the chemical nature and surface area of the impurity in question, according to McKee\textsuperscript{[94]}, who has studied many different catalytic oxidation reactions of graphite. The catalytic reaction is known to promote either the formation of etch pits, when for example iron is present, or channelling along the basal plane, for impurities such as copper or cobalt.

In previous work, McKee\textsuperscript{[95]} has studied the copper-catalysed oxidation of graphite in some detail, using thermal gravimetric analysis, finding that copper oxide is the active species between 500 and 800\degree C. McKee states that the catalytic effect involves the “localised reduction of CuO by graphite, followed by rapid re-oxidation of the resulting metal”, which causes channelling along a graphite basal plane as the catalytic particle
effectively oxidises a path through the graphite. Images of this channelling phenomenon have been produced by transmission electron microscopy (TEM), which can be seen in Figure 26 for cobalt oxide.

![Figure 26: Catalytic Channelling by Cobalt Oxide Particles on Natural Graphite Flake During Oxidation at 700°C in O₂](image)

A document produced by Snead and Burchell\cite{78} of Oak Ridge National Laboratory, discussing oxidation of high quality graphite, states that “the onset [temperature] of oxidation can be significantly increased by utilising highly crystalline materials with very low metallic impurity concentration.” The authors then give the example that if a commercially available intermediate quality graphite were to be purified, the oxidation onset temperature could be increased by approximately 100°C, indicating the importance of purification during manufacture and the magnitude of the catalytic effect.

It is very difficult to model or predict the behaviour due to catalysis in a bulk piece of graphite because the distribution of catalytic impurities is unlikely to be homogeneous, the corresponding effects are relatively local, and the temperature dependence and behaviour of each catalyst differ somewhat. It has been seen in Section 2.2 of this literature review that nuclear grade graphites for UK Magnox- and AGR-design reactor moderator
material are manufactured to a very high purity, though even these ppm levels of impurity encountered could have an influence on the bulk oxidation behaviour.

2.4.10 Summary of Section 2.4

The main findings of this section of the literature review, appropriate to thermal treatment of irradiated graphite, are:

- There are multiple oxidants which could contribute to the oxidation of irradiated graphite, including oxygen, carbon dioxide, steam and hydrogen, though the relative reaction rate of carbon with oxygen far exceeds that of other molecules.
- A number of controllable and uncontrollable oxidation influencing factors have been identified for the experimental arrangement utilised, with discussion as to how these will influence the oxidation behaviour and how they might be controlled.
- On a graphite bulk oxidation scale, the variation in oxidation regimes with temperature has been described. It is found that the location of mass loss to an irradiated graphite sample during treatment in an oxidising atmosphere will likely vary depending on the temperatures utilised, with high temperature oxidation corroding the outer geometric surfaces of the sample, low temperatures allowing for oxygen ingress into the sample before reaction and consequently corroding all surfaces throughout the internal porosity.
- The precise transition temperatures between oxidation regimes varies depending on the source data and will likely be affected by the graphite grade in question, its density, microstructure and impurity content, which could assist in explaining the inconsistency in the literature. Generally, oxidation temperatures below 600°C in oxygen are thought to be Regime I, and temperatures above 900°C thought to be Regime III.
- It is seen that the oxidation rate increases with increasing oxidant cover gas pressure, though the reaction rate approximately doubles for a factor of four increase in pressure irrespective of temperature suggesting that significant pressure changes are required to influence the oxidation behaviour.
The fundamentals of oxidation behaviour have been investigated on an atomic scale, where it is found that oxidation occurs more readily along the basal planes of graphite, in a slightly anisotropic fashion whereby the ‘zig-zag’ face of a basal plane will oxidise approximately 1.2 times faster than the perpendicular ‘armchair’ face (Figure 24).

The majority of sources suggest that neutron irradiated graphite oxidises more readily than similar unirradiated graphite, likely due to irradiation damage causing disorder in the structure, damaging basal planes and causing dislocations, producing a greater number of active sites available for oxidation. The disparity between the irradiated and unirradiated oxidation rates appears to diminish with increasing temperature.

Carbonaceous deposits, which form on the graphite surfaces during reactor operation due to complex irradiation induced interactions in the coolant phase, are known to oxidise more readily than the graphite substrate, which is how the presence of these are identified on irradiated graphite samples trepanned from UK reactor cores.

Catalytic oxidation of graphite can occur locally if some metallic impurities are present, significantly increasing the overall rate of oxidation of the bulk material. Nuclear grade graphite is usually purified to ppm levels of impurities, though even these can have some influence, reinforcing the importance of purity in graphite used for neutron moderator material in a reactor environment.
2.5 Thermal Treatment

As seen in Section 1.5, a disposal route has not yet been decided for UK irradiated graphite waste, though the UK Nuclear Decommissioning Authority baseline strategy for graphite waste in England and Wales is burial in a geological repository. Many alternative solutions for graphite waste have been proposed, and will be considered by Radioactive Waste Management (RWM) prior to its disposal, one of which is decontamination by thermal treatment, which is a process under investigation worldwide. This section of the literature review will now assess the current global knowledge of thermal decontamination of irradiated graphite, for inert and partial oxygen environments specifically, drawing on experience from many nations and reactor designs, for comparison and applicability to UK irradiated graphite waste.

2.5.1 Inert Atmosphere Treatment

One idea for removal of radioisotopes, particularly those that are potentially mobile in the graphitic lattice, such as $^3$H, or located near a geometric or pore surface, such as $^{14}$C, is to treat the samples at elevated temperatures in an inert environment, using only temperature related effects and the reaction of graphite with its surface bound adsorbed oxygen to remove a significant proportion of the radioactivity into the gas phase[92], in the forms of HT and HTO for $^3$H and $^{14}$CO and $^{14}$CO$_2$ for $^{14}$C.

A research group from Forschungszentrum Jülich (FZJ) research institute, contributors to the EU CARBOWASTE project outlined in Section 1.6, studied radioactive release in irradiated graphite by thermal processes[33]. Their experiment was designed to observe the release of $^3$H and $^{14}$C from irradiated graphite at elevated temperatures in both a flowing inert and reduced oxygen environment, using a tube furnace and bubbler system, and liquid scintillation counting to analyse the beta-particle emitting radioisotopes caught in bubblers. The experimental setup used can be seen in the schematic in Figure 27. This is the same experimental arrangement as described by the same authors in a similar paper considering thermal treatment of graphite[65], which will be discussed in parallel.
Following gasification of a sample, this experimental arrangement allows for capture of radioisotopes at multiple stages in the process, such that radioactive releases in the form of HT and CO can be analysed independently of the HTO and CO₂ releases; unlike the latter pair, the former molecules will travel through the bubbler train relatively unhindered until they undergo oxidation in the oxidiser, seen here after bubbler 4, after which they will become susceptible to capture in bubblers 5 to 8. Initial HTO capture occurs in 0.1M HNO₃ at washing bottles 1 and 2, and CO₂ from the sample will be captured in bubblers 3 and 4 using 4M NaOH.

Care is required with a long system of radioisotope traps and apparatus such as this that there are no leaks in any of the joints, which is easily supported in the first half of the system by the gas analyser, and that the radioactivity, particularly superscript ³H, has been taken up into the tubing or apparatus, affecting the measurement. Extraction and scintillation counting of multiple samples from the separate washing bottles for each isotope introduces the possibility of greater uncertainty in the measurement obtained. The method for taking a liquid sample from the washing bottles is not described in detail, and so it can only be assumed that each sample withdrawn was sufficiently mixed such that the radioactivity was evenly distributed in the fluid before withdrawal, and that gaseous losses or introductions were not incurred. This system does allow for a ‘real time’ gas analysis to be conducted,
indicating the proportions of CO and CO₂ produced during the treatment experiments, which could yield useful information about the mechanics of the oxidation process occurring. The ability to withdraw samples from the bubblers at any instance during the treatment allows an approximate time profile for the release from individual samples to be developed.

The limitations to this experimental arrangement are acknowledged by the authors, lending credibility to the data produced. There were issues with both the oxygen detector and the amount of oxygen present in the system; the oxygen detector is sensitive to pressure fluctuations which are largely unavoidable in a system such as this with bubblers, and the amount of oxygen ingress to the system following installation of the sample into the combustion zone caused an initial spike in oxidation. The authors accept that analysis of the oxygen content is only semi-quantitative.

The three sample types used for these experiments were from the Merlin pool-type test reactor thermal column, trepanned from Saint-Laurent A2 (SLA2) UNGG reactor, which is a carbon dioxide gas-cooled reactor similar to the UK-designed Magnox reactors, and graphite from Oldbury Magnox reactor 2, though the provenance of the Magnox reactor graphite is not described.

The results of inert atmosphere experiments conducted at 1100°C for the Oldbury Magnox reactor samples and 1300°C for the remainder, in a nitrogen cover gas, are shown in Figure 28 to Figure 31. It should be noted that for Figure 28 and Figure 30 the quoted absolute releases are estimates based on expected inventories, increasing the uncertainty surrounding this data especially given then known inhomogeneous distribution of radioactivity in irradiated graphite, whereas the release fractions for Figure 29 and Figure 31 are obtained by summation following complete gasification of the samples to determine the total inventory.
Figure 28: $^3\text{H}$ Release from Graphite Bulk Samples in Nitrogen at 1300°C\textsuperscript{(33)}

Figure 29: Release of $^3\text{H}$ from Oldbury Reactor 2 Graphite in Nitrogen at 1100°C (Mass loss after 11h: 0.14%\textsuperscript{(65)})
Figure 30: $^{14}$C Release from Graphite Bulk Samples in Nitrogen at 1300°C\(^{[33]}\)

Figure 31: Release of $^{14}$C from Oldbury Reactor 2 Graphite in Nitrogen at 1100°C (mass loss after 11h: 0.14%)\(^{[35]}\)

It can be seen from these graphs that in most instances, excluding the Oldbury Magnox reactor graphite data, the $^3$H release was far more successful than the relatively small releases of $^{14}$C observed, yielding over 90% final $^3$H release for the Merlin samples and
over 60% for the SLA2 sample. Although there is a noticeable difference in release efficiency between the 1100°C and 1300°C data, these experiments were performed on different graphites and so there are too many variables to identify from these graphs whether this may be a temperature effect or characteristic of the graphites in question, with their differing microstructures, impurity contents and irradiation histories.

The higher weight losses achieved in Figure 28 and Figure 30, indicated by the number preceding ‘M’ in the legend, and ¹⁴C release seen in one Merlin graphite sample more so than the other is a consequence of author acknowledged cracking glassware allowing a small amount of oxygen into the system. The initial mass and geometry of the samples is unknown. The sharp rise in ³H release for the SLA2 sample between approximately 6 and 10 hours is proposed by the authors to be a delayed release of ³H, as there is no mirror effect in the ¹⁴C data for this sample, nor any indication from the gas analyser to suggest air ingress, malfunction or an artefact of the system. One phenomenon that should be noted is that there is an apparent faster initial release rate for both radioisotopes at both temperatures investigated in all of the samples except one, the SLA2 sample. This could be indicative of exhaustion of any residual oxygen from installation of the sample, or the effects of a diffusion process as suggested by Vulpius.

A programme of research by Podruzhina, contributing to a doctoral thesis produced within the same institution as performed the treatment research above, FZJ, investigates thermal treatment of slightly different irradiated graphite samples, this time including graphite powder and solid material from the Merlin pool-type, and powder from the AVR pebble bed-design test reactor. Powder samples will have a significantly higher surface area for reaction, compared to its solid counterpart. It should be highlighted that these samples are derived from reactors quite dissimilar to the Magnox reactors and AGRs found in the UK, though the behaviour of the ³H and ¹⁴C release during treatment may still be similar. The experimental arrangement is similar to that shown in Figure 27, except that the second washing bottle for trapping ³H in 0.1M HNO₃ has been removed from the system and the gas analyser replaced with an infrared spectrometer. Thus, similar assumptions and limitations apply to this data as those seen above. The samples for this work were taken to full destruction, and their total radioisotopic inventory determined, yielding a better indication of the true releases during the treatment, as opposed to comparison with an estimated inventory.
The results for $^3$H release in an inert atmosphere for the graphites described are seen in Figure 32.

![Figure 32: $^3$H Release from Merlin and AVR Graphite in an Argon Atmosphere](image)

Similarly to the behaviour seen in Figure 28 and Figure 29, a faster rate of $^3$H release is observed towards the start of the experiment than elsewhere, which could either be an effect of treatment at an elevated temperature in an inert environment, such as a diffusion process as suggested by Vulpius$^{65}$, due to residual oxygen from ingress during sample placement, as acknowledged for the previous FZJ data, or air ingress during the experiments. A defined temperature effect does appear to be apparent, however, as noticeably less $^3$H is released from the graphite at lower temperatures. The increase in the release rate in the Merlin graphite powder at approximately 10 hours is thought to be due to air ingress$^{51}$. There is little apparent difference in $^3$H release rates between the solid and powdered Merlin graphite samples. The $^{14}$C releases occurring during this experiment are presented in Figure 33.
A similar trend of an initially faster removal rate can be deduced from this data, though it is less pronounced for $^{14}$C than $^3$H. The effect of the air ingress at 10 hours for the Merlin graphite powder sample appears to have more of an influence on the $^{14}$C release than the $^3$H release suggesting that oxygen may play a pivotal role in radiocarbon extraction.

A 2013 presentation delivered by Rizzato et al.\cite{96}, also of FZJ, contains the graphs seen in Figure 34 and Figure 35 for $^3$H and $^{14}$C release in an inert environment. This time the fractional release of radioisotopes is compared to the weight loss of the sample, which yields an indication as to the remaining sample’s structural integrity and release efficiency with mass loss. The experimental arrangement is the same as that represented in Figure 27.
Since the experimental arrangement is the same, initial high release rates of $^3$H and $^{14}$C in this inert environment could be as a consequence of air ingress whilst inserting the sample into the furnace. At these temperatures, $^3$H extraction is more successful than $^{14}$C, particularly at 1300°C. Since there is only a single sample treated in nitrogen, which is also the only sample treated at an elevated temperature of 1300°C, it is not clear from these
experiments whether it is the temperature or cover gas that has caused the efficient fractional release of $^3$H of over 200:1 with weight loss. The initial faster rate of release can also be seen in this data, consistent with previous analyses. Using the $^3$H release data presented thus far, a positive correlation between $^3$H release in an inert atmosphere and temperature can be drawn. The author of the presentation has included a note that it is the exhaustion of reactants that is the limiting factor for this experiment. Walker’s[52] review paper notes that a proportion of chemisorbed oxygen has been observed on graphite samples, and suggests that this can only be removed from the surface as oxides of carbon, corresponding to the exhaustion of reactants noted by FZJ. The overall release of $^{14}$C during these experiments was relatively small, with the largest release yielding less than 15% $^{14}$C removal.

Inert environment treatment appears to be mostly effective for $^3$H release from irradiated graphite, potentially through a process of diffusion[65]. It should be noted that despite the many different grades and forms of graphite being examined, all of the data considered has arisen from the same research institution using the same experimental apparatus and will therefore be subject to the same experimental limitations and uncertainties, and potentially consistent errors. Thus far, only $^3$H and $^{14}$C releases have been considered, as the dominant radioisotopes of concern, with the behaviour of other radioisotopes neglected.

### 2.5.2 Oxidising Atmosphere Treatment

The addition of oxygen to the treatment process could both accelerate and direct the release of radioisotopes by chemical oxidation and corrosion to the graphite surface. As seen in Section 2.4 there are a wide array of factors that can affect the oxidation behaviour of graphite, and so careful selection of experimental parameters should be made to obtain a desired result.

As a continuation of the work detailed above, seen in Figure 29 and Figure 31, the researchers at FZJ also performed some experiments on the same graphites with the addition of minute concentrations of oxygen, of 0.1 or 0.3% depending on the data set, the results for which are found in Figure 36 and Figure 37[33].
Figure 36: $^3$H Release from Graphite Bulk Samples in Nitrogen - Low Oxygen Environments\textsuperscript{[33]}

Figure 37: $^{14}$C Release from Graphite Bulk Samples in Nitrogen - Low Oxygen Environments\textsuperscript{[33]}
Under these conditions all graphite types except for the Merlin thermal column graphite retain the majority of their $^3$H inventory, and that excluding a single somewhat anomalous Magnox reactor graphite sample in which 100% of the $^{14}$C was released incurring only a 0.7% sample mass loss, the other $^{14}$C releases including another Magnox sample are generally less than 10%. These results are all estimates based on expected inventories, and as such the author believes the high fractional $^{14}$C release rates achieved from the Magnox sample could be a consequence of underestimating the actual inventory of the sample. Although difficult to see because of some of the data lines’ proximity with the x-axis, the initial fast rate of release can also be observed for these experiments including small amounts of oxygen in the system. The $^3$H and $^{14}$C release rates achieved for the Merlin graphite samples in Figure 36 are not dissimilar to those achieved previously by Podruzhina$^{[51]}$, demonstrating some consistency in results though little benefit from addition of small amounts of oxygen into the cover gas. It is possible that either the small addition of oxygen was not sufficient to influence the data in any noticeable way, or that the temperature, at 900°C, is so high that the corrosion is operating within the third boundary layer-controlled oxidation regime, attacking only the outer geometric surface of the sample and neglecting releases from deeper within the sample which may be attainable at lower operating temperatures.

The authors use these results to conclude that “radiocarbon is not homogeneously located in the graphite body: it is chemisorbed at the inner and outer surfaces at the pores of the graphite structure where nitrogen was absorbed before irradiation” $^{[33]}$. Though the data suggests that a preferential fractional release can be achieved and therefore the $^{14}$C may not be evenly distributed, arguably more investigation would be required to definitively prove that the release was not a consequence of another chemical- or temperature-based process, and that there is not a significant contribution from any $^{13}$C-derived radiocarbon locked into the graphitic structure. It is possible that the author has other background knowledge and data that are not cited in this report, which may have contributed in drawing them to their conclusion.

A group at Idaho State University have also performed thermal treatment on irradiated graphite specimens using varying concentrations of oxygen$^{[54]}$, this time following artificially inducing carbon-14 formation at the graphite sample surface. NBG-18 nuclear grade graphite and high surface area graphitic foam samples have been immersed in liquid nitrogen to significantly increase the nitrogen content at the graphite surface before being transferred to a materials test reactor and exposed to a flux of neutrons. It is known from
previous sections of this literature review that nitrogen, one of the precursor isotopes of $^{14}\text{C}$, has a relatively large neutron absorption cross section, and as such one might expect that a large proportion of nitrogen-derived $^{14}\text{C}$ will be induced at the surface of these samples. The samples are treated in differing reduced oxygen atmospheres and temperatures. The oxygen concentrations used were 0, 3 and 5% $\text{O}_2$ in an argon balance gas, and the temperatures used were 700, 900 and 1400$^\circ\text{C}$. Figure 38 shows a schematic of the experimental arrangement for this work.

*Figure 38: Experimental Design for Thermal Treatment of Nuclear Graphite to Remove $^{14}\text{C}$* [54]

The instrument ‘G.A.’ in Figure 38 refers to a gas analyser. Similarly to the FZJ experimental arrangement, the oxidised graphite passes a gas analyser before catalytic oxidation in a designated oxidising furnace and then collection in a bubbler system. The fractional releases of $^{14}\text{C}$ achieved, determined by full oxidation of the sample after treatment to determine the actual full inventory of each sample, can be seen in Figure 39.
It should be remembered that the dominant source of $^{14}$C in these samples has been deliberately induced at the sample surface, in contrast to power production reactor samples where the distribution of the $^{14}$C can be somewhat more complex, as explored in Section 2.3.4. The graph in Figure 39, though relatively difficult to interpret as the $^{12}$C and $^{14}$C releases for each treatment regime are plotted separately, does indicate that generally the fractional release of $^{14}$C in most samples is significantly higher than that of the weight loss, with many samples appearing to release greater than 80-90% of their $^{14}$C inventory. The initial high release rate seen in previous FZJ data is also observed here, though it is unclear whether this is a chemical phenomenon, air ingress during sample installation or a combination of the two; a gas analyser is installed to the circuit so it is assumed that the operator would not have allowed oxidation to occur with residual air registering in the gas phase. The author suggests from their results that ‘the oxygen level has the greatest influence on the selective release rate followed by temperature’, with lesser concentrations of oxygen appearing to be more effective for selective removal of $^{14}$C. Neither temperature explored, 700°C nor 1400°C, appears more effective than the other despite a likely clear distinction between oxidation regimes. This could be because of sample geometry, since a large concentration of $^{14}$C has been induced at the sample surface and as such, depending on the geometry of the sample, each oxidation regime could be similarly effective for removal under these conditions. For a large sample requiring significant oxidant

![Figure 39: Normalised Average Percent of Carbon-12 and Carbon-14 Released During Time at Experiment Temperature](image-url)
penetration depths into the bulk to oxidise the surfaces of internal pores, one might expect oxidation experiments at 700°C to be the most effective for selective $^{14}$C removal.

Some treatment of irradiated graphite research has also been conducted in Russia\cite{97}, using graphites obtained from the Leypunsky Institute for Physics and Power Engineering (IPPE) and Kursk Nuclear Power Plant, which is an RBMK design. The precise source of the IPPE graphite is unknown as there were multiple test reactors onsite. As noted in Section 2.3.2, RBMK graphite is usually irradiated in a helium-nitrogen environment and so one may expect a higher proportion of nitrogen-derived $^{14}$C to be found at the graphite surface compared to UK graphites, as there is no bulk mass loss through radiolytic oxidation coupled with a higher concentration of nitrogen in the immediate environment of the graphite surfaces. The samples have been treated at 650°C, typically oxidation regime I or II, in a flow of air as a cover gas, though details of the precise experimental arrangement or how activity measurements have been made are unavailable. The results obtained are shown in Figure 40 and Figure 41.

![Graphite mass loss vs. time of oxidation](image)

*Figure 40: Decontamination of Reactor Graphite Bushings from IPPE - Graphite Mass Loss and $^{14}$C Release with Treatment at 650°C*\cite{97}
Again, a preferential fractional release can be observed in each case, though the radiocarbon in the IPPE graphite appears to be more easily liberated than that of the Kursk graphite. Relatively high graphite mass losses are incurred in the Kursk graphite, suggesting that perhaps this treatment regime is not so effective for this source of irradiated graphite. It is probable that the high efficiencies of this treatment compared to other sources of data could be attributable to a large concentration of $^{14}$C found at the surface of RBMK reactor graphite attributable to its irradiation in a helium-nitrogen atmosphere, allowing for this treatment technique to be particularly effective for RBMK graphite. It should be noted that although the selective removal efficiency of $^{14}$C may be higher for RBMK graphites, the activities of $^{14}$C encountered are significantly higher than those in other reactor types. Though the simplicity of using air as a cover gas could certainly have its benefits, the consequent concentration of oxygen used is considerably higher than those utilised in the rest of the literature reviewed. The data presented in Figure 39, from the liquid nitrogen immersion experiments, suggests that a higher concentration of oxygen is not so efficient for selective removal of $^{14}$C, which appears to be supported by the data produced through this treatment experiment in air where large sample mass losses are incurred, though the sources of graphite treated are so different one would have to be cautious drawing conclusions from this. The mass losses encountered for these experiments are large, up to 55%, at which point any form of remaining structural integrity in the graphite is unlikely.
Employing a relatively low temperature for the treatment of this graphite will allow ingress of some of the oxygen in the cover gas to the internal porosity of the sample, as per oxidation regime I or II\(^{[52]}\) causing an internal corrosion of pore surfaces through at least some of the internal porosity of the sample.

It is seen in this Section, from the large quantity of available FZJ data, that the introduction of very small amounts of oxygen to the system do not appear to drastically alter the radioisotope release characteristics, although arguably the temperatures utilised are so high that the oxidation will likely occur in the third oxidation regime, at the outer geometric surfaces, reducing the effectiveness of the oxygen to remove radiocarbon through the remainder of the bulk material. First oxidation regime thermal treatment in air appears particularly effective for RBMK-derived graphites, which is to be expected because they have been irradiated in a helium-nitrogen environment, and as such the distribution of \(^{14}\)C will likely predominate at the graphite surfaces, and so the combination of low temperature treatment allowing oxidant to penetrate throughout the majority of the material and the presence of a high concentration of surface \(^{14}\)C yield high removal rates. It should be emphasised that the work so far has concentrated on the \(^3\)H and \(^{14}\)C behaviours, as these are generally the radioisotopes of highest activity and greatest concern in irradiated graphite, leaving analysis of the metallic radioisotopes neglected.

### 2.5.3 Thermal Treatment of Graphite: A Model

A 2005 modelling paper published by Yang et al.\(^{[98]}\) investigates the effect of excess air incineration on irradiated graphite samples, in order to understand the chemical nature of radioactive species under these conditions using equilibrium model analysis, in the context of developing an incineration plant for disposal of irradiated graphite waste; chemically, the radioactive isotopes will behave as their inactive equivalents. The authors assume that thermodynamic equilibrium is maintained in the thermal treatment furnace and that radioactive species are homogeneously distributed, or ‘intimately mixed’, throughout the graphite, which as seen previously is not necessarily the case. The initial impurity data has been experimentally determined using graphite from the pool-type Korea Research Reactor I (KRR1), yielding 99.8% fixed carbon, <200 ppm ash content and <0.001% hydrogen and oxygen content. A specific note is included regarding the chlorine impurity, which has been observed to vary greatly between 0.1 and 49 ppm, and so two separate models have been produced including 0 and 50 ppm chlorine content respectively. This
disparity in measurements is consistent with the chlorine measurements discussed in the literature in Section 2.2. It should be emphasised that a 50% excess of air is used for these models, to mimic an incineration process, and as such the graphite will undergo complete gasification and destruction. This is not so dissimilar to the processes expected during thermal treatment in a limited oxygen environment, where partial destruction will occur. The variety of radioisotopes analysed in these incineration models encompass all of the prominent radioisotopes previously identified in Section 2.2.2, which are not presented in other works reviewed and are listed below:

\[ ^{3}H, ^{14}C, ^{36}Cl, ^{60}Co, ^{90}Sr/^{90}Y, ^{133}Ba, ^{134}Cs, ^{137}Cs, ^{152}Eu, ^{154}Eu, ^{155}Eu \text{ and } ^{241}Am \]

The authors state that the results of these models show \(^{3}H, ^{14}C\) and \(^{36}Cl\) will partition into their gas phase under these conditions, though temperature ranges are not provided, with the likely chemical forms being HTO for tritium, \(^{14}CO_{2}\) for the radiocarbon and \(H^{36}Cl\) for radiochlorine.

It is found that for treatment temperatures below approximately 1000\(^{\circ}\)C, with no HCl present, barium exists almost solely as a solid phase, \(BaCO_{3}\), and is predominantly solid \(BaCl_{2}\) at 1000\(^{\circ}\)C even when gaseous HCl is present. This can be seen in the equilibrium distributions presented in Figure 42 and Figure 43.

![Figure 42: Equilibrium Distributions of Barium and Strontium Species under Incineration Atmospheres: (a) in the absence of HCl(g)][98]
The models indicate that “the volatility of strontium is relatively small when compared to that of barium” [98], with less than 10% of the strontium existing as gaseous \( \text{Sr(OH)}_2 \) at temperatures of 1200°C, irrespective of HCl presence. Figure 42 and Figure 43 suggest that below approximately 1000°C strontium will be stable, and will exist as solid phase \( \text{SrO} \) or \( \text{SrCO}_3 \).

The behaviour of caesium is somewhat more complex, and is affected by the surrounding gaseous environment and temperature. In the absence of HCl, caesium exists predominantly as \( \text{CsOH(g)} \) above 1000°C, whilst below 500°C most caesium species exist as \( \text{CsNO}_3(g) \), with a varying proportion of the two phases existing between these temperatures. The equilibrium analyses suggest that caesium will not exist in a solid phase below 300°C. In the presence of HCl, the volatility of caesium is expected to decrease significantly, as the most stable form of caesium is caesium chloride, \( \text{CsCl} \). Above 600°C this \( \text{CsCl} \) will become entirely gaseous. For thermal treatment of irradiated graphites, the chlorine content is largely unknown and variable, and so the possibility exists that the caesium behaviour will vary between samples undergoing thermal treatment, though will likely be gaseous at temperatures exceeding 300°C in air, or 600°C if HCl is present.

Cobalt is found to be unaffected by HCl in the cover gas, and likely to exist as solid \( \text{Co}_3\text{O}_4 \) at temperatures below 600°C and solid \( \text{CoO} \) above 600°C. It is possible that small
amounts of CoO(g) could be formed at temperatures over 1000°C, though the theoretical maximum volatilility is seen to remain below 13% at temperatures up to 1200°C, and so this will not present any significant concern during treatment at temperatures below this.

The models find that europium and americium isotopes will not transform into the gas phase at the temperatures considered here, irrespective of the presence of HCl. It can be seen from Figure 44 and Figure 45 and that there are no gaseous oxides or hydroxides of europium or americium even at 1200°C. The single partially gaseous element in the diagram is uranium, a fraction of which is in the form of UO₃(g) above 800°C.

*Figure 44: Equilibrium Distributions of Europium, Americium and Uranium Species under Incineration Atmospheres: (a) in the absence of HCl(g)²⁹⁸*
This modelling paper allows predictions to be drawn as to the behaviour of the metallic radioisotopes in irradiated graphite, such as $^{60}$Co, in an oxidising atmosphere at elevated temperatures, which the remainder of the experimental literature reviewed does not. The chemical nature of $^{36}$Cl remains slightly ambiguous, with this paper suggesting that it will volatilise into gaseous HCl with ease at elevated temperatures. The majority of the metallic radioisotopes will remain stable in their solid form, excluding caesium which is likely to volatilise and then condense if the temperature reduces to below 300°C. As well as providing a useful indicator as to the oxidation behaviour of the dominant radioisotopes found in irradiated graphite, this paper allows for some confidence to the safety of an operator of a laboratory scale thermal treatment system, yielding useful indications as to the final locations of various radioisotopes.
2.5.4 Summary of Section 2.5

The main findings of this section of the literature review, appropriate to thermal treatment of irradiated graphite, are:

- Independent of the reactor source of irradiated graphite, a preferential fractional release of both $^3$H and $^{14}$C from the samples can be achieved.

- Radioisotope releases of tritium and $^{14}$C can be achieved during thermal treatment in an inert environment, with an initial faster rate of release, thought to be largely a diffusion release process for $^3$H and oxidation of $^{14}$C at the sample surfaces by residual adsorbed atmospheric oxygen. The $^{14}$C release is thought to be limited by exhaustion of reactants.

- The radioisotope release process may be sensitive to temperature, with $^3$H release exhibiting a defined dependence on temperature in an inert environment, and $^{14}$C less so. Tritium release efficiencies appear to be higher for temperatures greater than 1000°C.

- The effectiveness of radioisotope release during inert cover gas treatment appears to vary considerably with the graphite source, with liberation of radioactivity from Oldbury Magnox reactor graphite proving less successful than other graphite sources.

- The addition of sub-1% levels of oxygen appear to be ineffective for treatments at high temperatures of approximately 1000°C and above.

- Using oxidation, the majority of $^{14}$C can be liberated from samples which have had the majority of their $^{14}$C inventory deliberately induced at the surface of the sample by immersion in liquid nitrogen prior to irradiation.

- The concentration of oxygen available appears to affect the efficiency of selective removal of $^{14}$C more so than temperature for liquid nitrogen immersed irradiated samples, with lesser oxygen concentrations appearing more effective.

- Thermal treatment of RBMK samples is particularly effective for removal of the $^{14}$C inventory, which is likely a consequence of irradiation in a helium-nitrogen atmosphere coupled with low temperature oxidation (650°C) allowing penetration of oxidant throughout much of the graphite internal porosity prior to oxidation.

- Models of incineration of irradiated graphite waste in excess air demonstrate that, aside from $^3$H, $^{14}$C, $^{36}$Cl and $^{134,137}$Cs, for treatment...
temperatures below 1000°C prominent metallic radioisotopes of concern will likely remain in a solid phase

- Only small amounts of literature exist for the thermal treatment of UK reactor derived irradiated graphites, which predominantly consider release characteristics at temperatures above 1000°C.
2.6 Major Conclusions of the Literature Review

The major findings of the literature review appropriate to thermal treatment of irradiated graphite samples are summarised as:

- The quality of the raw ingredients and impurity content of the finished product will likely influence the final radionuclide inventory in irradiated graphite, and potentially the location of $^{14}$C, affecting its treatability.
- Radioactivity associated with irradiated graphite waste predominantly arises from neutron interaction with impurities within the manufactured graphite product.
- There are a number of prominent radioisotopes of concern that can be found in irradiated graphite waste of varying half lives.
- The production and hazards associated with each of the radioisotopes have been explored, with many radioisotopes such as $^3$H, $^{14}$C, $^{36}$Cl and $^{90}$Sr requiring additional care during reactor dismantling and graphite handling because of their high mobility amongst the bio- and geosphere.
- The dominance of either the carbon- or nitrogen-derived $^{14}$C production route is extremely sensitive to the nitrogen impurity content in the graphite, with an equilibrium in production from $^{13}$C and $^{14}$N source isotopes occurring at a mere approximately 10 ppm nitrogen impurity.
- There are many discrepancies in the literature as to the actual amount of nitrogen in a graphite moderated reactor system, as it is difficult to measure and seems to vary heavily between batches of graphite, reactor type, operational history and locally within the graphite. Values range from 0.5 to 100 ppm nitrogen impurity in the graphite, with a ‘typical’ value for UK Magnox reactors suggested as just over 10 ppm.
- Carbon-14 derived from $^{15}$C will likely be randomly distributed throughout the bulk material in the graphite. There is evidence in the literature that a decreasing nitrogen concentration profile exists from the surface of the graphite inwards, over a lengthscale of typically hundreds of nanometers, which following activation by neutron irradiation and subsequent fast neutron interactions will likely result in an elevated concentration and distribution of nitrogen-derived $^{14}$C near the surface of the graphite.
A $^{14}\text{C}$ rich surface has been experimentally identified on the surface of irradiated graphite by multiple sources using multiple techniques, with a UK source suggesting that there was no evidence of $^{14}\text{C}$ enrichment on the surface of their Wylfa Magnox reactor samples and an alternative UK source suggesting $^{14}\text{C}$ enrichment on the surface of Oldbury Magnox reactor samples.

Some of the $^{14}\text{C}$ attributable to the graphite could also arise from the carbon dioxide coolant, either as a source of nitrogen and oxygen impurities, or through accumulation of potentially radioactive carbonaceous deposits that form on the geometric surfaces of the graphite following complex interactions in the gas phase, evidenced by one source looking at the radiocarbon content of the deposit on graphite from the UK Oldbury Magnox reactors.

It is found that the location of mass loss to an irradiated graphite sample during treatment in an oxidising atmosphere will likely vary depending on the temperatures utilised, with high temperature oxidation corroding the outer geometric surfaces of the sample, low temperatures allowing for oxygen ingress into the sample before reaction and consequently corroding all surfaces throughout the internal porosity.

A preferential fractional release of both $^3\text{H}$ and $^{14}\text{C}$ from the samples has been achieved for varying sources of irradiated graphite waste.

Radioisotope releases of tritium and $^{14}\text{C}$ can be achieved during thermal treatment in an inert environment, with an initial faster rate of release, thought to be largely a diffusion release process for $^3\text{H}$ and oxidation of $^{14}\text{C}$ at the sample surfaces by residual adsorbed atmospheric oxygen. The $^{14}\text{C}$ release is thought to be limited by exhaustion of reactants.

The effectiveness of radioisotope release during inert cover gas treatment appears to vary considerably with the graphite source, with liberation of radioactivity from Oldbury Magnox reactor graphite proving less successful than other graphite sources.

The addition of sub-1% levels of oxygen appear to be ineffective for treatments at high temperatures of approximately 1000$^\circ\text{C}$ and above.

Models of incineration of irradiated graphite waste in excess air demonstrate that, aside from $^3\text{H}$, $^{14}\text{C}$, $^{36}\text{Cl}$ and $^{134,137}\text{Cs}$, for treatment...
temperatures below 1000°C prominent metallic radioisotopes of concern will likely remain in a solid phase

- Only small amounts of literature exist for the thermal treatment of UK reactor derived irradiated graphites, which predominantly consider release characteristics at temperatures above 1000°C
2.7 Research Statement: Aims and Objectives

The aims and objectives for this programme of research, deduced from analysis of the literature, are to:

- Familiarise with and optimise the existing thermal treatment process, and investigate the sources of uncertainty
- Quantify the radioactivity of prominent radioisotopes in Oldbury Magnox reactor installed set graphite
- Determine whether a preferential release of $^{14}$C can be achieved from Oldbury Magnox reactor-sourced graphite
- Investigate the selective release efficiency that can be achieved for $^{14}$C from Oldbury Magnox reactor-sourced graphite
- Determine the maximum fraction of $^{14}$C that could be released from irradiated graphite, whilst retaining sample structural integrity
- Use thermal treatment to estimate the fraction of $^{14}$N-derived $^{14}$C compared to $^{13}$C-derived in UK graphite
- Investigate the effects of thermal treatment on $^{3}$H and metallic radioisotopes
3. Experimental Methodology

This section of the thesis will describe the methodology behind the experiments of this programme of research, including the irradiated graphite samples provenance, a detailed outline of the thermal treatment process used, the characterisation techniques used, and a section discussing data validation and the measures used to ascertain a high quality of data.

3.1 Samples: Irradiated Graphite Samples and Provenance

The cylindrical samples used for this programme of research are of great value for acquisition of meaningful data because they are reactor exposed Pile Grade A (PGA) graphite samples, machined from spacer pieces of an installed set Type A carrier retrieved from inside the graphite moderated Oldbury Magnox reactor 2, and as such have experienced similar environmental conditions and neutron flux as the graphite core.

An ‘installed set’ in this context is an arrangement of graphite test samples of the same origin as the bulk material, which may be in differing conditions of, for example, compression, tension, unrestrained or exposed to a restricted coolant flow, placed inside a carrier vessel and slotted into an interstitial channel in designated regions of the graphite core. The carriers and test samples are subject to neutron irradiation similarly to the rest of the core. The carrier vessel is typically composed of a steel shell and a titanium tie rod through the centre, along the entire length, with the majority of other components such as the sample holders and spacer pieces are constructed of graphite so that the neutron exposure received at the test samples mimics that of the bulk moderator material. The purpose of these installed sets is to analyse material property behaviour under exposure to reactor core conditions, to assist in predicting whole core behaviour. A schematic and photograph of typical installed sets is found in Figure 46[42].
Figure 46: A) Schematic of a Type A Installed Set Carrier, B) Photograph of an Installed Carrier after Removal from a Magnox Reactor\cite{42}

The samples used for this research originate from installed set spacer pieces supplied by the National Nuclear Laboratory (NNL), similarly to those indicated in Figure 46(A), which are made from the same PGA nuclear grade graphite as the core of Oldbury Magnox reactor 2. The pieces were extracted from channel S77 of Oldbury Reactor 2 in June 2005, by which time they had received an estimated ‘Adjacent Fuel Dose’ (AFD) or burnup, a value provided by NNL and derived from dosimetry data of Olbury Reactor 1, of 52827 MWd/t at an irradiation temperature of 543 K\cite{99}. The precise location of channel S77 in the reactor core is unknown to the author. There were three approximately 73 mm diameter disc shaped spacer pieces retrieved from the same carrier, with two of approximately 27 mm thickness and one of approximately 17mm thickness. The two 27 mm thickness retrieved spacers are shown in Figure 47, as received by the University of Manchester and stored at the Amec Foster-Wheeler graphite laboratory at Risley.
A number of cylindrical samples of approximately 4.5 mm diameter were produced from these irradiated graphite spacer pieces using a bench drill with a core drill bit attached, inside a glove box, from the upper flat surfaces of the discs as seen in Figure 47 into the bulk of the discs. Machining was conducted by AMEC Foster-Wheeler at their graphite laboratory at Risley. The thinner disc was machined prior to the commencement of this programme of research, into 24 cylindrical samples which were designated OM1 to OM24. The thicker discs were machined into cylinders in a similar manner, using a bench drill from the flatter surfaces of the disc into the bulk material. Since the drill bit did not penetrate through the entire depth of the discs, most of the samples were still attached at the base, and had gentle lateral forces applied to cause fracture at the base and allow the samples to be retrieved, leading to a somewhat variable sample length and a rough surface on the end of one cylinder. The longest of these samples were then manually cut in half to produce two shorter cylinders, to increase the total number of samples available. A schematic of this is presented in Figure 48. These cylindrical samples were all collected into the same large polythene sample bag. There is a possibility that some of the radioactivity associated with these samples may have been lost during the machining process, due to elevated temperatures at the drill bit causing oxidation within the fume cupboard. If this has occurred, then this will likely affect the more volatile radioisotopes, such as $^3$H and $^{36}$Cl, more than other more stable isotopes. The temperatures would need to be considerable (> 400°C) before any measurable losses of $^{14}$C by this mechanism would occur, and it is unlikely that this much heat has been generated.
The excess powder produced as a projectile by-product of the drilling process is collected onto a clean sheet of paper, before contact and potential contamination from other surfaces in the glove box, and poured into fresh vials.

The cylindrical samples and two separate vials of collected powder were shipped to the University of Manchester, where the samples were retrieved from their large sample bag, placed in individual polythene sample bags and designated sample names OMTT1 to OMTT160.

The irradiation conditions of these graphite samples differ slightly from the ‘typical irradiation’ received by the rest of the reactor core as a consequence of the titanium tie rod used through the centre of the carrier. The neutron absorption cross section for a neutron-gamma reaction with $^{48}$Ti, the most naturally abundant isotope of titanium, is 7.9 b, as opposed to 3.5 mb for $^{12}$C$^{[40]}$. This suggests that for a similar neutron dose a considerable number more nuclear reactions will take place in the titanium than the surrounding graphite components, with each reaction releasing gamma radiation thus significantly increasing the gamma dose received to the graphite in the immediate vicinity. This accelerates the rate of gamma radiation dependent radiolytic oxidation, leading to higher weight losses in this graphite than might be encountered in the core bulk material. Estimated typical weight losses for these samples, based on an unirradiated density of 1.73 g/cm$^3$, are of the order 40%$^{[99]}$.  

*Figure 48: Typical Machined Sample Geometry, showing the approximately flat top surface, rougher fractured surface at the bottom, and approximate location of additional cut for samples halved*
3.2 Methodology

This section of the report will describe the thermal treatment method and apparatus in detail, including observations and considerations to be made whilst conducting the procedure, learned from familiarisation and critical analysis of the system. The precise time, temperature and cover gas protocols used for differing experiments will be highlighted in the relevant results chapters.

3.2.1 Thermal Treatment

Generally, each irradiated graphite cylinder sample was handled in the same format from pre-treatment characterisation to complete destruction, following the order described in Figure 49 below.

![Figure 49: Typical Methodology applied to each Irradiated Graphite Sample](Image)

The samples each undergo pre-treatment characterisation using non-destructive techniques before undergoing thermal treatment and radioisotope activity analysis using a tube furnace to induce gaseous radioactive release, post-treatment characterisation using the same techniques employed previously and then full oxidation of the sample at 1000°C in pure oxygen in the tube furnace, and a second radioisotope activity analysis, to determine the real fraction of radioactivity released during the treatment stage. These fundamental stages in the lifetime of a sample for this programme of research will be described in greater detail later in this section.

Given the nature of radioactivity, the detectable activities in this irradiated graphite will be reducing with time because of radioactive decay, as per each individual radioisotope’s half life. Some activity determinations have been made with a considerable period of time in between, with the thermal treatment and full oxidation runs for a given sample sometimes performed months apart, during which time a noticeable proportion of shorter-lived radioisotopes may have decayed. All radioactivity measurements have

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consequently been normalised to the same date, the start date of this programme of research which was the 18th September 2012, to negate the effect of time between experiments on the effective radioisotope release rates. This correction has been performed using radioactive decay data from the National Nuclear Data Center database NuDat version 2.6\textsuperscript{[45]} and the radioactive decay equation as per Equation (10),

\[ A = A_0 e^{-\lambda t} \]  \hspace{1cm} (10)

where ‘\( A \)’ is the final activity, ‘\( A_0 \)’ the initial activity, ‘\( t \)’ the time elapsed between \( A \) and \( A_0 \), and ‘\( \lambda \)’, the decay constant for each radioisotope as defined by Equation (11),

\[ \lambda = \frac{\ln(2)}{\tau_{1/2}} \]  \hspace{1cm} (11)

where ‘\( \tau_{1/2} \)’ is the half life of that particular radioisotope.

### 3.2.1.1 Irradiated Graphite Sample Preparation

The evening before a sample treatment run is scheduled, the sample is put on to ‘degas’. This involves placing the sample under vacuum at 300°C overnight, in a bid to remove any surface adsorbed gases, notably oxygen which could affect the oxidation process. This is the same sample preparation technique used for surface area analysis by the Brunauer-Emmett-Teller (BET) method, to remove adsorbed impurity elements, known to become attached to graphite surfaces\textsuperscript{[52]}, and it was conducted using a Micromeritics VacPrep 061 Sample Degas System which is capable of initiating and maintaining an effective seal for the duration of the degas, determinable by the instrument’s pressure gauge. Data presented in a paper by Causey et al.\textsuperscript{[100]}, investigating \(^3\)H retention in graphite tiles taken from a fusion test reactor, shows that multiple sources find negligible release of \(^3\)H from graphite in a vacuum for temperatures under approximately 400°C, and as such an assumption is made that this degassing process will remove only the adsorbed surface impurities, and not the \(^3\)H inventory.

Following degassing, the samples are allowed to cool in the vacuum before being exposed to atmosphere for several minutes as they are moved to another laboratory for mass measurements, using the 4d.p. balance described in Section 3.2.2.3, and installed into
the thermal treatment furnace, and so questions can be raised as to the effectiveness of this degassing process as gases will adsorb during this period. Since a large number of experiments had already been conducted using this method, it was decided to continue with degassing the samples throughout this experimental programme, unless otherwise stated, to maintain consistency in the data.

### 3.2.1.2 Liquid Scintillation Counting

Liquid scintillation counting is a commonly used method for quantifying radioactive emission by alpha- or beta-particle decay within a fluid, and is particularly suitable for radioisotopes that do not have a gamma signature. In this research, it is the experimental technique used to determine $^3$H and $^{14}$C activities released from irradiated graphite samples during thermal treatment, and so this technique should be explored before considering the treatment process.

A basic overview of the process includes mixing of a test fluid with a chemically compatible ‘scintillation cocktail’ into a vial, in which emitted beta particles cause excitation of phosphor molecules, subsequent de-excitation and emission of a pulse of visible light, and then counting for a specified time in a liquid scintillation counter, which uses a photomultiplier tube (PMT) to amplify light signals before detection. The liquid scintillation counter used for this programme of research is a Perkin Elmer Tri-Carb 3100TR Liquid Scintillation Analyser. Scintillation cocktails used for this research include Goldstar$^{101}$, Scintisafe III$^{102}$ and Carbon Count$^{103}$.

One difference for beta activity analysis methods, as opposed to gamma spectrometry, is that the radiation emitted is a spectrum of energies instead of a single discrete energy gamma ray, and as such it is especially difficult to distinguish between radioisotopes if there are more than one present in a sample. The maximum energy of a $^3$H beta particle is 18.6 keV and the maximum energy of a $^{14}$C beta particle is 156 keV, though in reality both of these radioisotopes will emit the majority of their particles at significantly below their maximums. The overlapping beta particle energy spectra for $^3$H and $^{14}$C can be seen in Figure 50.
A liquid scintillation counter will output data obtained from user-specified ‘energy windows’, such that any emissions recorded outside of those energy bounds will be discarded for this count. The most common energy windows to specify for individual radioisotope counting are 0 to 18.6 keV for $^3$H and 0 to 156 keV for $^{14}$C, though it is possible to perform dual counting with a liquid scintillation counter, where both $^3$H and $^{14}$C can be measured in a sample simultaneously, by specifying two energy windows of 0 to 18.6 keV for $^3$H and 18.6 to 156 keV for the $^{14}$C emissions. Dual counting is particularly useful for samples with unknown activities of each radioisotope, since a positive $^3$H count could actually be interference from lower energy $^{14}$C beta emissions because of the beta emission energy overlap, as seen in Figure 50. Conversely, a positive $^{14}$C count during dual counting can never be $^3$H because the minimum threshold of the specified energy window, at 18.6 keV, exceeds that of the maximum energy of a $^3$H beta particle. The $^3$H and $^{14}$C radioisotopes are frequently chemically separated, as is the case for this programme of research, to avoid the issue of overlapping beta particle energy spectra.

Quantitative activity determination becomes more difficult when there are further radioactive contaminants in the sample, such as volatile $^{36}$Cl to be highly mobile in irradiated graphite, whose spectra will also overlap, increasing the uncertainty that the
positive count detected in a given energy window is not the radioisotope expected. It has been seen in Section 2.2, however, that the typical activities of other volatile radioisotopes, compared to $^3$H and $^{14}$C, are orders of magnitude lower, and as such if contamination were to occur they will contribute negligibly to the liquid scintillation counting at worst.

A schematic of the outlined process, from radioactive decay to the PMT, is presented in Figure 51.

![Schematic of the Liquid Scintillation Counting Process](image)

**Figure 51: A Schematic of the Liquid Scintillation Counting Process, adapted from Perkin Elmer[^105]**

The sample for analysis, generally comprising of a liquid scintillation cocktail and compatible liquid sample mixed together, are analysed in vials of specific geometries for liquid scintillation counting. Two different vial types have been used for this research, plastic and glass, because of chemical compatibility issues. Glass vials, which can hold up to 22 mL of fluid, have superior light transmission properties due to their transparency, though are known to have a higher amount of natural background radiation, notably $^{40}$K, which could interfere with the measurement. Glass vials are also prone to shatter if dropped and are relatively expensive. Plastic vials, which can hold up to 20 mL of fluid, are semi-opaque, though have considerably lower background levels of radiation than glass vials. There are issues with static electricity build up on plastic vials which can produce erroneous measurements, and though a static controller is installed on the NGRG liquid scintillation counter it is not always successful. Sample vials are counted one after the other in order in a rack, for a user determined amount of time. For this research, the first vial in the rack is always a background vial, mimicking the contents of the test vials with non-radioactive equivalents, and the counts determined from the background vial are subtracted from the remaining data obtained.
3.2.1.3 Thermal Treatment Apparatus and Method

All thermal treatment experiments have been performed using a commercially available Carbolite MTT \(^3\)H and \(^{14}\)C Analyser tube furnace system designed for extracting \(^3\)H and \(^{14}\)C from samples using thermal decomposition[106]. This system was already installed and in use prior to this programme of research, though some adaptations and improvements have been made, which will be described in Section 3.3.1.1. A schematic of the furnace and bubbler train arrangement can be seen in Figure 52.

![Figure 52: A schematic of the Thermal Treatment Tube Furnace and Bubbler Train](image)

The process used for initiating thermal treatment will now be described in detail, in chronological order:

The cover gas of choice enters the tube furnace at the right side of Figure 52, at a user-specified flow rate. A constant flow rate of 100 cc/min is maintained across all experiments using a manual flow rate controller, to remove the flow rate and consequent pressure variation in the combustion tube as a variable, since an increased gas pressure will increase the density of the oxidising gas and thus could increase the rate of oxidation, as seen in Section 2.4 of the literature review.

The digital sample zone temperature controller allows detailed programs to be constructed where the furnace will automatically regulate the sample zone temperature depending on the programmed ‘segment’ in which it is operating. Typically, the furnace will be programmed to ramp the temperature up at a constant rate of 20°C/minute to the desired temperature, which is similar to the 23.3°C/minute suggested in the operator manual[107], and then dwell at this indicated temperature for a given amount of time, often in hours, before halting all sample zone heating and allowing the sample to cool. It should
be noted that the furnace thermocouples registering the digital display of ‘indicated’
temperature of the furnace are positioned outside of the quartz tube itself, where the
temperature is likely to be somewhat higher than in the centre of the quartz tube. Analysis
of the temperature at the sample has been performed using a thermocouple, which will be
presented later in Section 3.3. The sample zone begins 20cm from the end of the furnace,
according to the furnace operating manual[107].

The cover gas flows along the quartz combustion tube passing the independently
heated sample zone and catalyst zone, which houses a copper oxide catalyst intended to
fully oxidise any passing gaseous species. As a graphite sample placed in the sample heating
zone is oxidised, tritium and carbon-14 will likely be gasified to HT or HTO and $^{14}$CO or $^{14}$CO$_2$
depending on temperatures and oxygen supply, as seen in Section 2.5 of the literature
review. The copper oxide catalyst works to ensure that all $^3$H is in tritiated water vapour
form and that all $^{14}$C is in carbon dioxide form, which is an accepted technique used by
others in the literature[54, 65], such that they can be efficiently trapped later in the process.
Separate heating elements allow the sample and catalyst to undergo heating almost
entirely independently of each other, such that the catalyst can be raised to a reasonable
working temperature, usually 750°C, before sample oxidation even begins.

The four bubblers, connected in series by ball and cup joints in a bubbler train and
denoted B1 to B4 in Figure 52, are designed to trap gaseous $^3$H and $^{14}$C radioisotopes.
Before their installation in the bubbler train, the bubblers are kept in an oven at 175°C for a
minimum of three hours to remove any significant surface moisture, and are allowed to
cool before their empty mass is taken using the 2d.p. mass balance described in Section
3.2.2.3. The bubbler must be at room temperature before the mass is taken because any
residual heat will effect a lowering in the density of the air around the mass balance,
causing a localised ‘lift’ force and consequent underestimated mass reading.

The appropriate trapping fluid is then transferred into each bubbler before they are
attached to the furnace. The first two bubblers connected in series, B1 and B2, contain 20
mL of 0.1M nitric acid (HNO$_3$) for trapping $^3$H by condensation of HTO, whilst the $^{14}$CO$_2$ in
the cover gas will travel onwards to bubblers B3 and B4 containing 40 mL of Carbon Trap, a
commercially available trapping agent for carbon dioxide containing 3-methoxypropylamine. This is the method used to chemically separate $^3$H from $^{14}$C to allow
effective independent liquid scintillation counting of each radioisotope, as described in
Section 3.2.1.2. Carbon Trap is capable of absorbing up to 4.8 millimoles of carbon dioxide
per 1 mL of trap\textsuperscript{[107, 108]}. One gram of graphite, which when fully oxidised is equivalent to 83.3 mmol of CO\textsubscript{2}, could theoretically be completely absorbed into 17.35 mL of Carbon Trap, and so 40 mL was chosen as a suitable trapping volume to allow some margin for error. Saturation of the B3 bubbler did not occur over the course of this experimental programme of research. The secondary bubbler of each trapping medium, bubblers B2 and B4, are always filled first to avoid any potential contamination from the measuring cylinders, by dust or otherwise, appearing in the primary analytical bubblers, B1 and B3. As these bubblers are upwards of 99% efficient trapping mechanisms for the radioisotopes of interest, the second bubbler of each trapping fluid, bubblers B2 and B4, are used as a precautionary measure to capture any radioisotopes that either evaporate from or successfully traverse the first bubbler, evading capture, or for large samples where the carbon trap could become unexpectedly saturated. It should be noted that 0.1M HNO\textsubscript{3} is used as a trapping agent for \textsuperscript{3}H, as opposed to deionised water, because the excess bubbler solution is stored in case future analysis should be required, and the weak acidic content is sufficient to prevent biological growth during this time. Evaporation of the trapping media does occur over the course of a treatment experiment, though the consequences of this are thought to have negligible influence on the combustion tube internal pressure and thus rate of oxidation. The bubblers are not interchanged, such that the bubblers are always attached in the same order and contain the same trapping agent, to avoid any unexpected change in trapping behaviour and to maintain consistency between experiments.

The joints for the inlet and outlet to the furnace are ground glass which does not form a perfect seal. The use of greases or other sealants is to be avoided, at the behest of the manufacturer\textsuperscript{[106]}, because of the presence of tritium, which is notorious for permeating into all kinds of materials\textsuperscript{[109]}. One of the appeals of this experimental setup is that it is almost entirely constructed from glassware, so tritium uptake into plastic components will not occur, though as a consequence it is acknowledged that a perfect seal cannot be achieved. This is accounted for using recovery checks, as will be described in detail in Section 3.3.1.2, where it is seen that this contribution, amongst others, to any losses in the system are relatively consistent and predictable. The ball and cup joints between the bubblers are tested using a leak detector spray, using which a consistent seal between bubblers has been observed throughout this experimental programme.

The system is exhausted into a 1 litre bottle of 0.1M HNO\textsubscript{3} solution before venting to atmosphere in a fume cupboard. This final trap is in place to capture any \textsuperscript{3}H or evaporated carbon trap that might traverse the exhaust system. This solution has never
returned a positive count of detectable radioactive contamination. The system is exhausted to a fume cupboard to prevent undesirable hazardous gases entering the laboratory environment.

Once the furnace system is assembled, the cylindrical graphite sample’s mass should be taken using the 4d.p. balance described in Section 3.2.2.3 prior to treatment, it should be placed lengthways into a ceramic combustion boat, maintaining the sample to boat configuration for consistency between experiments, before removing the furnace inlet and sliding the sample and boat into the sample zone of the furnace, determined by a marking 20cm along the rod used to insert the sample.

The process used for dismantling and analysing the thermal treatment experiment will now be described in detail:

At the end of a treatment experiment, the sample zone cooling process can take upwards of an hour depending on the treatment temperature required. A graphite sample will not be removed from the furnace and exposed to atmosphere until the sample zone is below an indicated 500°C, to prevent any significant oxidation occurring during sample extraction into the laboratory environment, following which relatively quick sample cooling in ambient temperature conditions will ensue. Time constraints prevent the operator leaving the sample in the furnace to room temperature, as the bubblers should not be detached from the furnace before the sample is retrieved, for radiological purposes.

The bubblers are detached one by one and their mass taken using the 2d.p. balance described in Section 3.2.2.3, to determine the total mass of trapping agent in each bubbler, before placing in a fume cupboard to prevent inhalation of ³H, ¹⁴C or volatile Carbon Trap. Inside this fume cupboard, the bubblers are decanted into clean beakers, which similarly to the bubblers are not interchangeable. An assumption is made that the radioactive isotopes are evenly distributed through the fluids in the bubbler, though every care should be taken to remove all of the trap fluid from a bubbler to mitigate for this.

The trap fluid in the beaker is thoroughly mixed and aliquots from each beaker are taken using a Rainin digital electronic pipette and dispensed into previously prepared liquid scintillation vials, which contain an appropriate amount of the relevant scintillation cocktail. For liquids obtained from bubblers B1 and B2, the ³H capture bubblers, 4 mL of the HNO₃ solution is taken and mixed with 16 mL Scintisafe, a HFP cocktail, to fill a 20 mL plastic vial.
For liquids obtained from bubblers B3 and B4, the $^{14}$C bubblers, 8 mL of the Carbon Trap bubbler solution is mixed with 14 mL of Carbon Count, a LFP cocktail which is designed for compatibility with Carbon Trap, in glass vials. Glass vials must be used for the $^{14}$C analysis because Carbon Trap and Carbon Count are chemically incompatible with plastic vials. The mixing ratios of cocktail to trap in a scintillation vial deviate slightly from those recommended in the operator manual [107] because the remaining empty volume in the vials has been filled with scintillation cocktail. The performance of a scintillation cocktail is improved if the ratio of cocktail-sample is increased [105, 110], and the surface area for observation is also increased by filling the sample vials. The masses of the vials are taken using the 4d.p. balance between each addition of a fluid to determine the total mass of radioisotope trap added to each liquid scintillation vial. Two sample vials are produced from the first analytical bubbler of each solution, from B1 and B3, and a single sample vial produced from the secondary trap bubblers, B2 and B4.

These vials are then taken for liquid scintillation counting, as described in detail in Section 3.2.1.2. It is paramount that the correct quench correction curve should be allocated to each liquid scintillation rack depending on the scintillation cocktail used and radioisotope under analysis. Each vial is counted twice for a period of one hour and the average activity over these two hours taken.

Once the sample and all bubblers have been removed from the furnace, a ‘flush’ is passed through the furnace, achieved by placement of a bath of deionised water in the furnace inlet and using the residual heat of the system to convert this to steam under a constant flow of dry, compressed air. The steam travels along the furnace collecting harboured radioactive species, notably $^3$H, before capture in a bubbler of deionised water. The flush is then analysed by dual counting for $^3$H and $^{14}$C using the liquid scintillation counter, in an equal parts 10:10 mL mixture of flush water and HFP scintillation cocktail Gold Star, to determine the quantity of any residual radioactivity remaining in the furnace. The measured radioactivity in the flush is generally less than 0.1% of the original sample activity. This ‘flush’ activity can also be a useful indicator of any issues within the furnace which may cause $^3$H to become trapped in the system.

The calculation method for quantifying the $^3$H and $^{14}$C liberated from a graphite sample involves using the measured activity and multiplying by various ratios determined by mass measurements to yield the total activity in a bubbler. The activity output by the liquid scintillation counter is for the total radioactivity in each particular vial. There are two
vials analysed per analytical (B1 and B3) bubbler, and since the mass of trap solution in each vial is known, an average specific activity of the trap solution can be deduced, and applied to the remainder of the total solution in the bubbler, known from bubbler mass measurements, to obtain the total activity trapped in a bubbler. Since this treatment system is not 100% efficient, the determined bubbler activity is adjusted as per the predictable system efficiency determined by recovery checks, which are described in detail in the upcoming Section 3.3.1.2, to estimate the actual activities of $^3$H and $^{14}$C liberated from the irradiated graphite samples.

The total activity remaining in a sample following treatment is determined by a second experiment used to fully oxidise the $^3$H and $^{14}$C inventory in the sample into the gas phase, in a treatment process identical to that described above except the process duration is 2 hours using pure oxygen at 1000°C to cause relatively rapid oxidation. A graphical representation of the furnace protocol used for this full oxidation experiment is found in Figure 53, where the dashed line represents uncontrolled cooling by natural processes, and as such the temperature profile will not behave linearly, as drawn.

![Figure 53: A Graphical Representation of the Furnace Protocol used for Full Oxidation of a Sample](image)

Collection of meaningful data from this thermal treatment system requires a considerable amount of operator time, for furnace preparation and dismantling, and liquid scintillation vial preparation and analysis, and as such one ‘run’ of the furnace, which is taken as one cycle of ramping up to a treatment temperature and allowing the furnace to
cool again, takes a considerable number of hours. In most instances it has been possible to perform one treatment run per day.

3.2.2 Characterisation Techniques

Characterisation techniques have been utilised, for application both before and after thermal treatment to observe any differences that might occur in the sample as a consequence. These will be described in detail in this section, as well as specific applications of the techniques to make them appropriate to measurements of irradiated graphite.

3.2.2.1 Germanium Gamma Spectrometry

Gamma spectrometry is a non-destructive technique whereby gamma radiation emitted, by radioactive decay or otherwise, can be detected. The energy of the gamma rays can be determined from the energy they deposit into the detector, though the energy resolution attainable is dependent on the particular detector system used. Analysis of the spectrum of gamma emissions from a sample allows specific radioisotopes to be identified according to their gamma ‘fingerprint’, determinable from the decay schemes seen in Appendix C, along with accurate determination of their activities.

There are several types of gamma spectrometer that can be used, often distinguishable by the type of detector crystal that they house. Two common types of gamma spectrometer include thallium-activated sodium iodide (NaI(Tl)) scintillation detectors and germanium (Ge) detectors, each with their own advantages and disadvantages, both of which are available for this programme of research. The relatively inexpensive NaI(Tl) detector, known for its versatility, uses a solid state crystal for detection, by analysis of the light pulses produced by a gamma ray interaction with one of the crystal electrons causing excitation followed by de-excitation and emission of a light photon. As a consequence of losses and inefficiencies in the detector, however, the resultant energy resolution is poor and the peaks in the spectra are broad. A Ge detector works by a slightly different principle of gamma ray energy deposition into a semiconductor crystal’s electrons. The germanium crystal allows for much improved energy resolution, with sharp, pronounced peaks, at the expense of requiring liquid nitrogen cooling and a
significant applied electric field. A comparison of these two detector types’ spectra is shown in Figure 54.

Figure 54: Comparative Pulse Height Spectra Recorded using a Sodium Iodide Scintillator and a Ge(Li) Detector

Figure 54 demonstrates that the energy resolution attainable using a germanium detector is far greater, with many peaks becoming lost in the continuum of the NaI(Tl) detector. The data presented in this programme of research has been collected by a germanium detector, selected over the NaI(Tl) detector because of its improved resolution, and so the NaI(Tl) detector will not be discussed further. The energy resolution for the
Nuclear Graphite Research Group (NGRG) germanium detector is 0.25 keV per channel over 8192 channels, allowing a full spectrum of gamma rays from 0 to 2048 keV to be observed.

There are three dominant interaction mechanisms between gamma rays and matter, known as Compton scattering, photoelectric absorption and pair production\cite{112}, each of which have energy regions in which they are most likely to occur, as shown by Evans\cite{113} in Figure 55.

\textbf{Figure 55: Relative Importance of the Three Major Types of Gamma Ray Interaction}^{[113]}

\textit{Compton Scattering:} For the majority of the gamma ray energies encountered in radioisotopes in graphite, described in Section 2.2, the Compton Scattering effect dominates. This is a process where an incoming gamma ray will impart some of its energy to an electron in the detector crystal, causing excitation, and then scatter off at an angle at a reduced energy level through the remainder of the crystal. The fraction of energy transferred occurs as per Equation (12)\cite{112}.

\begin{equation}
E' = \frac{E}{1 + \frac{E}{m_0c^2}(1 - \cos \theta)}
\end{equation}

where ‘$E$’ is the resultant gamma ray energy following scatter, ‘$E'$’ is the original energy of the gamma ray, ‘$m_0c^2$’ is the rest mass of the electron (511 keV) and ‘$\theta$’ the angle of scatter.
It should be noted that the maximum energy transfer occurs when $\theta = 180^\circ$, or the gamma ray scatters in the opposite direction of travel, yet the equation will never yield a value of 1 indicating that the entire energy of a gamma photon cannot be transferred by this mechanism. Since the gamma ray must come to a complete halt within the crystal for its full energy to be detected, there is a high probability that the gamma ray will escape the crystal before this occurs, leading to a measurement of a fraction of the incident gamma ray energy. This phenomenon of Compton Scattering leads to two artefacts on a gamma spectrum, known as the Compton continuum and the Compton edge. The Compton continuum appears as an elevated background due to the distribution of recorded energies as a consequence of the varying angles of scatter. The Compton edge occurs because there is a maximum amount of energy that can be transferred to an electron by Compton Scattering, when the scatter angle is $180^\circ$, and so the continuum for a given gamma ray energy cannot extend beyond this energy yield. A representation of how these might be observed in a gamma spectrum can be found in Figure 56.

Photoelectric Effect: In the lower energy regions, for less energetic gamma rays, the photoelectric effect dominates. This is a process whereby the energy of the entire gamma photon is absorbed by the atom and an energetic electron is released, often from one of the inner shells of the atom\textsuperscript{112}, at approximately the same energy minus the binding energy required to remove the electron from its position in the lattice. This energetic photoelectron is then likely to deposit its entire energy into the detector which can be quantified into a recorded full energy photopeak. A representation of the full energy photopeak can be found in Figure 56.

Pair Production: Pair production occurs predominantly following interaction between atoms and high energy gamma rays, where the entire of the gamma ray photon is lost into the atom and replaced by an electron-positron pair, requiring minimum gamma ray energy of twice the rest mass of an electron (1022 keV) to make this energetically possible. Any excess energy carried by the lost gamma ray is transferred into kinetic energy shared between the electron and positron. The positron, as a particle of antimatter, will annihilate on interaction with a surrounding electron, which are available in abundance, producing two further gamma rays travelling in opposite directions of exactly 511 keV each. Should one or both of these annihilation gamma rays escape the detector crystal without interaction then precisely 511 or 1022 keV of the initial gamma rays energy will be lost from the detector. This phenomenon leads to single and double ‘escape peaks’ appearing in the
spectrum, occurring at the energy corresponding to the full photopeak minus the lost energy. A representation of the single and double escape peaks can be found in Figure 56.

![Spectrum from 1460 keV gamma rays emitted by a $^{40}$K source](image)

**Figure 56:** Spectrum from 1460 keV gamma rays emitted by a $^{40}$K source$^{[112]}$. ‘SE’ and ‘DE’ refer to single escape and double escape peaks at 949 and 438 keV respectively. Image adapted by the author

For gamma spectrometry of irradiated graphite, a high activity of cobalt-60 compared with other radioisotopes, with prominent peaks at both 1172 and 1332 keV, can cause a significantly raised Compton continuum across much of the spectrum, leading to losses of information for less prominent and lower activity radioisotopes as their peaks exist below the continuum and thus remain undetectable. It should be emphasised that this occurs predominantly to lower activity radioisotopes, which are usually of less concern to irradiated graphite waste management for this reason.

Given the excellent resolution of a germanium detector, and assuming regular and correct calibration, identification of radioisotopes is relatively simple by cross-referencing the peaks with the gamma energies expected from their radiation fingerprint. Quantitative analysis of the activity of these radioisotopes is more difficult, because of multiple effects that could affect the number of counts detected, including radiation attenuation through the detector, self-attenuation of radiation leaving a sample, multiple gamma photons released from a given radioisotope with varying natural intensity as seen in Appendix C, variable detector efficiency and interaction mode depending on incoming gamma photon
energy, and differing sample geometries and consequent distances from the detector. The majority of these can be accounted for using a software package called ISOCS\textsuperscript{[114]} in conjunction with the collection software, Genie2K\textsuperscript{[115]}, which allows the user to generate a model of the sample, including geometry, density and position information, which can be related to the particular detector efficiency data determined by the manufacturer and radioisotope libraries containing decay intensity information. An ISOCS image of a modelled graphite cylinder atop the NGRG germanium detector can be seen in Figure 57, showing data collection parameters.

\textit{Figure 57: An ISOCS\textsuperscript{[114]} Model of Sample OMTT21 on the NGRG Germanium Gamma Spectrometer}

In order to determine quantitative activity data from a germanium gamma spectrometer, the software processes used are, in order:
• Peak Analysis: the GENIE2K software mathematically determines the location of peaks in the spectrum by differentiating the curve and analysing significant changes in the third derivative
• Peak Area: the area under each peak is now calculated, by integration under the previously located peaks
• Background subtract: the peak area analysis from a previous appropriate background scan of the same duration as the sample scan is subtracted from the spectrum, on a peak by peak basis
• Geometry Modelling: a model of the sample for analysis can be produced in ISOCYS, including geometry, density and position relative to the detector
• Geometry Efficiency: geometry efficiency data points are determined by the software based on manufacturer defined detector efficiency parameters and the modelled geometry provided, and applied to the spectrum to account for individual collection efficiencies of each recorded gamma energy
• Nuclide Identification (with Interference Correction): the GENIE2K software compares the peak positions with a user-defined radioisotope library to identify the radioisotopes in the spectrum. For isotopes with multiple gamma emissions, the recorded gamma peaks are weighted according to their decay intensity. The total activity for each radioisotope is determined by the software, based on the efficiency corrected peak area

3.2.2.2 Autoradiography

Autoradiography is a non-destructive technique not dissimilar to old fashioned photography techniques of exposing films to light radiation. The differences lie in the sources of energy, this time beta and gamma radiation as opposed to visible light, and the film used for detection, which is this time a phosphor storage screen\textsuperscript{[116]} as opposed to silver halide impregnated plastic film.

The storage phosphor screens used are composed of fine crystals of BaFBr:Eu\textsuperscript{2+} in an organic binder\textsuperscript{[117]}. Incoming radiation, from beta or gamma emissions, excites the Eu\textsuperscript{2+} ions in the film to a state where its electrons can move within the conductance band of the rest of the crystal and become trapped in bromine vacancies which were induced during the manufacturing process\textsuperscript{[116]}. The result is that the Eu\textsuperscript{2+} becomes oxidised to Eu\textsuperscript{3+} and the
barium fluorobromide reduced to BaFBr\(^{-}\). When the radiation source is removed from the screen, the crystals remain in this balanced oxidised-reduced state, and so the energy from the radiation is ‘stored’ in the BaFBr phosphor. A second radiation source, a red laser of wavelength 633 nm, is then used to liberate this stored energy in the phosphor by scanning across the surface of the screen causing further excitation of the BaFBr crystal, allowing its electrons freedom to move, which reduce the Eu\(^{3+}\) to an excited state of Eu\(^{2+}\), which falls to its original ground state for stability emitting a blue light of wavelength 390 nm in the process\(^{117}\). The blue light is detected and collected by a GE Healthcare Typhoon 9410 imager, which uses a photomultiplier tube (PMT) to analyse the intensities of 390 nm light emitted and relate this to radiation exposure intensity in the screen as a two-dimensional intensity map. A schematic of this process can be seen in Figure 58.

![Schematic Representation of the Storage Phosphor Process](image)

**Figure 58: Schematic Representation of the Storage Phosphor Process\(^{116}\), adapted by the author**

Before a radiograph is taken, the screens must be cleared of any radiation that has been accumulated in them, including background radiation. This is done by exposing the screens to a bright white light, using a device designed for precisely this purpose, for approximately 20 minutes. This is sufficient to deionise all of the crystals in the screens, which can be confirmed by an immediate scan of the screen. A radiograph is collected by placing irradiated graphite samples onto the screen, noting their relative positions for the post-processing, and allowing them to irradiate the screens for a given length of time.
Other researchers have determined that an exposure time of 20 hours is suitable for autoradiography of Oldbury Magnox reactor graphite of similar activities\cite{42}, and so this exposure time has been continued. The samples are kept in their polythene bags, to prevent graphite dust contamination of the screens themselves. The low energy beta-particle emissions of tritium will likely be completely shielded by the sample bag, though this will not affect the experiment because the screens are not sufficiently sensitive to detect tritium. The sample bag will also likely shield a reasonable proportion of the $^{14}$C beta-particles from detection, though the gamma emissions will only be negligibly affected. The sample bags are carefully arranged such that one bag does not interfere with another sample’s radiation ‘shine path’ to the screen, so that there is one single layer of polythene between the sample and the screen.

One specific note that should be emphasised for autoradiography of irradiated graphite is that this technique cannot distinguish between radioisotopes, as it only yields the absolute amount of radiation that has interacted with the film. Thus, for a given intensity output on the screen, it would be impossible to determine whether the cause was a low activity of a relatively high energy emitting radioisotope, such as $^{60}$Co, or a high activity of a relatively low energy emitting radioisotope, such as $^{14}$C. Some other sources have attempted quantitative autoradiography of irradiated graphite samples using multiple scans with differing filters applied between each, to shield progressively higher energy radiations from the screen\cite{65}.

A $^{14}$C standard is placed alongside the samples, for the same 20 hour exposure time as the samples, though because of the difficulties with quantitative imaging of irradiated graphite described above this is mostly useful for ascertaining the repeatability of measurements and that the phosphor storage screens have retained their capability to store energy between scans, rather than obtaining any quantitative information about the samples themselves.

### 3.2.2.3 Metrology

For this research, it is appropriate to record the mass of the samples between characterisation processes, to ensure that unrecorded sample mass losses are not occurring through the sample handling procedures. Determination of the sample bulk geometries both before and after thermal treatment using a digital micrometer is useful for analysing
changes in bulk density and allows an estimate as to which oxidation regime, as described in Section 2.4.4, is the dominant mechanism of oxidation.

Two mass balances have been used for this research, for different mass ranges measured. The first is a Denver MAXX Series 612 balance, which has a measurable range of 0-200 g and is sensitive to 2 decimal places of a gram (0.01 g)\(^\text{118}\), which will be referred to from here on in as the ‘2d.p. balance’. This balance is suitable for determining the mass of larger components, such as the bubblers attached to the furnace. All measurements using the 2d.p. balance are inclusive of the mass of a plastic beaker used to stabilise bubblers during mass measurements, though this mass is subtracted from itself during the calculation stages and so does not contribute to the analysis. The other balance is a Denver SI-64 balance, which has a measurable range of 0-60 g and a resolution of 4 decimal places of a gram (0.0001 g)\(^\text{119}\). This balance is more appropriate for determining small sample mass losses during oxidation experiments. All mass measurements are taken by first placing a weighing boat on the balance, taring the balance, then adding the sample to the boat to obtain the sample mass.

The bulk geometry of the sample has been determined using a Mitutoyo Series 293 Digimatic Micrometer with a range of 0-25 mm and a resolution of 0.001 mm, from which bulk volume data can be ascertained. This micrometer has a ‘constant-force device’, a ratchet stop mechanism, which applies a measuring force of between 5 and 10 N\(^\text{120}\).
3.3 Data Validation

As with any large experimental programme, a number of sources of uncertainty associated with the data produced for this programme of research can be identified. This section aims to identify those sources of uncertainty, and how they may be mitigated if possible, with a view to establishing confidence in the data produced by acknowledgment of their nature, magnitude and potential effects on the results.

3.3.1 Thermal Treatment System Adaptations and Validation

3.3.1.1 Adaptations to Existing Process

A critical analysis of the entire furnace treatment system described in the Methodology section was conducted during the early stages of this programme of research, following some familiarisation with the process, with a view to reducing the uncertainties and increasing process efficiency of an already successful thermal treatment process, wherever possible. The major adaptations made to the process are listed below:

- All joints in the gas delivery system have been inspected, both visually and using leak detector spray, and those that were seen to be leaking have been dismantled, cleaned, repaired and retested. No detectable leaks exist in the gas delivery system
- The inclusion of a T-piece to the cover gas delivery system has allowed for switching between a low oxygen environment and an inert environment to be seamless, avoiding exposure to atmosphere by disconnection of the gas lines to the furnace and consequent inevitable ingress of higher concentrations of oxygen in air to the system. This T-piece also allows the operator to maintain a relatively constant gas flow and pressure within the combustion tube
- An additional rack for liquid scintillation counting has been introduced during a recovery check. There are two types of quenched standards correction curve installed for each radioisotope, LFP and HFP depending on the chemical construction of the scintillation cocktail in question, as described in Section 3.2.1.2. Previously, all $^{14}$C samples were assigned to a single rack for counting in the LSC, meaning that all vials were counted and compared to a single installed quenched standards correction curve. It will be seen in a following section that one sample, the 1 mL $^{14}$C standard taken for direct LSC counting is sucrose
dissolved in deionised water, and as such is compatible with HFP Gold Star and not LFP Carbon Count. The samples taken from the bubblers are ¹⁴C dissolved in LFP Carbon Trap, which is compatible with LFP Carbon Count and not with HFP Gold Star. Consequently, these ¹⁴C samples require counting compared to separate quench correction curves, and so an additional rack has been introduced to implement this, reducing uncertainty in the liquid scintillation counting whilst increasing the analysis duration by a further 2 hours.

- The frequency of analytical recovery checks of the thermal treatment system, as will be described in more detail in Section 3.3.1.2, has been increased from between every 5 runs to every 4
- The acceptable analytical recovery limit for each isotope during a system radiosotope recovery check has been raised from the operator manual suggested 75%[^107] to 90%, as will be seen in more detail in an upcoming section
- The maximum temperature at which a graphite sample is to be retrieved from the furnace has been set to 500°C, to avoid any significant uncontrolled oxidation on exposure to atmosphere

^3.3.1.2 Recovery Checks

'Recovery checks' are an analytical evaluation of the operating efficiency of the thermal treatment system, as suggested by the Carbolite process manual[^107]. The evaluation works by applying the thermal treatment process outlined in the Section 3.2.1.3 of the Methodology, using a known quantity of ³H and ¹⁴C radioactivity as the sample instead of irradiated graphite. The ratio of collected radioactivity in the bubblers, determined by liquid scintillation counting, to the known quantity put into the furnace is the analytical recovery rate.

Losses of detectable radioactivity can occur through gas leaks in the system, inefficient catalytic oxidation of any ¹⁴CO radioactivity into ¹⁴CO₂ form that can be trapped, or issues with the liquid scintillation counting process, and so performing regular recovery checks ensures that each component of the system is working efficiently.

The frequency with which recovery checks can be performed is chosen by the operator, though it should be noted that data points collected between the previous passed recovery check and a failed recovery check, where an unacceptable level of
radioactivity was collected in the bubblers, could be thrown into suspicion if the cause of the failure is unknown. For instance, a crack may have developed in the quartz tube the day after a successful recovery check, meaning that the following number of days’ data is not reliable and may need discarding. Thus, a compromise must be reached between the frequency of performing time consuming recovery checks, which require a full day and a half from the start of the procedure to obtaining the results from the liquid scintillation counter and performing the analytical calculations, and the quantity of data which may require discarding should the system fail. This is especially difficult to determine because of the nature of the irreplaceable irradiated graphite samples. It was decided that the frequency of recovery checks should be reduced from the previous system’s every 5 runs to every 4, to reduce the risk of losing large swaths of data and to coincide with a 5 day working week where the lengthy recovery check scintillation counting process can be left counting over a weekend.

The limit of acceptable analytical recovery is recommended by the Carbolite process manual to be 75%, meaning that 75% of the known radioactivity inserted into the furnace is detected. Below this limit, the manual suggests replacing the copper oxide catalyst, which may have degraded with time and operation. It has been decided to increase the acceptable analytical recovery limit to 90% for this programme of research, which is achievable and reduces the uncertainty in the thermal treatment data produced.

The known quantities of radioactivity are in the form of $^3$H- and $^{14}$C-labelled sucrose standards, commercially available from Perkin Elmer$^{[121,122]}$. These are glass capsules sealed in plastic, with a labelled sucrose coating on one surface. These standards are immersed into a known quantity of deionised water, determined using the 4d.p. balance, into which they will readily and homogeneously dissolve in a relatively short period of time, as seen in Figure 59. Care is taken not to take a sample of the standard within the first few minutes of immersion, to ensure that full mixing has occurred. At the date of manufacture in April 2010, each $^3$H standard capsule had an activity of $210200 \pm 0.78\%$ disintegrations per minute (DPM) and each $^{14}$C standard capsule had an activity of $101500 \pm 0.91\%$ DPM. The subsequent loss of activity in the standards due to radioactive decay is accounted for in the calculations.
Samples of approximately 1 mL volume are withdrawn from each of the standards vials using a 1 mL capacity disposable manual pipette, recording the mass before and after with the 4d.p. balance to determine the precise quantity of standard taken, before transferring to a ceramic boat. It was found that the ceramic boats were slightly porous, and so to avoid loss of radioactivity and contamination of the laboratory, this transfer of liquid was conducted at the furnace inlet, requiring minimal contact with the sample boat.

Unlike the thermal treatment process, the recovery check is performed using compressed air and oxygen as cover gases because the goal is to effect full oxidation of the radioisotopes into the gas phase. The cover gas is switched from air to O₂ at a temperature of 600°C as per the furnace operator manual[107]. The temperature is ramped up to a final temperature of 700°C at a rate of 10°C/minute, which is slower than typical for a treatment protocol. This is to avoid overwhelming the catalyst or bubbler system by mass transfer of considerable volumes of tritium or ¹⁴C along the quartz tube. A graphical representation of the recovery check operational protocol is given in Figure 60.
Figure 60: A Graphical Representation of the Furnace Protocol used for Recovery Checks

The dashed line represents uncontrolled cooling by natural processes, and as such the temperature profile will not behave linearly as is drawn in Figure 60. The catalyst zone for recovery checks performed earlier in the experimental programme is held at 750°C, and in later recovery checks elevated to 850°C for reasons that will be explained in the following paragraph.

One issue encountered with the recovery check process, that does not occur during oxidation of irradiated graphite samples, is that a large volume of the $^3$H laden water travels through the furnace between temperatures of approximately 100 and 150°C, which occurs over a relatively short period of time. As the tritiated water vapour leaves the catalyst zone of the quartz tube it is met with a relatively cold region of glassware and begins to condense and accumulate, with the original small pool of tritiated water promoting condensation of further water vapour. This is not a particular issue, as long as the pool has evaporated and condensed into the first bubbler by the end of the experiment, except at the previously identified ground glass joint where a perfect seal cannot be achieved. There is significantly less moisture associated with oxidation of irradiated graphite samples, and so this phenomenon of moisture conglomeration does not occur. This has been countered by the use of a heat gun to raise the temperature of the glassware between the furnace and the first bubbler throughout the first half of a recovery check, to prevent this pool of tritiated water the opportunity to form. It was found that raising the catalyst zone temperature to 850°C did not adversely affect the working of the catalyst and provided
sufficient heat to the moisture to assist in maintaining a gas phase water vapour through to the first bubbler, and so this was adopted as standard practice.

The calculation method for recovery checks is similar to that described for thermal treatment in Section 3.2.1.3, except that the analytical recovery is taken as a ratio of the measured radioactivity in the bubbler system against the measured activity in a similar 1 mL unprocessed sample from the standards vials, counted in the liquid scintillation counter with 10 mL of HFP Gold Star cocktail. This method somewhat removes liquid scintillation counting and fluid transfer errors using the 1mL disposable pipettes from the uncertainty in the final result, because both quantities under comparison have been processed similarly.

The results of the recovery checks performed since the commencement of this programme of research are shown in Figure 61.

![Figure 61: Recovery Check Results Obtained over the Duration of this Programme of Research](image)

The analytical limit line, the user defined pass-fail limit, is seen to increase from 75 to 90% as of the 18th November 2013, as described above.

The $^3$H data is quite variable, and some difficulties with $^3$H recovery were encountered in the latter few months of experimentation. Several components of the tube furnace were cleaned or replaced as a consequence, including replacement of the copper
oxide catalyst and the quartz combustion tube, with some limited success in raising the average $^3$H recovery result. One theory is that dust in the quartz tube, likely arising from the ceramic combustion boats, is harbouring tritium in the quartz work tube, though a correlation is not seen in the steam flush data, in which one would expect to see an increase in $^3$H activity for flush data over recent months if this were the case. Another idea is that greater proportions of $^3$H are escaping the furnace through progressively worn ground glass joints at the ends of the furnace, evading capture in the bubbler system, though if this were true a similar trend would be expected of the $^{14}$C recovery, which is not seen. It should be highlighted that despite this apparent ‘poor’ $^3$H recovery, all values of $^3$H recovery remain above the Carbolite user manual recommended analytical recovery limit of 75%. The average $^3$H recovery, inclusive of ‘failed’ recovery checks, is $91.89 \pm 5.98\%$ (1σ) over the entire duration of this research, and $93.34 \pm 4.98\%$ (1σ) since the raised 90% analytical limit was introduced.

Since the introduction of the 90% analytical limit, the $^{14}$C recovery appears fairly consistent aside from a single poor recovery data point on the 13th June 2015 attributed to improper mixing of the $^{14}$C-labelled sucrose standard and deionised water. The average $^{14}$C recovery over the entire programme of research, inclusive of any ‘failed’ recovery checks, is $93.58 \pm 4.14\%$ (1σ), and the average recovery is $95.13 \pm 0.91\%$ (1σ) since the 90% limit was introduced, exclusive of the 13th June failed recovery noted above. This consistency in the data allows a great deal of confidence in the apparatus and thermal treatment process for oxidation and capture of $^{14}$C.

Assuming that this method for recovery of $^3$H and $^{14}$C behaves similarly to that for oxidation of irradiated graphite, these recovery check values can effectively be used as calibration values. If it is known that 95.13% of the $^{14}$C expected is consistently recovered, then the same value can be assumed for graphite and the ‘missing’ 4.87% accounted for.

The recovery fraction for $^3$H is seen to vary across this experimental programme of research, and so defining a single average recovery fraction for the entirety of the data is therefore not necessarily reflective of each particular data set. Consequently, an average recovery fraction for $^3$H and $^{14}$C for experiments performed between two given dates corresponding to differing groups of experiments have been defined and applied to the appropriate experiments, which is particularly important for uncertainty calculations, which are yet to be discussed in detail. The applied recovery fractions for experiments performed within given time periods, with uncertainties given to 2σ, are given in Table 11.
### Table 11: Differing Recovery Fractions applied to Experiments between Specific Dates

<table>
<thead>
<tr>
<th>Dates</th>
<th>Applied $^3$H Recovery (%)</th>
<th>Applied $^{14}$C Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3rd March ’13 - 9th April ’13</td>
<td>87.38 ± 13.66</td>
<td>90.31 ± 11.52</td>
</tr>
<tr>
<td>8th August ’13 – 24th March ’15</td>
<td>94.02 ± 12.54</td>
<td>94.44 ± 2.24</td>
</tr>
<tr>
<td>28th March ’15 – 1st August ’15</td>
<td>91.20 ± 8.81</td>
<td>95.19 ± 2.17</td>
</tr>
<tr>
<td>19th August ’15 – 4th September ’15</td>
<td>88.24 ± 4.55</td>
<td>95.57 ± 1.47</td>
</tr>
</tbody>
</table>

### 3.3.1.3 Sample Temperature Profile Validation

The furnace thermocouples informing the digital display are located outside of the quartz work tube, and so the precise temperature at the graphite sample is unknown. An experiment was devised, using an external K-type thermocouple, to try and determine the actual temperature at the graphite sample. The K-type thermocouple was tested using ice water and boiling water immediately prior to this experiment, and was found to be accurate to 0 and 100°C respectively within approximately 1°C. The experiment was performed by drilling a hole into a ceramic combustion boat as used for the graphite samples, through which a thermocouple was passed such that the end of it was in a similar position to a graphite sample, before sliding the ceramic boat and thermocouple unit into the sample zone of the furnace. Introduction of the thermocouple was done via an additional T-piece at the inlet of the furnace such that a 100cc/minute flow of an inert argon cover gas could be maintained during the measurement, imitating the conditions of an inert treatment run. The furnace sample zone temperature was then raised from room temperature at 20°C/minute in steps of 100°C, up to 800°C, with intended dwell times of approximately 5 minutes at each temperature step to allow the furnace to stabilise, as depicted graphically in Figure 62, though in reality the dwell times were slightly variable and often closer to 10 minutes because of software issues. This does not affect the experiment, because it is the settled sample zone temperature and time to settle that is of interest. The indicated catalyst zone temperature was 750°C throughout the experiment. The furnace indicated and registered thermocouple temperatures were recorded simultaneously. The furnace digital display temperatures were recorded by hand, and the thermocouple temperatures were recorded both by hand and using a Pico Technology TC-08 Thermocouple Data Logger and the corresponding software[123].
The results obtained from the staggered temperature thermocouple testing match the intended profile well, as seen in Figure 63.

**Figure 63: Results of the Staggered Temperature Thermocouple Testing of the Carbolite Furnace**

The blue continuous line represents continuous data received from the thermocouple, at a sampling rate of approximately two temperature measurements per
second, and the red square data points are the temperatures indicated on the digital display of the Carbolite furnace itself. Figure 63 shows that the furnace is more stable at higher temperatures, overshooting the intended dwell temperature less at elevated temperatures and stabilising faster. This can be seen numerically in Table 12 where the ‘Temperature after 10mins Dwell’ refers to the thermocouple measured temperature inside the furnace 10 minutes after the digital display has registered the correct dwell temperature. For 500°C and above, the temperatures all reside within ±1% of the intended dwell temperature following 10 minutes of stabilisation.

Table 12: Numerical Evaluation of Staggered Temperature Thermocouple Test

<table>
<thead>
<tr>
<th>Dwell Temperature (°C)</th>
<th>Overshoot (°C)</th>
<th>Temperature after 10mins Dwell</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>16.81</td>
<td>No Data</td>
</tr>
<tr>
<td>200</td>
<td>12.74</td>
<td>No Data</td>
</tr>
<tr>
<td>300</td>
<td>7.22</td>
<td>306.21</td>
</tr>
<tr>
<td>400</td>
<td>6.21</td>
<td>404.50</td>
</tr>
<tr>
<td>500</td>
<td>7.42</td>
<td>503.95</td>
</tr>
<tr>
<td>600</td>
<td>7.24</td>
<td>602.47</td>
</tr>
<tr>
<td>700</td>
<td>6.69</td>
<td>No Data</td>
</tr>
<tr>
<td>800</td>
<td>6.18</td>
<td>801.01</td>
</tr>
</tbody>
</table>

Another test was performed, ramping straight from room temperature up to 800°C at a rate of 20°C/minute, without staggering the temperature, because it was recognised that in a thermal treatment run the temperature would not be elevated in stages, but in one single ramp, preventing stabilisation at each 100°C step.
Figure 64: Furnace Temperature Test using 20°C/minute Ramp from Room Temperature to 800°C

The results of this second test are shown in Figure 64, where the red line represents the intended temperature profile programmed into the furnace, and the blue line yields the resultant temperature as measured by the thermocouple. It can be seen that beyond approximately 400°C the two temperature profiles match closely, until the furnace overshoots by 20.34°C. Within ten minutes of stabilisation, from when the furnace digital display registers 800°C, the measured temperature at the thermocouple has fallen to 807.7°C.

These temperature tests using an external thermocouple attached to a ceramic combustion boat in a 100cc/minute flow of argon allows confidence in the registered furnace temperature correlating with the actual temperature at the sample, and any insulating effects of using a ceramic combustion boat. It was decided following these tests that a 10 minute stabilisation period should be introduced to the furnace temperature profile programming, to allow the temperature to fall within ±1% of the intended temperature. Given the consistent temperature profiles and behaviour, it is expected that this will hold approximately true for other intended treatment temperatures, between 600 and 800°C.
3.3.1.4 Gas Composition Determination

Without testing, there is some uncertainty as to the actual gas composition within the sample zone of the work tube, and so an experiment has been designed to determine both the composition of the treatment gas, expected to be 1% and certificated to 1.01% oxygen in an argon carrier gas, and upon switching cover gases the time taken for the environment in the work tube to change from an inert environment to the desired concentration of oxygen.

This experiment has been performed collaboratively with a colleague\textsuperscript{[124]}, using a Hiden Analytical Quantitative Gas Analyser system attached to a Carbolite MTT \textsuperscript{3}H and \textsuperscript{14}C Analyser furnace identical to that for this programme of research. The gas analyser probe has been positioned between the catalyst zone and the sample zone of the furnace. The argon cover gas is provided from a different bottle located in the test laboratory, though the 1% oxygen test cover gas is exactly the same bottle as used for thermal treatment. All cover gases are passed through the furnace at 100 mL/minute, as indicated by a Vögtlin ‘MIX_146 red-y compact’ digital flow rate controller. The temperature in the furnace was approximately 350°C, as it had been used prior to this experiment for other work. Over approximately the first 25 minutes, the furnace is purged using argon before introduction of the test gas.

The results of the test are presented in Figure 65, showing the fractional composition of argon, oxygen and nitrogen, which has been used as an indicator of air leaks or ingress.
It can be observed from Figure 65 that the introduction of argon at the beginning of the test has successfully flushed a major proportion of the oxygen and nitrogen, which is assumed to be analogous to air, from the furnace tube. The increasing concentration of nitrogen at approximately 16 minutes, which is suspiciously linear, is a consequence of misrepresentation of the raw data by the software. Following introduction of the test gas into the tube at approximately 26 minutes, there is a considerable spike of nitrogen and oxygen, registering a maximum of 6.5% of the total gas composition, which will be a consequence of air and residual gas from the previous experiment (60% oxygen) being pushed through the gas line attached to the 1% oxygen bottle. This spike would not be expected to be as large for the experimental arrangement used in this programme of research because the argon and 1% O₂ treatment gas lines are shorter and attached to each other by a T-piece, so that during argon purging at the start of the experiment the majority of residual air (oxygen) will be flushed through the lines, and exposure to atmosphere is not required between switching cover gases. It remains plausible, however, that a small fraction of oxygen could be introduced to the furnace environment from trapped air during this cover gas changeover, though given the length of the run times, in the order of hours, this will likely have negligible effects on the data.

**Figure 65: Furnace Gas Composition Test, Gas Analyser Results**
According to the raw data, the relative fractions of oxygen and argon in the treatment test gas, over a five minute period once stabilised and following background subtraction, are $0.844 \pm 0.005\%$ oxygen and $99.110 \pm 0.006\%$ argon, with the remaining $0.046\%$ consisting of minute impurity concentrations of gases such as carbon monoxide and methane. In this experiment, the time taken for half of the oxygen spike to dissipate is 4.75 minutes, and the time for the furnace environment to change from the argon purge gas to 1% oxygen in argon is 9.51 minutes, which is small compared to even the shortest thermal treatment run times conducted, at 4 hours. This transition time from one gas to another is expected to occur faster in the system used for this programme of research because there should be less of an oxygen spike, for the reasons described above, allowing an equilibrium to be reached faster.

This transition time between the purge gas and treatment gas cannot be easily accounted for, as the test gas will inevitably take a finite amount of time to occupy the work tube, though this experiment has demonstrated that this uncertainty should have negligible effects on the data because the transition time between gases is small compared to the duration of a treatment run, and any oxygen introduced dissipates quickly.

3.3.2 Data Validation for Other Characterisation Techniques

3.3.2.1 Germanium Gamma Spectrometry

3.3.2.1.1 Energy Calibration

Regular energy calibration of a gamma spectrometer is essential for collecting meaningful quantitative data, as the spectra will drift away from their correct energies with time. When the detector is in use, calibrations are performed weekly. This is conducted by collecting a spectrum using sealed standards of known radioisotopes emitting gamma rays of known energies, and using the GENIE2K software to correlate their peaks with their correct position on the spectrum. It is helpful to have standards emitting gamma rays that might be expected in your sample, and emissions of energies across a good breadth of the energy spectrum to be analysed, which in this instance is from 0 – 2000 keV.

The standards used for calibrating the NGRG gamma spectrometer are $^{60}$Co, $^{137}$Cs, $^{152}$Eu and $^{241}$Am, which had activities of approximately 40 kBq each at their time of manufacture in 2013, and have half lives extending into multiple years. The precise activity is not important for calibration purposes, as the standards are simply placed on the
detector for approximately 5 minutes, to allow the formation of pronounced and well resolved peaks in easily definable positions on the spectrum, and so as long as there is a reasonable amount of detectable radioactivity remaining in the standards then they will be suitable for calibration. The energies of the prominent peaks which appear in the spectrum are as seen in Table 13, in energy order.

Table 13: Germanium Gamma Spectrometer Calibration Standard Peak Energies

<table>
<thead>
<tr>
<th>Source Radioisotope</th>
<th>Gamma Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{241}$Am</td>
<td>59.541</td>
</tr>
<tr>
<td>$^{152}$Eu</td>
<td>121.782</td>
</tr>
<tr>
<td>$^{152}$Eu</td>
<td>244.680</td>
</tr>
<tr>
<td>$^{152}$Eu</td>
<td>344.279</td>
</tr>
<tr>
<td>$^{137}$Cs</td>
<td>661.657</td>
</tr>
<tr>
<td>$^{157}$Eu</td>
<td>778.904</td>
</tr>
<tr>
<td>$^{152}$Eu</td>
<td>964.079</td>
</tr>
<tr>
<td>$^{152}$Eu</td>
<td>1085.869</td>
</tr>
<tr>
<td>$^{152}$Eu</td>
<td>1112.069</td>
</tr>
<tr>
<td>$^{60}$Co</td>
<td>1173.228</td>
</tr>
<tr>
<td>$^{60}$Co</td>
<td>1332.492</td>
</tr>
<tr>
<td>$^{152}$Eu</td>
<td>1408.006</td>
</tr>
</tbody>
</table>

A good breadth of the energy spectrum has been used for calibrating the detector, exploiting the reliable low energy emission from $^{241}$Am and the multiple strong emissions from a $^{152}$Eu source across the energy spectrum. An obtained calibration spectrum using the described sealed radiation sources is found in Figure 66.
Figure 66: Calibration Spectrum using $^{60}$Co, $^{137}$Cs, $^{152}$Eu and $^{241}$Am on the NGRG Germanium Gamma Spectrometer

3.3.2.1.2 Scan Time Determination

Since the confidence in gamma spectrometry data partially arises from the number of counts received at the detector, a suitable scan time must be determined for these irradiated graphite samples, reaching a compromise between uncertainty in the data and the volume of data that can be collected. When a sample activity is quantified, the GENIE2K software is able to determine the mathematical uncertainty for each radioisotope by performing an algorithm based on factors such as the sample geometry, number of counts for a given energy peak, the efficiency of the detector at a given energy, the proportion of detector dead time, amongst others. Thus, a suitable means for determining a reasonable scan time is by observation of this uncertainty relative to the time taken to collect that data.

An irradiated graphite sample was selected at random for this sensitivity study; this was sample OMTT21. The radioactivity in the sample was quantified for the gamma-emitting radioisotopes highlighted as prominent in Section 2.2.2 and using the full process
outlined in Section 3.2.2.1, varying the live scan time from 30 seconds to 16 hours, and the uncertainties for each radioisotope determined. The results can be seen in Figure 67.

![Figure 67: Sensitivity Study for Gamma Spectrometry Uncertainty and Live Scan Time](image)

Figure 67 demonstrates that there is a defined relationship between time and activity uncertainty, which varies between radioisotopes though almost exclusively reduces with increasing live scan time. It should be noted that the activities of americium-241 are low in this graphite, and so the uncertainty in its activity is relatively high and it could not even be confidently detected for scan times less than 30 minutes. It was decided using this data that the relative benefit of scanning a sample for any longer than 2 hours (7200 seconds) did not justify the additional time required to do so, and so this was selected as a suitable scan time to adopt for confident quantitative radioactivity determinations on these irradiated graphite cylinders.

This experiment has also proved that the cylindrical irradiated graphite samples are of suitable radioactivity to be scanned with the sample in contact with the upper surface of the detector, as seen in Figure 57. If the samples were too radioactive, the dead time of the detector would be so high as to cause large uncertainties in the data, and they would require distancing from the detector to reduce the effective counts at the detector. A dead time proportion above 5% begins to raise doubts about the data produced. These scans
have shown that the detector dead time during scans of sample OMTT21 was approximately 1%, which is suitably low for representative data.

3.3.2.2 Autoradiography

The most efficient means of performing autoradiography on these samples is by exposure of multiple samples to the screen at the same time. Consequently, large periods of time can elapse where the phosphor storage screens go unused. It is useful therefore to have a standard, using which the screens can be compared between scans for any changes in performance. The $^{14}$C standards used are placed on the screen, as though they were a graphite sample, adhering to the same duration of exposure as the samples. There are six tabs aligned parallel to each other with known and differing activities per unit of surface area, the effects of which on the phosphor storage screens can be seen in Figure 68. These standards are also useful for demonstrating that the screens have a linear response with increasing energy deposition, as can be seen in Figure 69.

![Radiograph of the $^{14}$C Standards used for Autoradiography](image)

Figure 68: Radiograph of the $^{14}$C Standards used for Autoradiography
Figure 69: The Linear Response of the $^{14}$C Standards on an Autoradiography Screen

The response of the autoradiography screen reduces with time, though since it has been acknowledged that quantitative activity data is not sought because of unknown contribution of other radioisotopes such as $^{60}$Co, as described in more detail in Section 3.2.2.2, this phenomenon is not of serious concern to this research. It can also be seen that the phosphor storage screen responds linearly with increasing energy deposition, with high $R^2$ fit values of 0.994, 0.9747 and 0.9818 irrespective of the relative efficiency of the screen. This allows confidence that radiographs produced by using these phosphor storage screens are reflective of energy deposition induced by the radioactivity in the irradiated graphite samples.

3.3.2.3 Metrology

3.3.2.3.1 Validation of Mass Balances

There is a contribution to the random uncertainty associated with the mass balances used for this research from the laboratory environment. The manufacturer specified uncertainties are not reflective of those for real measurements because of the negative pressure ventilation systems installed in the radiation laboratory. The 2d.p. balance is situated on a bench top and the 4d.p. balance, which has a protective housing, is
placed inside a fume cupboard because of the nature of the samples requiring mass measurements. It is therefore necessary to quantify the additional uncertainty, to ensure that these balances are suitable for the role.

An experiment has been devised to determine the random error associated with these balances, accountable largely to the ambient pressure differences in the laboratory, by taking repeat measurements of multiple vials containing differing volumes of deionised water. A total of 11 plastic vials were made up, with one empty and the remainder differing by 1 mL of water in each between 1 mL and 10 mL.

For the 4d.p. balance, the mass of each individual vial is recorded 10 times, taking the reading following 10 seconds on the balance and then allowing a 10 second unloaded period for the balance to stabilise before the next measurement. The balance is tared between vials. It was noted during early measurements that the vials appeared to be losing mass with time, though it was discovered that this was a consequence of heat energy from the author’s hand affecting the mass measurements, as the vials were held between measurements, and so these results were repeated taking care to place the vial on the base of the fume cupboard between measurements and reduce the handling time. This effect was not noticeable in the following data.

For the 2d.p. balance, it was recognised that it will be used for determining larger masses than the 4d.p. balance, and so the vials were measured by addition of the next vial to the existing vials on the balance. Bubbler mass measurements are conducted using a plastic beaker to stabilise them, and so this beaker is inclusive in this analysis. The measurement is taken similarly to those for the 4d.p. balance, by recording the mass following 10 seconds on the balance and allowing 10 seconds for the balance to stabilise when unloaded.

The results of the 4d.p. balance mass measurements can be found in Appendix D.

If the standard deviations for the measurements corresponding to each vial are taken, they are found to be reasonably similar, suggesting that the variation between measurements is quite consistent. The average mass and standard deviations (σ and 2σ) for the results of the 4d.p. balance mass measurements are shown in Table 14.
Table 14: 4d.p. Mass Balance Test Results Analysis

<table>
<thead>
<tr>
<th>Vial</th>
<th>Average Mass (g)</th>
<th>σ (g)</th>
<th>2σ (g)</th>
<th>2σ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.2497</td>
<td>0.000294</td>
<td>0.000589</td>
<td>0.009421</td>
</tr>
<tr>
<td>2</td>
<td>7.45497</td>
<td>0.000411</td>
<td>0.000822</td>
<td>0.0110288</td>
</tr>
<tr>
<td>3</td>
<td>8.4622</td>
<td>0.000732</td>
<td>0.001464</td>
<td>0.0172961</td>
</tr>
<tr>
<td>4</td>
<td>9.3024</td>
<td>0.000408</td>
<td>0.000816</td>
<td>0.0087773</td>
</tr>
<tr>
<td>5</td>
<td>10.27368</td>
<td>0.000343</td>
<td>0.000685</td>
<td>0.0066683</td>
</tr>
<tr>
<td>6</td>
<td>11.3096</td>
<td>0.000327</td>
<td>0.000653</td>
<td>0.0057756</td>
</tr>
<tr>
<td>7</td>
<td>12.2473</td>
<td>0.000365</td>
<td>0.000731</td>
<td>0.0059654</td>
</tr>
<tr>
<td>8</td>
<td>13.25962</td>
<td>0.000469</td>
<td>0.000937</td>
<td>0.0070676</td>
</tr>
<tr>
<td>9</td>
<td>14.25935</td>
<td>0.000071</td>
<td>0.000141</td>
<td>0.0008698</td>
</tr>
</tbody>
</table>

The uncertainty in measurements taken using the 4d.p. balance, reflective of the uncertainty across a range of masses, has been taken as the average second standard deviation (2σ) from Table 14, which equates to 0.000733 g.

Table 14 also shows that 2σ is small as a percentage of the average mass, and reduces in magnitude with additional mass, allowing confidence that this balance is suitable for this programme of research and will not contribute any significant uncertainty to the data.

The results of the 2d.p. balance mass measurements can be found in Appendix D.

Similarly to the 4d.p. data, the standard deviations for the measurements corresponding to each group of vials are found to be similar, suggesting that the variation between measurements is quite consistent. The average mass and standard deviations (σ and 2σ) for the results of the 2d.p. balance mass measurements are seen in Table 15.

Table 15: 2d.p. Mass Balance Test Results Analysis

<table>
<thead>
<tr>
<th>Vial</th>
<th>Average Mass (g)</th>
<th>σ (g)</th>
<th>2σ (g)</th>
<th>2σ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beaker</td>
<td>55.083</td>
<td>0.011595018</td>
<td>0.02319</td>
<td>0.0421002</td>
</tr>
<tr>
<td>1</td>
<td>61.335</td>
<td>0.011785113</td>
<td>0.02357</td>
<td>0.0384287</td>
</tr>
<tr>
<td>1-2</td>
<td>68.795</td>
<td>0.012692955</td>
<td>0.025386</td>
<td>0.0369008</td>
</tr>
<tr>
<td>1-3</td>
<td>77.259</td>
<td>0.01197219</td>
<td>0.023944</td>
<td>0.0309924</td>
</tr>
<tr>
<td>1-4</td>
<td>86.552</td>
<td>0.010327956</td>
<td>0.020656</td>
<td>0.0238653</td>
</tr>
<tr>
<td>1-5</td>
<td>96.823</td>
<td>0.004830459</td>
<td>0.009661</td>
<td>0.0099779</td>
</tr>
<tr>
<td>1-6</td>
<td>108.131</td>
<td>0.012866839</td>
<td>0.025734</td>
<td>0.0237986</td>
</tr>
<tr>
<td>1-7</td>
<td>120.383</td>
<td>0.008232726</td>
<td>0.016465</td>
<td>0.0136776</td>
</tr>
<tr>
<td>1-8</td>
<td>133.635</td>
<td>0.007071068</td>
<td>0.014142</td>
<td>0.0105827</td>
</tr>
<tr>
<td>1-9</td>
<td>147.909</td>
<td>0.014491377</td>
<td>0.028983</td>
<td>0.0195959</td>
</tr>
<tr>
<td>1-10</td>
<td>163.309</td>
<td>0.011005049</td>
<td>0.02201</td>
<td>0.0134776</td>
</tr>
<tr>
<td>1-11</td>
<td>179.563</td>
<td>0.010593499</td>
<td>0.021187</td>
<td>0.0117992</td>
</tr>
</tbody>
</table>
The uncertainty in measurements taken using the 2d.p. balance to two standard deviations, reflective of the uncertainty across a range of masses, has been taken as the average second standard deviation (2σ) from Table 15, which equates to 0.021244 g. Table 15 indicates that 2σ is small as a percentage of the average mass, and reduces in magnitude with additional mass, allowing confidence that this 2d.p. balance is also suitable for this programme of research and will not contribute any significant uncertainty to the data.

A further confidence that these balances are operating correctly can be gleaned when the data they produce is compared. Addition of the average mass of the vials from the 4d.p. data should be equivalent to the ‘1-11’ mass recorded by the 2d.p. balance minus the mass of the beaker. The uncertainties are combined in quadrature, as per Equation (13).

\[ E_{Total} = \sqrt{(E_1)^2 + (E_2)^2 + \ldots + (E_n)^2} \] (13)

The term ‘n’ represents the number of uncertainties for consideration. The 4d.p. combined mass measurements equate to 124.4919 ± 0.0023 g, and the 2d.p. multiple vial mass measurements equate to 124.48 ± 0.03 g, and so the 4d.p. measurement lies within the uncertainty of the 2d.p. measurement. This demonstrates that each balance is operating correctly, and the uncertainty introduced by the fluctuating atmosphere in the laboratory has not detrimentally affected the data.

The two balances used for this research have been calibrated by an external company twice over the course of this research, with United Kingdom Accreditation Service (UKAS) endorsement. A 100 g standard weight was placed on the 2d.p. balance daily to ascertain that the balance has remained true to the calibration. No determinable shift is observed over many months, with measurements lying within the random uncertainty of the balance, as determined above. Repeat mass measurements of irradiated graphite samples sometimes 2 years apart demonstrate that the 4d.p. balance also remains true to its calibration, with mass values varying within the determined random uncertainty.

### 3.3.2.3.2 Geometry Measurements

Unless otherwise specified, three measurements of the length and three diameter measurements along the length of each irradiated graphite cylinder have been taken, and an average calculated. A compromise has been reached between number of measurements
and associated hazard, since a greater number of measurements leads to a greater accrued operator radiation dose, as measurements on small cylinders with a micrometer require placing hands within close proximity of the radioactive samples.

### 3.3.2.4 Liquid Scintillation Counting

The correct operation of a liquid scintillation counter can be confirmed by analysis of the manufacturer provided Self-Normalisation and Calibration (SNC) vials which are to be passed through the counter every 24 hours, or directly before counting samples if longer than 24 hours since the previous SNC to confirm appropriate counter performance. There are three SNC vials including a background, a $^3$H and a $^{14}$C vial of known activities, which the liquid scintillation counter uses to self-calibrate and adjust the quench correction curves previously described in Section 3.2.1.2.

One of the outputs from the SNC vials is the counting efficiency of $^3$H and $^{14}$C as a percentage. The precise efficiencies will vary from counter to counter and can be seen to slowly fall with time, as components within the scintillation counter degrade, though should typically lie above 60% for $^3$H and 95% for $^{14}$C.

The SNC determined efficiencies for $^3$H and $^{14}$C for the liquid scintillation counter used over this programme of research are shown in Figure 70.
Figure 70: $^3$H and $^{14}$C Counting Efficiencies for the NGRG Liquid Scintillation Counter

The jump in $^3$H efficiency seen in Figure 70, corresponding to March 2013, indicates where counter components have been replaced during a routine service, significantly improving the $^3$H counting efficiency. The same effect has occurred for counting of $^{14}$C, though it is less pronounced. Counting performance is otherwise found to be consistent over the duration of this programme of research, allowing confidence in the LSC results.

3.3.3 Thermal Treatment Uncertainty Calculations

As the treatment process is a relatively lengthy and complex procedure involving many pieces of apparatus, a detailed assessment of the accumulated uncertainties associated has been conducted, to determine a final uncertainty value.

There are many measurements taken over the course of a typical treatment run, meaning that calculating the uncertainty on a particular data point is not a simple process. The chronological order in which these measurements are conducted, and thus the order of introduction of uncertainties, can be seen in the schematic below, Figure 71. The terms ‘2dp’ and ‘4dp’ refer to the precision of the mass balance used, to the number of decimal places of a gram.
This schematic could be misleading, however, as it does not indicate which measurements are dependent on others. The activity measurement for instance, taken using liquid scintillation counting, is independent of the mass measurements used to determine a mass difference. As different instruments of varying precision and accuracy are used, it is sensible to conduct an order of magnitude study to determine whether the uncertainties associated with some measurements can be neglected as negligible in comparison to others.

As seen in Section 3.3.2.3.1, it has been experimentally determined the mass balances yield a relatively consistent 2σ uncertainty of 0.000733 and 0.021244g for the 4d.p. and 2d.p. balances respectively. When compared to the masses measured, these fluctuations yield relatively small uncertainties for all mass differences measured, except the graphite sample mass difference, which in some instances can be small enough to be difficult to measure using this apparatus.

The liquid scintillation counters calculate a statistically determined 2σ percentage uncertainty for each and every measurement taken, which is an output of the LSC data. As each absolute activity of a sample vial is determined by comparison with the activities of standards for the appropriate quench correction curve, the uncertainty associated with these standards should also be included in these calculations. It is the combination of these two values that is used to determine the total uncertainty associated with the liquid scintillation counting process.

The uncertainty associated with the furnace is more arbitrary and difficult to determine, though in this instance the data retrieved from numerous recovery checks can be used to deduce a realistic uncertainty for the specific setup and furnace used for this experimental programme. One additional complication, or possibly advantage to this approach, is that a recovery check will include the uncertainties introduced by human operation, as fluctuations in the final result could be as a consequence of human error. It is found from the recovery check data, seen in Section 3.3.1.2, that the performance of the system varies slightly depending on when the data was taken. The average uncertainty to 2σ for $^{3}$H and $^{14}$C, over the entire programme of research, are 5.98 and 4.14% respectively.
The expected orders of magnitude of errors to be found throughout the treatment process can be compared, as seen in Figure 72, to reveal that some uncertainties are orders of magnitude lower than others, indicating that they can be deemed to bear a negligible influence on the total uncertainty, and consequently can be systematically removed from the calculations. Those measurements that are relatively insignificant and can be removed from the uncertainty calculation are highlighted in green in Figure 72, whilst the noteworthy uncertainties are highlighted in red with a bold border.

From this, it can be deduced that the uncertainties associated with the masses of the bubbler, trap and vials are significantly less than those seen elsewhere, and as such will be neglected from any following error determinations. The combined uncertainty of the mass difference of a sample, the efficiency of the furnace and the activities determined by liquid scintillation counting will require calculating.

Uncertainties can be combined in quadrature, as seen in Equation (14), which is applicable to both summation and product functions, and the combining of these. The division of each uncertainty by their respective measurement, as per Equation (14), yields a fraction without units, allowing their combination into a total uncertainty.

\[
\frac{E_T}{Total} = \sqrt{\left(\frac{E_A}{\text{Measure } A}\right)^2 + \left(\frac{E_B}{\text{Measure } B}\right)^2}
\]  

(14)

The uncertainties should be combined appropriately to the property measured. For instance, a property of key interest is in the form of released radioactivity per gram of graphite mass loss, or specific release activity (Bq/g). To obtain the uncertainty of the specific activity property to two standard deviations, which corresponds to 95.45% confidence that the measured value will lie within the specified range, the uncertainties of interest remaining in Figure 72 will be combined as seen in Equation (15).
\[
\frac{2\sigma_{LSC}}{2\sigma_{Mass\ Loss}} + 2\sigma_{Furnace}
\]

where \(2\sigma_{LSC}\) is the uncertainty associated with liquid scintillation counting, \(2\sigma_{Mass\ Loss}\) is the uncertainty associated with the mass measurements of the sample taken before and after treatment, and \(2\sigma_{RC}\) is the uncertainty associated with the performance of the furnace as determined by analysis of the recovery checks.

Using the uncertainty combination rules described above, the total uncertainty equation for the specific activity of release for each radioisotope can be derived.

Firstly,

\[
2\sigma_{LSC} = \sqrt{(2\sigma_{LSC-QSTD})^2 + (2\sigma_{LSC-Act})^2}
\]

where \(2\sigma_{LSC-QSTD}\) is the uncertainty in the activity of the quench correction curve standards, and \(2\sigma_{LSC-Act}\) is the statistical uncertainty in the activity in a vial as calculated by the liquid scintillation counter for each measurement.

It therefore follows that,

\[
2\sigma_{LSC-Mass} = \sqrt{\left(\sqrt{(2\sigma_{LSC-QSTD})^2 + (2\sigma_{LSC-Act})^2}\right)^2 + \left(\sqrt{(2\sigma_{Mass1})^2 + (2\sigma_{Mass2})^2}\right)^2}
\]

where \(2\sigma_{Mass1}\) and \(2\sigma_{Mass2}\) are the uncertainties of the mass measurements of the sample taken before and after treatment. Inclusion of the uncertainty associated with the furnace system yields,

\[
\frac{2\sigma_{LSC}}{2\sigma_{Mass}} + 2\sigma_{RC} = \sqrt{\left(\sqrt{(2\sigma_{LSC-QSTD})^2 + (2\sigma_{LSC-Act})^2}\right)^2 + \left(\sqrt{(2\sigma_{Mass1})^2 + (2\sigma_{Mass2})^2}\right)^2 + (2\sigma_{RC})^2}
\]
where $2\sigma_{RC}$ is the uncertainty associated with the performance of the furnace as determined by analysis of the recovery checks. The uncertainty in the specific activity of release for each radioisotope during treatment can therefore be determined as shown in Equations (16) and (17).

$$2\sigma_{\text{Treatment-3H}} = \sqrt{\left(\sqrt{(2\sigma_{\text{LSC-STD-3H}})^2 + (2\sigma_{\text{LSC-Act-3H}})^2} \right)^2 + (2\sigma_{\text{Mass}})^2 + (2\sigma_{\text{Mass}})^2} + (2\sigma_{\text{RC-3H}})^2$$

(16)

$$2\sigma_{\text{Treatment-14C}} = \sqrt{\left(\sqrt{(2\sigma_{\text{LSC-STD-14C}})^2 + (2\sigma_{\text{LSC-Act-14C}})^2} \right)^2 + (2\sigma_{\text{Mass}})^2 + (2\sigma_{\text{Mass}})^2} + (2\sigma_{\text{RC-14C}})^2$$

(17)

Each sample undergoes two separate experiments in the furnace to obtain the full treatment data, as described in Section 3.2, including the treatment experiment where a preferential release of radioactivity and a remaining solid sample are sought, and a second full oxidation of the sample to determine the actual amount of remaining radioactivity and thus the precise efficiency of the treatment process used. This further complicates the uncertainty calculation since the treatment data point uncertainties from each individual experiment, determined by the equations above, must be combined in quadrature, such that the final uncertainty in the data, following propagation of all of the uncertainties through multiple measurements and experiments, can be described by Equations (18) and (19).

$$2\sigma_{\text{Final-3H}} = \sqrt{(2\sigma_{\text{Treatment-3H}})^2 + (2\sigma_{\text{Full Oxidation-3H}})^2}$$

(18)

$$2\sigma_{\text{Final-14C}} = \sqrt{(2\sigma_{\text{Treatment-14C}})^2 + (2\sigma_{\text{Full Oxidation-14C}})^2}$$

(19)

Although the precise form and complexity of the uncertainty calculation will vary depending on the property of interest, this section has outlined the typical method used to estimate the uncertainties of specific activity measurements in the thermal treatment data, inclusive of a number of sources of uncertainty through multiple measurements and experiments.
3.3.5 Carbonaceous Deposit on Oldbury Magnox Installed Set Samples

Two Oldbury Magnox installed set cylindrical samples from the selection of samples used for this programme of research have been analysed for carbonaceous deposit by the National Nuclear Laboratory (NNL). This has been conducted by thermal gravimetric analysis (TGA) of each sample in laboratory grade air at 450°C for 54 hours\(^{125}\). As seen in Section 2.4.8, the ‘deposit’ is classed as “material that oxidises at a higher rate than substrate graphite”, which is how it is identified and quantified in irradiated graphite specimens. The rate of reaction of the bulk material can be extrapolated backwards to quantify the additional accelerated mass loss due to any deposit at the beginning of the experiment. This post-processing has been performed by NNL. It should be noted that an observed accelerated rate of oxidation could also incorporate material that has a higher rate of reactivity due to catalytic contamination, which is an acknowledged source of uncertainty with this method. It is unclear whether any relatively high surface area dust contamination displaced into the pores during the machining process may also contribute to any accelerated mass loss measurements.

Section 2.3.5 indicates that a carbonaceous deposit may also be relatively rich in \(^{14}\)C, and as such it is important to determine the extent to which a deposit exists on the irradiated graphite specimens used for this programme of research to assess their contribution to any \(^{14}\)C releases observed during thermal treatment.

The results for the two samples analysed can be seen in Table 16.

**Table 16: Concentration of Carbonaceous Deposit on Oldbury Magnox Reactor Graphite Samples, as determined by NNL**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample Mass (g)</th>
<th>Deposit Concentration (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMTT33</td>
<td>0.2059</td>
<td>2716</td>
</tr>
<tr>
<td>OMTT40</td>
<td>0.1719</td>
<td>1989</td>
</tr>
</tbody>
</table>

The measured deposit concentrations on these samples are relatively small compared to the mass of the bulk material, corresponding to 0.0006 and 0.0003 g of samples OMTT33 and OMTT40 respectively, which lie within the limit of detection of the mass balance as determined in Section 3.3.2.3.1.

It is seen from this data that a small concentration of reactive ‘deposit’-like material exists on these samples exhibiting a faster rate of oxidation than the substrate graphite,
with unknown $^{14}\text{C}$ content. Assuming that first regime oxidation is achieved, any contribution of $^{14}\text{C}$ from this source should not interfere with thermal treatment results beyond limit of detection mass losses as this identified deposit will be relatively quickly liberated from the sample by thermal oxidation.

### 3.3.6 Remaining Assumptions and Limitations

A number of sources of uncertainty associated with the data produced over the course of this programme of research have been discussed so far in Section 3.3, and so this section aims to describe the remaining identified assumptions, and how they may be mitigated if possible.

The first assumption is that variations in cylindrical sample length, from approximately 8 to 13 mm in length will not significantly affect the radioisotope release behaviour or thermal oxidation characteristics in these irradiated graphite samples, despite an increase in total activity and surface area. The radius of the cylinders remains approximately constant.

The second assumption is that $^3\text{H}$ and $^{14}\text{C}$ radioisotopes are evenly mixed in the traps in the bubbler. An observation has been made that the gases passing through the bubbler accumulate as a large bubble on one side of the filter, before being forced into several small bubbles to increase their surface area, as shown in Figure 73.
The possibility exists that gaseous radioactivity passing through the bubbler will interact with the fluid in the bottom of the bubbler, physically separated from the remainder of the trap fluid by a large gas bubble, before having opportunity to reach the remaining trap above the filter, because of the pressure-induced separation effect that can be seen in Figure 73. This could lead to a concentration of radioisotopes in this portion of the fluid. Care should be taken when transferring this bubbler fluid to a beaker that as much of the trap is transferred as possible, as this portion of separated fluid in the lower chamber of the bubbler could have more of an influence on the result than would be expected if the radioactivity was homogeneously distributed.
3.4 Summary of Section 3

The main findings of the methodology section of this thesis, appropriate to thermal treatment of irradiated graphite conducted during this programme of research, are:

- The precise nature and origin of the irradiated graphite samples have been described in detail, inclusive of any machining processes
- The overall method has been described, from pre-treatment characterisation to treatment, post-treatment characterisation and then full oxidation of the sample
- The characterisation techniques have been described in detail, including how they operate and the consequences for measurements of irradiated graphite
- The thermal treatment process has been outlined in detail
- Adaptations to the existing thermal treatment process have been highlighted
- The methods used for validation of the data produced from each characterisation technique and the thermal treatment process have been discussed in detail, demonstrating by quantification of the individual sources of uncertainties that confidence in the data is high
- The methodology for quantification of the uncertainty of individual data points is described, demonstrating by an order of magnitude study that many sources of uncertainty are comparably negligible due to their precision and repeatability
- A carbonaceous deposit-like layer has been identified on the samples used for this programme of research, though the quantity of deposit is relatively small, within the limit of detection of the mass balance, and so this should not significantly influence thermal treatment results
4. Results and Discussion: The Effects of Oxygen on Radioisotope Release

This chapter of the thesis describes the preliminary results, collected with guidance and in collaboration with other researchers at the earliest stages of this programme of research. The data produced, however, has been independently analysed, which led to subsequent experiments. A part of this data contributed to the European consortium CARBOWASTE, and has been internally reviewed and published\textsuperscript{[33]}. 

4.1 Hypothesis and Experimental Protocol

An experimental programme was conducted to investigate the release of $^3$H and $^{14}$C from irradiated graphite samples from the same source as the remainder of this programme of research, using both an inert and oxidising atmosphere. The hypothesis for these experiments is that an unknown proportion of the $^{14}$C formed in an irradiated graphite sample will derive from randomly distributed nitrogen impurities and $^{13}$C, as described in Sections 2.1 and 2.3, and a proportion of the formed $^{14}$C will also exist near the sample surfaces, for reasons outlined in Section 2.3.4. Controlled thermal oxidation can be used as a mechanism for removal of any surface or near-surface $^{14}$C. Thermal treatment in an inert argon atmosphere should yield small releases of $^3$H and $^{14}$C accountable to surface adsorbed oxygen, and possibly a diffusion process in the case of $^3$H, as seen in the literature in Section 2.5. Thermal treatment in a limited oxygen atmosphere, using 1% oxygen in argon, could initiate controlled oxidation of the graphite surfaces throughout the internal porosity.

For these initial investigations, 700°C and 800°C were selected as suitable treatment temperatures, comparable to some of the treatment in the literature\textsuperscript{[54, 97, 126]} and exhibiting oxidation characteristics of reaction in the first and second oxidation regimes, as per Table 10 in Section 2.4.4.

The treatment process was conducted as described in Section 3.2.1.3, with a 100 cc/minute flow of cover gas and 20°C/minute ramp up to treatment temperature, except for these experiments the ramp up to temperature and ramp down were conducted in the respective treatment gases for that experiment. Also atypical of following treatment experiments, the samples were removed from the furnace at temperatures typically
between 650 and 700°C. It is assumed that the temperature of the sample fell sharply following exposure to air at ambient temperatures in the laboratory, though it is possible that a negligible amount of oxidation occurred during this period. The sample treatment durations were between 4 and 8 hours in increments of 1 hour, and each sample was treated only once such that every data point pair, of \(^3\)H and \(^{14}\)C release for a given treatment environment, represents the radioactive release behaviour of a single sample. Full oxidation of each sample is used to determine the actual fractional release, by summation with the total determined \(^3\)H and \(^{14}\)C inventories.

It should be noted that at a later juncture in this programme of research the mass loss data for the 1% oxygen data points was found to be inconsistent with repeat data produced from later experiments, with average graphite mass losses per hour occurring a factor of 6 times faster in the early data. Gamma spectrometry results did not suggest unexpectedly high metallic impurity content in these samples, and so catalytic oxidation by metallic impurities is not suspected. Logically, the most likely reason for this high rate of mass loss is because of higher concentrations of oxygen being present in the earlier data than the repeat data. Following several tests and data validation experiments such as testing the gas composition of the 1% O\(_2\) treatment bottle, as described in Section 3.3.1.4, a conclusive reason for this discrepancy was not found, though insufficient purging and consequent air contamination in the lengthy gas lines is strongly suspected. The gas lines were purged for a significant length of time before the remaining bulk of the data for this programme of research was produced, and so this is not thought to have affected the later data.

The uncertainties for this data have not been calculated because of the unknown magnitude of uncertainty caused by the discrepancy in the data noted above. Consequently, this data will be simply considered in terms of treatment in an inert and an oxidising environment.

Graphical representations of the protocols used for inert and oxidising atmosphere experiments are found in Figure 74, showing the furnace temperature profile and cover gas with time.
4.2 Results

The radioactive releases with time observed for treatment at elevated temperatures in an inert environment are given in Figure 75. The radioactive releases in an inert environment are small, at typically less than 2.5% under these conditions. Mass losses are also typically small, at less than 1% for all samples except one exhibiting 1.8% mass loss. Each data point pair, of $^3$H and $^{14}$C release for a given treatment environment, represents a separate sample, treated once, and so some statistical noise is expected in the data, especially given the known inhomogeneous properties of irradiated graphite as seen in Sections 2.2 and 2.3.

Figure 74: Furnace Protocols used for Preliminary Thermal Treatment Experiments
It is interesting to note that each data set, for $^3$H and $^{14}$C at 700 and 800°C, appears to display a general positive correlation between time and radioactive release, meaning that more radioactivity is liberated from the samples with time. It is unclear from this data whether this is because of $^3$H diffusion and surface $^{14}$C oxidation by adsorbed oxygen, as suggested by the literature[65], or whether small quantities of oxygen ingress into the furnace is occurring. The gas analyser data in Section 3.3.1.4, from an identical Carbolite furnace, suggests that air ingress is negligible. If surface adsorbed oxygen is responsible for these small releases, then one would expect the reactants to become exhausted with more time, and the release rate of $^{14}$C to halt. There is no definitive trend with variation in temperature for this data.

The radioactive releases with time observed for treatment at elevated temperatures in an oxidising environment are shown in Figure 76. It is immediately noticeable that the releases per unit time observed are significantly larger for this oxidising environment than that observed in Figure 75 for an inert environment, and since the only variation between these sets of data is the addition of an oxidising cover gas, it is clear that oxygen is the cause of these releases. This result was to be expected, as oxidation of the
graphite sample, inclusive of its impurity content, will inevitably cause oxidation of the chemically identical radioisotope equivalents.

![Graph of radioisotope releases with time and temperature]

**Figure 76: Releases of $^3$H and $^{14}$C with Time observed during Thermal Treatment in an Oxidising Environment**

Any positive trends are less pronounced in Figure 76 than Figure 75, though it appears that generally further radioisotope release is occurring with time. A marked difference between the radioisotope releases with temperature can be observed, as the $800^\circ$C data releases noticeably and consistently more radioactivity from the sample. This data does not yield any information as to the selective release efficiency of radioactivity, however, as there is no indication as to any sample mass losses by oxidation.

The radioactive releases with mass loss observed for treatment at elevated temperatures in an oxidising environment can be seen in Figure 77. The magnitudes of the mass losses during these experiments are typically high relative to the mass at the beginning of the experiment, extending to over 55% mass loss in some instances. The mass loss accumulated in samples treated at $700^\circ$C is noticeably less per unit of radioactivity released.
Figure 77 shows that the $^3$H release data is sporadic, and it is difficult to identify any trend. The $^{14}$C release data behaves more consistently, however, and an apparent approximately linear release with mass loss can be identified, as demonstrated by the linear best fit lines plotted using Microsoft Excel software. The equations of these best fit lines show that their gradient is approximately unity, signifying that for each percentage of $^{14}$C release an equal percentage of mass loss occurs in the sample. This shows that selective removal of $^{14}$C-rich graphite is not occurring at these temperatures and mass losses, between 4 and 8 hours. If the y-axis intercept values are deduced from the best fit line equations, however, then this predicts that if this linear trend were true and consistent a release of approximately 15 and 3.5% of the $^{14}$C would have been observed for the 700 and 800°C data respectively, at 0% weight loss. This is not physically possible, as the treatment processes have not begun at this stage, yet this positive y-axis intercept does prove that a preferential fractional release of $^{14}$C to fractional mass loss was achieved at some earlier point during both temperatures of treatment. Since each $^{14}$C data point represents the release behaviour of a separate sample, this trend is consistent across several graphite samples treated.
The mass losses encountered during these oxidation experiments are large, especially considering that the samples had reached mass losses of the order 40% compared to the unirradiated material on retrieval from Oldbury Magnox Reactor 2, before any thermal treatment process had been conducted. This can have detrimental effects on the structural integrity of the samples, as demonstrated in Figure 78, showing three cylindrical samples following thermal treatment, and one pre-treatment sample.

**Figure 78: Sample Degradation Following 5 Hours of Thermal Treatment**

Figure 78 demonstrates that samples treated in an inert environment, where mass losses are typically less than 1%, are visually unaffected by the treatment process, with samples treated at 700°C showing signs of slight degradation, as indicated by graphite dusting around the sample. The sample treated at 800°C, the temperature which incurred the highest mass losses, has received significant structural damage, leaving a fragile bulk cylinder and powdered remains. This has poor consequences for post-treatment sample handling and characterisation, which is hindered significantly by sample fragility, powder dispersion, and the radiological risk associated with handling of these samples, which is applicable to both this programme of research and the wider ramifications for adopting a thermal treatment technique for decontamination of the UK inventory of irradiated graphite waste; the graphite material may be difficult to handle requiring additional engineering controls, and incurring cost and radiological risk.

Further to this, if the sample fractional mass loss and volume loss are compared for the 700 and 800°C oxidising treatment data, some indication as to the operating oxidation regime can be obtained. This comparison is presented in Figure 79.
Recalling from Section 2.4.4 that the lower temperature first oxidation regime induces mass losses throughout the entire bulk of the sample, and that the higher temperature third oxidation regime induces mass losses from the outer geometrical surfaces inwards, with the second regime somewhere between these two, one would expect the ratio of mass loss to bulk volume loss to equal unity if the oxidation were occurring solely by the third oxidation regime. Figure 79 shows that for the 800°C treatment data, this 1:1 relationship between volume and mass is almost true, strongly suggesting that the kinetics of oxidation at 800°C are occurring predominantly by the third regime. This is in contrast to the 700°C data in Figure 79, in which large mass losses are seen per unit bulk volume loss, meaning that mass loss must be incurred from internal surfaces of the open porosity within the sample. This data suggests that lowering the temperature to 700°C allows the oxidation process to operate in the first or second oxidation regime.

Since it is selective removal of surface $^{14}$C throughout the open porosity of the bulk material that is sought, the data shown in Figure 79, along with the sample degradation seen in Figure 78, indicate that treatment at 800°C is inappropriate for this research. It is acknowledged that there was likely a higher concentration of oxygen for these treatment
experiments than desired, though this will not significantly affect the oxidation regime and as such sample degradation at the outer geometric surfaces of the sample will likely still occur even for lesser concentrations of oxygen, though at a slower rate.

4.3 Conclusions Reached in Section 4

The main findings of the preliminary experiments are:

- Releases of $^3$H and $^{14}$C from irradiated graphite samples are achievable at elevated temperatures in an inert environment
- Faster releases of $^3$H and $^{14}$C from irradiated graphite samples are achievable at elevated temperatures in an oxidising environment, as opposed to an inert environment
- Large mass losses are incurred to the samples during treatment at 700 and 800°C in an oxidising environment
- The total fractional releases of radioactivity are higher per unit mass loss for treatment at 700°C than at 800°C
- The ratio of release of $^{14}$C to mass loss for both 700 and 800°C treatment data between 4 and 8 hours treatment approaches unity, suggesting that selective removal of $^{14}$C is not occurring between these times
- Selective removal of $^{14}$C can be achieved and must have occurred at some point earlier in the treatments, which is more pronounced for treatment data at 700 than 800°C
- Significant sample degradation occurs during oxidation at 800°C in an oxidising environment, for these treatment conditions
- Treatment at 800°C exhibits oxidation characteristics of the third oxidation regime, whereas 700°C treatments are more indicative of first or second oxidation regime processes
- Treatment at 800°C is inappropriate for selective removal of surface $^{14}$C throughout the open porosity of the bulk irradiated graphite material
5. Results and Discussion: The Effects of Time and Temperature

This results chapter explores the influence of temperature and time on the selective release efficiency of $^{14}$C from irradiated graphite samples.

5.1 Hypothesis and Experimental Protocol

It has been observed from the results in Section 4 that a preferential fractional release of $^{14}$C from the bulk material can be achieved. Although the accurate concentration of oxygen present during these experiments is unclear, the sample mass losses during treatment at 700°C and 800°C in an oxidising atmosphere are relatively large, with the higher temperature treatments compromising the structural integrity of the samples as seen in Figure 78. It has also been seen that oxidation at 800°C exhibits behaviour of the third regime of oxidation, whereas reduction of the temperature to 700°C shows first or second oxidation regime behaviour, as significant mass losses are recorded corresponding to a smaller fractional sample geometric volume loss than at 800°C, as per Figure 79.

Reduction of the oxidation temperatures will ensure that the corrosive oxidation reactions are occurring predominantly by the first chemical oxidation regime, causing mass losses at the surfaces throughout the internal open porosity of the sample, desirable for removal of near surface $^{14}$C as documented in Section 2.3.4. This could increase the selective removal efficiency for $^{14}$C, as less non-radioactive bulk material is unnecessarily oxidised. The rate of oxidation will slow with decreasing temperature, and therefore it may take a longer duration of treatment to effect a release of $^{14}$C comparable to higher temperature treatments.

If an elevated concentration of $^{14}$C exists near the surfaces of the irradiated graphite specimens used for this research, and oxidation parameters are selected to focus the corrosion process at the graphite surfaces, then a faster release of $^{14}$C should be observed earlier in the experiment, with the rate of $^{14}$C removal slowing as the $^{14}$C-enriched surface region becomes exhausted and oxidation of the bulk material underneath begins.

The reduced temperature selected for investigation was 600°C, followed by the introduction of data at 650°C treatment temperature, as the oxidation rate at 600°C in a 1% O$_2$ environment is slow, as will be seen. The treatment protocol has been adapted from the preliminary experiments for this data, to align with the method outlined in Section 3.2.1.3
also applicable to the remaining data for this research. In addition, the 700°C data is repeated to ensure that the adaptations do not significantly affect the data. Initially, the duration of treatments is kept consistent with previous data, varying between 4 and 8 hours of treatment in one hour increments. Thermal treatment is applied to each sample only once, and as such each release data point produced represents the behaviour of an individual sample. The $^{14}$C recovery fraction applied to correct these results is $94.44 \pm 2.24\%$, which corresponds to the average $^{14}$C recovery achieved during recovery checks over the period that these experiments were conducted, extending from August 2013 to March 2015, with an uncertainty of two standard deviations.

A graphical representation of the protocol used for these experiments is given in Figure 80.

![Figure 80: Furnace Protocols used for Thermal Treatment Experiments with Varying Temperature and Duration](image)

5.2 Results

The releases of $^{14}$C with time observed for treatment at elevated temperatures in 1% oxygen in an argon balance environment are shown in Figure 81, where the temperature is having a pronounced effect on the liberation of $^{14}$C from the bulk material that can be achieved within a given time.
Figure 81: Releases of $^{14}$C with Time during Treatment in a 1% Oxygen Environment

The data point corresponding to treatment for 4 hours at 650°C in Figure 81 is significantly higher than the average trend seen for other samples. The mass loss data appears relatively consistent with other data, and so ingress of air to the system is not suspected though equally cannot be disproved. This result may also be a statistical anomaly arising from comparison of multiple samples of a material known for localised inhomogeneity. It can also be seen in Figure 81 that there is a defined positive correlation between time and release, which appears to be linear, demonstrating that with increasing time and increasing oxidation a quantity of $^{14}$C liberation is still occurring, though how this trend might differ beyond 8 hours is difficult to ascertain from this graph.

Care should be taken drawing any conclusions or comparison between these data points, as the temperature has a significant effect on the oxidation rate of graphite. With respect to time, treatment at 700°C is more effective for absolute removal of $^{14}$C from the bulk material, though this may not be reflective of the selective removal efficiency.

It should be emphasised that each data point in Figure 81 corresponds to the $^{14}$C release behaviour of a different sample, and the release fraction achieved has been ascertained by full oxidation of the sample at a later date, to determine the remaining $^{14}$C in the sample following treatment. The quantified activities from each experiment have been
normalised to the same date, corresponding to the start date of this programme of research, to negate the influence of radioactive decay between experiments. The half life of $^{14}$C is long compared to the time between experiments that this correction will only affect this data negligibly, though will become more influential for analysis of other shorter-lived radioisotopes as found in the upcoming Section 7. The uncertainties throughout this results section are calculated per data point, as per Section 3.3.3, and represent the uncertainty to 2σ confidence.

A plot of the mass loss per sample against time is seen in Figure 82. If it is assumed that the rate of mass loss is approximately linear over the 4 to 8 hour timescale used, neglecting any increase or reduction in surface area due to porosity development, and that this rate of oxidation is consistent from the beginning of the experiment, then the gradient of a linear trend line through the origin for each data set is reflective of the average rate of oxidation, in units of grams per hour. It should be noted that the y-axis in Figure 82 is logarithmic to clearly represent the differences between the data sets, and therefore a linear relationship will appear curved.

![Figure 82: Mass Loss per Sample with Time at Differing Treatment Temperatures](image)

Figure 82 demonstrates that the average rates of oxidation for oxidation in 1% oxygen at 600, 650 and 700°C are 0.0002, 0.0009 and 0.0025 g/h respectively,
demonstrating an order of magnitude difference in the rates of oxidation over this oxidation temperature range. This indicates that comparison of $^{14}$C releases with sample mass loss will prove more indicative of the selective removal of $^{14}$C from the bulk material than the data presented in Figure 81.

It is assumed that the influence of the slightly differing geometries between samples does not significantly affect the oxidation behaviour, and as such the mass loss data presented in Figure 82 are comparable. The uncertainty in mass loss per data point is equivalent to approximately 0.001g, deduced from two measurements using the 4d.p. balance, and has not been included in the plot for clarity of the data. This uncertainty is only significant for the relatively small mass losses of the 600°C treatment data. The 700°C treatment data from the preliminary results, seen in Section 4, are included here to support the conclusion that an increased amount of oxygen was present for those experiments, as the mass losses encountered are significantly higher than those observed for the later repeated data.

The releases of $^{14}$C with mass loss observed for treatment at elevated temperatures in a 1% oxygen in argon environment are seen in Figure 83. Lower treatment temperatures are more effective for selective release of $^{14}$C, showing typically a greater average release of $^{14}$C per unit mass loss, as indicated by the gradients of the linear trend lines through each data set which are applied for demonstrative purposes rather than suggesting the trend of the data. There is a single anomalous data point in the 650°C experiments exhibiting over 15% $^{14}$C release, which is thought to be a consequence of inhomogeneity in the source material. The gradient of the linear trend line for treatment at 600°C indicates that an average 4.0953% $^{14}$C is liberated from an irradiated graphite sample per 1% mass loss, compared to 2.149 and 1.7054% $^{14}$C releases for 650 and 700°C respectively. The positive y-intercept values for each temperature set’s linear trend line indicate that, at some instance prior to the minimum experimental time of 4 hours, a faster initial release of $^{14}$C must have been achieved, and so the overall $^{14}$C release profile cannot be linear.
As a consequence of the differences in oxidation rates between treatment temperatures, the mass losses achieved during each treatment temperature explored do not overlap, and as such it is difficult to determine from Figure 83 whether a change in temperature causes a marked effect on the $^{14}$C release characteristics, or whether each of these samples are exhibiting a similar behaviour irrespective of the treatment temperature utilised, though at differing rates. Further data has been collected for treatment at 600°C for longer durations, extending from 12 hours up to 32 hours in increments of 4 hours, which will confirm whether the apparent increased efficiency for selective removal of $^{14}$C during treatments at lower temperatures is consistent into higher sample mass losses. The same experimental protocol as seen for Figure 80 is utilised, with increased duration at treatment temperature and exposure to a 1% atmosphere.

The releases of $^{14}$C with mass loss observed for treatment at elevated temperatures in a 1% oxygen in argon environment, inclusive of additional data extending up to 32 hours of treatment in 4 hour increments, is presented in Figure 84. The $^{14}$C recovery fraction applied to correct these additional results is 95.19 ± 2.17% with an uncertainty of two standard deviations, which differs from previous data because these results were collected over a different time period extending from March 2015 to August 2015, as described in Section 3.3.1.2.
A limitation on the maximum duration of treatment that could be achieved was imposed by evaporation of the bubblers into each other, causing minor cross-contamination and more significant issues for liquid scintillation counting. One 40 hour duration treatment was performed, though a visible separation between the Carbon Trap and a chemically incompatible aqueous solution thought to have arisen as evaporation from the attached nitric acid bubbler could be observed at the bottom of a liquid scintillation vial. Assuming the \(^{14}\)C is not present within the aqueous portion in the vial, an activity is still determinable, though the precise mass of trap in the liquid scintillation vial is now unknown and so this activity cannot be extrapolated to the total release from the sample. The proportion of aqueous contaminant is small following 40 hours of treatment, and so this effect is not thought to have significantly affected the data taken prior to this discovery.

Figure 84 shows the additional longer treatment duration data for treatment at 600°C overlaid on the data sets presented in Figure 83, which are now semi-transparent for demonstrative purposes. The additional mass losses incurred by increasing the duration of treatment now overlap with the data obtained for the \(^{14}\)C release behaviour during treatment at 650°C. Since the \(^{14}\)C release behaviour for longer duration treatments at 600°C...
relate strongly to treatment at 650°C, Figure 84 strongly suggests that the overall release profile for \(^{14}\)C from irradiated graphite is largely unaffected by the temperature utilised between 600 and 700°C, which further suggests that these temperatures all cause oxidation by similar oxidation regimes, and as such the same region of graphite is oxidised at all temperatures though at different rates.

Two trend lines have been applied to the data in Figure 84, one linear and one a power law relationship, because the \(^{14}\)C release profile is not immediately apparent from this data and these appear to best fit. The \(R^2\) coefficient of determination values for the linear and power trends are 0.8358 and 0.8124 respectively, indicating that there is some uncertainty as to whether these are truly reflective of the data. There will inherently be some scatter in the data, as a consequence of using multiple samples of an inhomogeneous material, though relative consistency in the data allows some confidence that the trends produced are reflective of the average behaviour over multiple samples.

The linear trend lines imposed on Figure 83 and Figure 84 indicate that the release profile for \(^{14}\)C from these irradiated graphite samples cannot be entirely linear, as the \(y\)-intercept value is greater than 0 showing that a faster release of \(^{14}\)C must occur at the start of the experiments. If the linear trend line applied to the data in Figure 84 is extrapolated forwards to 100% mass loss, by substituting a value of 100 for ‘\(x\)’ in the trend line equation, the predicted \(^{14}\)C release is 188.34%, which is not physically possible. If the power law trend equation is similarly extrapolated to 100% mass loss, the predicted \(^{14}\)C release is 50.00%, which is also not physically possible in this instance because all of the \(^{14}\)C must be gasified and liberated from the sample at the total sample destruction of 100% mass loss. This indicates that neither a linear nor power law trend alone is reflective of the \(^{14}\)C release profile, and a realistic profile is likely to be a combination of both.

Further information can be obtained about the \(^{14}\)C release profile if the specific activity of the oxidised portion of the graphite converted into the gas phase, in units of becquerels per gram oxidised, is considered. The specific activity of \(^{14}\)C with mass loss observed for treatment at elevated temperatures in a 1% oxygen in argon environment can be seen in Figure 85. The data presented in Figure 85 is inclusive of the additional longer duration data introduced in Figure 84, and the uncertainties presented are calculated individually, as per the method described in Section 3.3.3. The mathematical uncertainties for samples associated with small mass losses are large, though it should be noted that the reason for this is because the measured mass losses are small compared to those
accurately measurable using the 4d.p. balance, with an instance of a measured 0.0001 ± 0.0010g mass loss, and so despite the large mathematical uncertainty associated with these data points, they are confidently reflective of the release behaviour during relatively small mass losses.

![Figure 85: The Specific Activity of $^{14}$C in the Oxidised Portion of Irradiated Graphite Samples against Mass Loss during Treatment in a 1% Oxygen Environment](image)

It is seen in Figure 85 that all of the treatment data sets exhibit a reduction in the specific activity of $^{14}$C in the gas phase with increasing mass loss, which is analogous to time in this instance, irrespective of the treatment temperature. This data strongly implies that a $^{14}$C-enriched graphite surface region undergoes oxidation early in each experiment, becoming exhausted with mass loss and leading to oxidation of the underlying bulk material, thought to contain a random and approximately even distribution of $^{14}$C, contributes to the $^{14}$C release. The specific activity of pure $^{14}$C is 165 GBq/g, as calculated in Appendix E, yet the largest specific activity achieved from the data in Figure 85 is less than 1 MBq/g indicating that despite these relatively high selective release efficiencies, a significant proportion of the recorded mass loss is attributable to non-radioactive $^{12}$C and $^{13}$C, with some likely contribution from moisture losses.

The data presented in Figure 85 behaves similarly irrespective of the treatment temperature utilised. It is found that a power law trend is appropriate to describe the
reduction in the specific activity of oxidised graphite with increasing mass loss, irrespective of the treatment temperature, with an $R^2$ coefficient of determination value of 0.9358 as seen in Figure 85. This supports the inclusion of a power law trend in the analysis of Figure 84.

A prediction of the release profile for $^{14}$C from irradiated graphite can be empirically deduced from the data presented in this results section. This prediction indicates that the likely release profile for liberation of $^{14}$C from the irradiated graphite specimens used for this programme of research is approximately describable using a power law for the initial faster release rate of $^{14}$C, assumed to arise from an enriched surface region of nitrogen-derived $^{14}$C. This is followed by a more linear fractional release of $^{14}$C with mass loss as the remaining bulk material, assumed to contain evenly and randomly distributed $^{13}$C-derived $^{14}$C, is oxidised.

Theoretically, following an infinite time of thermal treatment, the release profile of $^{14}$C from any post-neutron irradiation graphite sample must traverse a (mass loss, release) $(x,y)$ plot from the origin (0,0)% to the opposite corner at (100,100)% This is because the sample must begin at an untreated state, where no mass losses or releases of $^{14}$C have occurred, and finish having undergone full oxidation into the gas phase, whereby all $^{14}$C will be in the form of carbon monoxide or dioxide and is thus released from the sample. A graphical representation of this can be found in Figure 86, with example $^{14}$C release profiles. The linear $^{14}$C release profile indicates how radioactivity would be released from irradiated graphite if it were evenly distributed, yielding no selective release of the radioactive carbon compared to the bulk material $^{12}$C and $^{13}$C. The arbitrarily defined example ‘surface-dominant’ profile is optimistic compared to the release profile suggested by the data seen in this results chapter and is indicative of what might theoretically be achievable for samples with high proportions of surface $^{14}$C formed from nitrogen, such as RBMK-reactor graphite. The predicted release profile is a trend of removal behaviour deduced empirically using the results presented in this results section. The specific activity of $^{14}$C in the oxidised irradiated graphite is seen to reduce approximately as a power law with increasing mass loss. The reducing power law equation for the trend in Figure 85 is seen in Equation (20).

$$y = 436642x^{-0.581}$$

(20)

It is the exponent of $x$ in this equation that dictates the shape of the $^{14}$C release curve, and since this curve represents the decrease in specific activity, it is not
unreasonable to suggest that if this trend is correct then the accumulated $^{14}$C release profile with weight loss will follow this same trend, with a positive exponent of $x$ of the same magnitude. The coefficient preceding $x$ will change as the units are different.

Earlier analyses suggest that the $^{14}$C release profile curve will obey a more linear trend after the majority of the $^{14}$C-enriched graphite near the surface has been oxidised, noting that Section 2.3.4 demonstrates that $^{14}$C resultant from irradiation of nitrogen impurities at the surface is thought to yield a $^{14}$C concentration profile with depth from the surface into the graphite bulk, and as such this profile may contribute to a lesser extent to the $^{14}$C release characteristics into relatively high mass losses. Consequently, if a linear portion is included in the power law trend defined in Equation (20), then the overall release prediction trend, with two currently unknown coefficients, $A$ and $B$, seen in Equation (21), can be reached.

$$ y = Ax^{0.581} + Bx $$ (21)

Using the known condition that when the mass loss, $x$, is equal to 100% then the $^{14}$C release must also be 100%, and selection of a data point residing on the desired trend, the unknown coefficients can be calculated by solving simultaneous equations seen in Equations (22) and (23). The selected second data point, from treatment of sample OMTT19 at 700°C for 5 hours, corresponds to 16.183% $^{14}$C release at 5.069% mass loss.

$$ 100 = (100^{0.581})A + (100)B $$ (22)

$$ 16.183 = (5.069^{0.581})A + (5.069)B $$ (23)

The solution of these simultaneous equations yields $A$ and $B$ coefficients of 4.588 and 0.334 (3d.p.) respectively. This allows the empirically determined $^{14}$C release profile prediction function seen in Equation (24) to be formed, which is the function plotted as the predicted release trend in Figure 86.

$$ y = 4.588x^{0.581} + 0.334x $$ (24)

It should be highlighted that this equation represents the prediction for the approximate $^{14}$C release profile for these irradiated graphite samples, though there is some
uncertainty attributed to the inherent inhomogeneity and variable distribution of radioactivity in irradiated graphite.

![Fractional Mass Loss against Fractional Release of $^{14}$C, including an ‘ideal’ release profile, a linear release profile and an empirically predicted release profile](image)

**Figure 86: Fractional Mass Loss against Fractional Release of $^{14}$C, including an ‘ideal’ release profile, a linear release profile and an empirically predicted release profile**

### 5.3 Conclusions Reached in Section 5

The main findings of this results section are:

- There is a positive correlation between $^{14}$C release from irradiated graphite and time during thermal treatment, yet a negative correlation between the specific activity of $^{14}$C and sample mass loss.
- The $^{14}$C release profiles are similar irrespective of the treatment temperature used, between 600 and 700°C, suggesting that between these temperature ranges selective removal of $^{14}$C is not heavily influenced by the treatment temperature.
- The specific activity of the oxidised graphite reduces quickly with mass loss, as a power law trend, indicating that a $^{14}$C-enriched surface region does exist in these Oldbury Magnox reactor sourced irradiated graphite samples.
The overall $^{14}$C release profile from these UK irradiated graphite samples cannot be entirely linear or as a power law, though is likely a combination of these two trends, exhibiting power law release behaviour at low sample mass losses and more linear behaviour at higher mass losses.

An empirically determined predictive $^{14}$C release profile function, inclusive of power law and linear components, can be deduced using the release data obtained from the experiments in this results chapter.
6. Results and Discussion: The Carbon-14 Release Profile

This results chapter explores the absolute fraction of $^{14}$C that can be retrieved from the UK irradiated graphite samples used for this programme of research. The $^{14}$C release profile during thermal treatment of irradiated graphite is explored further.

6.1 Hypothesis and Experimental Method

It has been demonstrated in Section 5 that an initial faster release of $^{14}$C is observed during thermal treatment of Oldbury Magnox reactor sourced irradiated graphite, and then the release rate of $^{14}$C from the sample reduces with further time and mass loss. Limitations in the apparatus, due to fluid evaporation from the bubbler system, mean that observations of the release of $^{14}$C into sample mass losses above 10% have not been recorded. The transition from an untreated sample at (0, 0)% (mass loss, $^{14}$C release) to complete liberation of all of the $^{14}$C in the sample at (100, 100)% defines the selective release efficiency of $^{14}$C with respect to mass loss, and so it is this release profile into higher mass losses which will be constructed.

Two major questions arise from the previous data:

1) What is the real $^{14}$C release profile for mass losses greater than 10% for thermal treatment of irradiated graphite using the first oxidation regime, and how does it compare to the prediction deduced in the previous results chapter?

2) What is the maximum attainable fractional release of $^{14}$C which can be achieved from irradiated graphite before sample disintegration occurs?

Previous experiments outlined in Section 5 indicate that successful treatment is possible for durations up to approximately 32 hours, the limiting factor for which is excessive evaporation and cross contamination of fluids between bubblers in the furnace bubbler train. Therefore, treating individual samples for periods greater than 32 hours is not suitable. An alternative approach has been chosen for this set of experiments, whereby a single sample is treated multiple times on consecutive days, allowing large accumulative treatment duration to be accrued. The $^{14}$C release following each treatment stage is determined by liquid scintillation counting, as previously, such that a detailed $^{14}$C release
profile for one single sample can be constructed over many days. The sample is to undergo treatments until sample disintegration occurs, to determine the fractional release that can be achieved before sample fragility is sufficiently severe that the graphite structure collapses. The samples will have their external geometry dimensions measured between each treatment run, and the most likely cause of sample disintegration is during handling or geometry measurement using the digital micrometer which applies a small measuring force, of between 5 and 10 N\textsuperscript{[120]}. The mass of the sample is to be taken between each movement or process applied to the sample, such as geometry measurements, to ensure that sample degradation and losses of $^{14}$C are not occurring during handling of the graphite sample between treatments.

The cover gas used for this set of treatment experiments is 1% oxygen in an argon balance gas, as per previous treatment experiments. The treatment temperature selected for this set of experiments is 600°C, because this temperature allows a slow and controlled oxidation rate to be maintained at the surfaces throughout the sample, allowing detail and precision in the constructed $^{14}$C release profile whilst inducing first regime oxidation behaviour. The compromise to using low temperature oxidation is that the entire process will take a greater number of days than similar treatment at higher temperatures. Since the oxidation rate is slow, multiple treatments of 12 hours duration have been selected as appropriate for maintaining safe laboratory operating hours, to effect an approximate 2% mass loss per treatment, as per the protocol seen in Figure 87. A single sample, OMTT36, has been chosen for these experiments, due to the visual uniformity of both of the end surfaces meaning that reasonable geometry measurements can be taken without inclusion of an uncertainty associated with a rough surface. This sample is therefore one machined at both ends and taken from the upper surface of the installed set, as seen in Figure 48, and therefore there is a likelihood that it was directly exposed to the reactor coolant flow. The $^{14}$C recovery fraction applied to correct these results is 95.57 ± 1.47%, which corresponds to the average $^{14}$C recovery achieved during recovery checks over the period that these experiments were conducted, extending from August 2015 to September 2015, with an uncertainty of two standard deviations.
An adaptation made for these experiments that differs from the experimental method outlined in Section 3.2.1.3 is that the sample has not been degassed between each experiment, as a consequence of time constraints. It is possible that some oxidant from the air may adsorb to the surface of the sample between treatment runs, potentially introducing additional oxidation to the system, though results of thermal treatment in an inert environment as per Section 4 suggest that this effect will be insignificant.

Reduction in the uncertainty of the bulk volume measurements has been achieved by introduction of 10 geometry measurements of both the length and diameter of the sample, increasing confidence in the data. This has not been performed for previous samples because of the consequent increased radiation exposure to the operator.

6.2 Results

The cumulative releases of $^{14}$C with time observed following multiple thermal treatments of sample OMTT36 at 600°C in a 1% oxygen in argon environment is shown in Figure 88. The $^{14}$C release data points presented in the previous results chapter, Section 5, each representing the release behaviour of different samples during their single respective treatment experiments are plotted in semi-transparent blue in Figure 88, demonstrating a correlation between data sets and providing confidence that this sample, OMTT36, is reflective of the remainder of the Oldbury Magnox reactor sourced irradiated graphite.
samples. This correlation supports that the degassing process, which was not applied for these treatment runs, has not significantly affected this data, as these treatments would exhibit an enhanced rate of oxidation and $^{14}$C release compared to previous data if the surface adsorbed oxygen were comparable in magnitude to the oxygen supplied to the graphite during the treatment experiments. The uncertainty in the data increases with each 12 hour treatment, up to an accumulated 120 hours treatment because the fractional release following each treatment is partially dependent on the confidence in the $^{14}$C release determined for the preceding treatments, and so the previous treatments’ uncertainties propagate through with each treatment iteration.

The accumulated hours of thermal treatment of sample OMTT36 came to a halt at 120 hours because of sample fragility caused by thermal oxidation, with a corresponding mass loss to the sample of 22.35%. Sample collapse occurred as the geometry was measured using the digital micrometer, which exerts a measuring force of between 5 and 10 N to the sample. The approximate cross sectional area of the cylinder ends following 120 hours of treatment is $17.154 \times 10^{-6}$ m$^2$, thus assuming the measuring force is applied to the entire end surface this equates to an applied stress of 583 kPa. If it is conservatively assumed that the measuring force is applied to 10% of the end surfaces of the cylinder to account for an imperfect surface then the equivalent applied stress is 5.83 MPa. These yield stress values are both significantly less than ‘typical’ expected minimum yield stresses for unirradiated PGA nuclear grade graphite, which are of the order 30 MPa$^{[127]}$, indicating that the structural integrity of this sample has been compromised following 120 hours of oxidation at 600°C in 1% oxygen, to the extent that sample collapse has occurred under a small external force. This level of sample degradation is not desirable for thermal treatment, because of the difficulties and radiological hazards associated with fragile and powdered irradiated graphite specimens.
Figure 88 shows that the release of $^{14}$C from this irradiated graphite sample appears to be consistently linear with increasing time, with an $R^2$ coefficient of determination value of 0.9999, excluding the initial 12 hour treatment where an elevated rate of $^{14}$C release is observed. The positive y-intercept of the linear trend line mathematically indicates that a faster release of $^{14}$C must occur earlier in the experiment. The precise release profile is not captured using a 12 hour sampling rate. Using the linear trend lines in Figure 88, the average rate of release between 12 and 120 hours is 0.2626% $^{14}$C per hour, approximately one third of the average rate of 0.7644% $^{14}$C per hour observed for the initial 12 hour treatment.

The linear correlation between $^{14}$C release and time seen in Figure 88 may not be expected, principally because the rate of oxidation of graphite is likely to change with oxidation as a consequence of porosity evolution, whereby pores are oxidised into larger pores, increasing the surface area available to the oxidant, before pore coalescence and lack of remaining material decrease the surface area available to the oxidant. The rate of oxidation is seen to vary with time for sample OMMT36, which is presented in Figure 89.
Figure 89: The Average Rate of Mass Loss from Sample OMTT36 per 12 hour Treatment

The initial higher average oxidation rate during the first 12 hours could be a consequence of gasification of carbonaceous deposit, though evidence presented in Section 3.3.5 suggests that the mass of carbonaceous deposit is negligible compared to the bulk material, more easily oxidised graphite dust remaining from the machining process or rougher higher surface area regions. Since the source of the higher rate of mass loss is unknown, it is unclear whether this coincides directly with the enhanced $^{14}$C release during this same period. The rate of oxidation following this initial treatment duration is then seen to increase measurably in a non-linear fashion, likely because of porosity evolution. This suggests that for the $^{14}$C release with time seen in Figure 88 to remain linear, the increasing rate of oxidation seen in Figure 89 must be compensated by a reduction in $^{14}$C specific activity with time. This has been observed in previous data and can be seen for OMTT36 in Figure 90 alongside $^{14}$C release data points from Section 5. The specific activity of $^{14}$C initially reduces with increasing time, which is consistent with previous data. Following approximately 12% mass loss, the specific activity then steadies around a value of approximately 70 kBq/g, indicative of a more linear release of $^{14}$C with increasing mass loss, which is to be expected, as per the predictions of a $^{14}$C release profile outlined in Section 5.2.
Figure 90: The Specific Activity of $^{14}$C in the Oxidised Portion of Sample OMTT36 against Mass Loss during Treatments in a 1% Oxygen Environment

The average specific activity determined in irradiated graphite sample OMTT36 prior to any thermal treatment is 55.53 ± 4.25 kBq/g, and so the specific activity of release seen in Figure 90 is likely to continue reducing further with mass loss, unrepresented in this data due to sample disintegration. Figure 88 demonstrates an apparent linear fractional release with time and Figure 90 shows a reducing specific activity with time, which is analogous to mass loss in this instance, because the sensitivity of the specific activity data displayed here in Bq/g on a logarithmic scale is higher than that of the fractional release in percent, using which any subtle changes in release rate are not captured.

The cumulative releases of $^{14}$C with mass loss observed following multiple thermal treatments of sample OMTT36 at 600°C in a 1% oxygen in argon environment is shown in Figure 91 where the $^{14}$C release profile for OMTT36 to higher mass losses follows the predicted release profile closely, albeit at a slightly higher absolute $^{14}$C release fraction. This could be because of inhomogeneity in this material, or because the predictive curve based on previous data is underestimating the releases. It is demonstrated, however, that the $^{14}$C release profile behaviour for samples of a similar irradiated graphite source is empirically predictable. There is less statistical scatter in this data than seen previously because the data is obtained from a single sample rather than multiple samples, allowing a more
consistent response to treatment which is in agreement with data obtained from multiple samples.

Figure 91: Cumulative Releases of $^{14}$C with Mass Loss following Multiple Treatments at 600°C in a 1% Oxygen Environment with the Empirically Predicted $^{14}$C Release Profile

The previous 600°C treatment $^{14}$C release data points presented in Section 5 allow confidence that the data produced from this single sample, OMTT36, is reflective of the other Oldbury Magnox reactor sourced irradiated graphite samples used for this research. The predicted $^{14}$C release profile deduced in Section 5.2 has been plotted alongside the treatment data, for comparative purposes. Similarly to Figure 88, the uncertainties associated with each consecutive treatment propagate through with each treatment iteration, and so the uncertainty in the fractional release of $^{14}$C increases with mass loss, which is a product of the data collection method of multiple successive treatments.

An estimate as to the original location of this $^{14}$C can be deduced from measurements of mass and sample geometry between measurements as per Figure 92. It is assumed that oxidation at 600°C in 1% oxidation exhibits first oxidation regime behaviour, whereby the sample surfaces of both the external geometry and throughout the internal porosity of the sample are oxidised equally. Since porous PGA grade graphites have a large internal surface area, the mass and geometry data should therefore show a larger fractional
reduction in mass than volume, as a large proportion of the mass loss is occurring from within the sample.

![Graph showing mass, volume, and density data for Sample OMTT36 during consecutive treatments.](image)

**Figure 92: Mass, Volume and Density Data for Sample OMTT36 During Consecutive Treatments**

Figure 92 shows that the fractional mass loss to the sample is occurring faster than the relatively consistent loss in geometric volume with time, and is accelerating as seen by the second order polynomial trend fit. This plot proves that the mass losses induced in the sample are not occurring from the outer geometric surfaces inwards, as might be seen for third regime oxidation, and strongly suggests that this temperature yields first regime oxidation of the internal open porosity surfaces throughout the sample. The circular data points represent the change in bulk density of the sample, the decreasing gradient of which showing that as time is elapsing the ratio of sample internal oxidation to external oxidation is increasing, signifying an increase in oxidising surface area within the sample as the internal porosity is developed by oxidation. Figure 92 allows confidence that the mass loss, and thus the $^{14}$C releases observed are occurring predominantly at the surfaces throughout the internal open porosity of the sample. The calculated uncertainties for the volume data have been plotted, though their relative magnitude is small and they are obscured by the data points.

The maximum achievable fractional $^{14}$C release by this method of multiple consecutive thermal treatments of sample OMTT36 was $37.26 \pm 2.34\%$ release.
corresponding to a sample mass loss of 22.35 ± 0.37%. This degree of mass loss, additional to the 40% reactor-induced mass loss in the original material yielding an estimated total 50.4% mass loss compared to the unirradiated material, caused a loss of structural integrity in the graphite sample. Thermal treatment to this extent of corrosion damage is therefore not appropriate if a solid treated graphite specimen is sought. Given that the predictive curve, which has been produced from previous data, aligns closely with the $^{14}$C release profile for sample OMTT36 into higher mass losses, the maximum achievable release seen for OMTT36 is thought to be indicative of the typical fractional release that might be achieved for UK reactor graphite from similar sources and reactors, though the absolute release fraction and initial gradient of the release profile for other irradiated graphites will be heavily influenced by the factors that affect $^{14}$C formation, such as the reactor operating history and environment, as explored in detail in Section 2.3 of the literature review.

It has been seen that extraction of approximately 35% of $^{14}$C from these samples leads to sample degradation, which is inappropriate for practical use. Assuming that the empirically derived predicted curve is reflective of the $^{14}$C release profile for UK reactor graphite of similar sources, and with minor adaptation to the profile equation to account for differing reactor operational conditions and environments, an approximation as to how much $^{14}$C can be effectively liberated from irradiated graphite waste can be obtained from the gradient of the predictive $^{14}$C release profile. The gradient of the release profile, determined by differentiation of the release profile equation, represents the fractional release of $^{14}$C per fraction mass loss, which is indicative of the selective release efficiency of $^{14}$C from irradiated graphite, as shown in Figure 93. The gradient is large at small mass losses, and then falls quickly, as supported by data collected in Sections 5 and 6. At higher mass losses, the gradient falls below 1, at which point selective release of $^{14}$C from the bulk material is no longer occurring as less than 1% of the $^{14}$C inventory is liberated per 1% mass loss of the sample, and thermal treatment from there on becomes completely ineffective.
Figure 93: The Empirically Predicted Release Profile of $^{14}$C and its Gradient with Mass Loss

The absolute release fraction that might be deemed ‘effective’ or ‘efficient’ for application to the UK inventory of irradiated graphite waste is an issue out of the scope of this programme of research, and as such efficiency milestones that could be deemed appropriate limits for a large scale industrial process of thermal treatment of UK irradiated graphite waste have been arbitrarily defined for demonstrative purposes. The empirically derived equation for the predicted release and its derivative, the gradient, can be used to estimate the mass loss at which milestone $^{14}$C release efficiencies including the $1/1$ ($^{14}$C release/$\%$ mass loss) changeover point seen at approximately 27% mass loss in Figure 93 are reached, following which selective release of $^{14}$C is not occurring and treatment becomes completely ineffective. Table 17 shows the predicted mass losses during a continuous treatment process, analogous to treatment durations, at which the efficiency of release with respect to mass loss falls below arbitrarily defined milestones, from 5/1 to 1/1. The fractional efficiency of $^{14}$C release falls from greater than 5/1 to 3/1 during the first 1% of mass loss and then maintains an average fractional release greater than 2/1 until approximately 3% mass loss. Further thermal treatment becomes entirely ineffective at approximately 27% mass loss, though in the instance of sample OMTT36 sample disintegration occurred before this milestone was reached. Table 17 also shows the average
sample release efficiency for the whole sample, in percentage $^{14}$C release per total sample mass loss, and equivalent to integrating under the predicted release profile curve and dividing by the mass loss. This shows that if the efficiency milestones of the empirically defined prediction curve are correlated to the estimated total release from a sample, the absolute efficiency of $^{14}$C release reduces with increasing mass loss, and thus a compromise must be reached between the desired fraction of $^{14}$C to be released and the efficiency with which it can be removed.

Table 17: Comparison of Empirically Predicted $^{14}$C Release Efficiencies in Real Time for Defined Efficiency Milestones

<table>
<thead>
<tr>
<th>Predicted Real Time Fractional Release Efficiency Milestone (% $^{14}$C Release / % Mass Loss)</th>
<th>Mass Loss (%)</th>
<th>Predicted Total Release of $^{14}$C (%)</th>
<th>Predicted Total Sample Release Efficiency (% $^{14}$C Release / % Mass Loss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 5/1</td>
<td>0.26</td>
<td>2.20</td>
<td>8.46</td>
</tr>
<tr>
<td>&gt; 4/1</td>
<td>0.47</td>
<td>3.11</td>
<td>6.62</td>
</tr>
<tr>
<td>&gt; 3/1</td>
<td>1.00</td>
<td>4.92</td>
<td>4.92</td>
</tr>
<tr>
<td>&gt; 2/1</td>
<td>3.07</td>
<td>9.83</td>
<td>3.20</td>
</tr>
<tr>
<td>&gt; 1/1</td>
<td>27.40</td>
<td>40.56</td>
<td>1.48</td>
</tr>
</tbody>
</table>

It is not possible to make a rigorous determination from this thermal treatment data as to the fraction of $^{14}$C produced from $^{13}$C or $^{14}$N, the two prominent source isotopes of $^{14}$C in irradiated graphite. This is because of the large uncertainty associated with the fraction of $^{14}$C lost through normal graphite moderated reactor operation processes such as radiolytic oxidation. This is of particular note because the samples used for this research were subject to an enhanced rate of radiolytic oxidation by gamma radiation emission from the titanium tie rod holding the installed set carrier together, as described in Section 3.1, and so a significant proportion of any surface formed $^{14}$C may have been oxidised and transferred to the coolant phase prior to thermal treatment.

The empirically predicted $^{14}$C release profile from these Oldbury Magnox reactor irradiated graphite samples can be approximated as a combination of linear and power law components, indicative of $^{13}$C and $^{14}$N-derived $^{14}$C respectively. Power law release behaviour is exhibited at low sample mass losses, followed by more linear behaviour at higher mass losses when the $^{14}$C-enriched surface region is exhausted and randomly distributed $^{13}$C-derived radiocarbon remains. The second derivative of the predicted $^{14}$C release profile function yields the rate of change of the efficiency of release with mass loss, which is taken as the fractional release of $^{14}$C per fraction mass loss, as shown in Figure 94 alongside the
predicted release function. The second derivative reduces quickly before flattening out, which indicates that the majority of the change in release efficiency occurs during the initial mass losses by oxidation, which suggests strongly that a transition from release of surface $^{14}$N- to bulk $^{13}$C-derived $^{14}$C is occurring.

![Figure 94: The Empirically Predicted Release Profile and the Derivative of its Gradient with Mass Loss](image)

If the limit for when the ‘surface $^{14}$C’ has been oxidised away is assumed to be when the second derivative reaches 1% of the ‘initial’ value then it is found that the majority of surface region $^{14}$C is oxidised by approximately 5% mass loss, corresponding to a predicted 13% total $^{14}$C release from the sample. A proportion of this release will include $^{13}$C-derived $^{14}$C, which is difficult to quantify because there is not a step transition in the release profile from one release zone to another, but a gradual transition. If it is assumed that the releases of radioactivity beyond this calculated transition mass loss milestone of approximately 5% contains evenly distributed $^{13}$C-derived $^{14}$C, then the gradient of the predictive function at a mass loss of 5% can be extrapolated back to the y-axis to subtract the fraction of $^{13}$C-derived randomly distributed $^{14}$C contributing to the initial fast release. The remainder, the positive y-intercept, is indicative of surface $^{14}$C, hypothesised to be derived from neutron activation of $^{14}$N. The calculations suggest that approximately 5% of the $^{14}$C liberated from these samples is derived from neutron absorption of $^{14}$N.
If the transition mass loss milestone is now set to that when the second derivative is 0.1% of the initial value corresponding to 27.6% mass loss, as opposed to 1% of the second derivative corresponding to 5% mass loss, then the estimated \(^{14}\)N derived fraction found in these samples increases to approximately 13%.

As these two \(^{14}\)N-derived \(^{14}\)C values differ significantly depending on where the gradient of the predictive function is taken, there is some ambiguity as to a true figure, though a confident estimate of the order of approximately 10% can be made. As previously noted, however, an unknown proportion of \(^{13}\)C and nitrogen-derived \(^{14}\)C atoms have been lost to the coolant during reactor operation, and so this programme of research suggests that a minimum of approximately 10% of the \(^{14}\)C formed in these irradiated graphite specimens is derived from nitrogen.

It should be highlighted that the empirically defined \(^{14}\)C release profile behaviour from which the above approximations have been deduced is specific to this source of irradiated material. The irradiation and operational history of each source of reactor graphite will influence the respective release characteristics of \(^{14}\)C during thermal decontamination, though some parallels can be drawn between the Oldbury Magnox reactor installed set material used for this research and other UK Magnox and AGR reactor graphites; each are subject to competing surface \(^{14}\)C production against radiolytic oxidation \(^{14}\)C removal processes, they are irradiated in a carbon dioxide coolant environment and each have a similar order of magnitude impurity concentration prior to irradiation. Significant differences in \(^{14}\)C release behaviour between graphites might arise from the extent of carbonaceous deposit on the graphite, the frequency of reactor outages and the position of the graphite in the core, which will affect the level of neutron irradiation, radiolytic oxidation and porosity evolution. Irrespective of graphite source there will likely exist some degree of \(^{14}\)N-derived near-surface region \(^{14}\)C, and so the respective release profile will likely contain both the power law and linear components identified previously, with differing magnitudes. Further research is required to confirm that the overall behaviour of release identified in this research is applicable to a broad range of UK irradiated graphites.

As previously stated, the appropriateness of application of this thermal decontamination technique to the entire UK inventory of irradiated graphite is out of the scope of this thesis. This decision will be predominantly based on whether the benefits of retrieval and segregation of the order of 10% \(^{14}\)C activity outweigh the associated
radiological risks and costs inherent in the manipulation, transport and processing of thousands of tonnes of radioactive material.
6.3 Conclusions Reached in Section 6

The main findings of this results section are:

- The $^{14}$C release data for multiple treatments of a single sample is consistent with the previous data for single treatments of multiple samples.
- A faster average rate of $^{14}$C release is observed in the initial 12 hour treatment period, followed by a positive linear correlation between time and $^{14}$C release up to 120 hours.
- Thermal oxidation at 600°C for 120 hours in 1% oxygen caused considerable damage to the graphitic structure, adversely impacting the structural integrity and resulting in compressive yield under an external force of 10 N.
- The specific activity of $^{14}$C in the oxidised portion of the graphite initially reduces sharply by nearly an order of magnitude with increasing mass loss, as per previous data, before stabilising.
- The $^{14}$C release profile observed, to approximately 23% sample mass loss, follows the predicted release profile closely.
- The sample mass loss is occurring predominantly at the surfaces of the internal open porosity throughout the sample, allowing confidence that it is releases of surface region $^{14}$C that are observed.
- Up to approximately 35% of the $^{14}$C in this irradiated graphite can be retrieved at the expense of selective release efficiency and sample structural integrity.
- The fractional selective release efficiency for $^{14}$C with mass reduces from greater than 5/1 to 3/1 in the first 1% mass loss, and reduces to 1/1 following a sample mass loss of approximately 27% and corresponding total $^{14}$C release of approximately 40%.
- The second derivative of the predicted $^{14}$C release profile function allows an estimate that a minimum of the order 10% of the $^{14}$C formed in these irradiated graphite samples is derived from nitrogen, though the real fraction could be higher due to unquantifiable surface $^{14}$C losses by corrosion processes in the reactor during operation.
7. Results and Discussion: Effects of Thermal Treatment on Tritium and Metallic Radioisotopes

This results chapter explores the effects of thermal treatment in a 1% oxygen atmosphere at elevated temperatures on $^3$H and the metallic radioisotopes found in irradiated graphite, such as $^{60}$Co. This chapter considering the release characteristics of predominantly shorter-lived radioisotopes is appropriate to the potential decision for an accelerated decommissioning programme in the UK, and highlights thermal release characteristics which could influence management of the UK inventory of irradiated graphite waste.

7.1 Hypothesis and Experimental Method

7.1.1 Releases of Tritium

Tritium is a radioisotope of concern for irradiated graphite waste research because of the large activities produced from the lithium impurity in graphite and its mobility within the bio- and geosphere, which is further discussed in Appendix C.

Tritium is captured and chemically separated from the gas phase in the first two bubblers of the thermal treatment experimental arrangement, before subsequent capture of $^{14}$CO and $^{14}$CO$_2$ in the final two bubblers. As such, radioanalysis of the $^3$H release from irradiated graphite during thermal treatment is a relatively convenient extension of the methods applied for analysis of the $^{14}$C content with differing scintillation cocktails and parameters, and so each $^{14}$C release data point seen in Sections 5 and 6 has an associated $^3$H release measurement. Tritium is a weak beta-particle emitter and is highly mobile, and so the uncertainties associated with $^3$H measurements are inevitably larger than that for $^{14}$C because of a reduced liquid scintillation counting efficiency and more variable analytical recovery rate during recovery checks, described in Section 3.3.1.2.

The results seen in Section 4, and more specifically those in Figure 76 showing tritium releases during treatment in an oxidising environment, suggest that an increase in temperature from 700 to 800°C is not beneficial for efficient removal of $^3$H with respect to sample mass loss, as similar fractional releases of $^3$H are achieved during the lower temperature as with higher temperature treatments, though with less sample degradation.
by oxidation and mass loss. This results chapter will demonstrate whether this trend continues to even lower temperatures and sample oxidation rates, as the $^3$H releases at $600\,^\circ C$, $650$ and $700\,^\circ C$ are considered. Section 2.5 suggests that $^3$H is released from irradiated graphite by a fundamentally differing mechanism than that for $^{14}$C, where $^3$H liberation is predominantly by a diffusion process through the graphite bulk rather than oxidation of surface radioisotopes$^{[65]}$. If this is correct, one would expect $^3$H release at $600\,^\circ C$ to be slower than at higher temperatures, as less thermal energy effecting movement of $^3$H through the bulk material is applied to the system. The release rate of $^3$H should reduce with time, as the remaining fraction of $^3$H in the graphite sample is depleted causing a reduced concentration gradient between the sample and the cover gas and decreasing the rate of $^3$H diffusion. Using the preliminary collected data to indicate how the rate of diffusion may differ with temperature, it is thought that the rate of sample oxidation increases considerably more quickly with temperature than the rate of $^3$H diffusion, and therefore lower temperature treatments should eventually exhibit similar fractional releases of $^3$H though with noticeably less mass loss and damage to the graphitic structure.

The experimental protocols utilised for the $^3$H release data in this results chapter are identical to those seen in Sections 5 and 6 for $^{14}$C release, as this data was collected in parallel.

### 7.1.2 Releases of Metallic Radioisotopes

The list of prominent radioisotopes to be found in irradiated graphite, discussed in Section 2.2.2, shows that the release characteristics of a number of isotopes of concern during thermal treatment have not yet been discussed in this programme of research. These are predominantly metallic radioisotopes derived from activation or fission of impurities in the graphite. The list of prominent radioisotopes, excluding $^3$H, $^{14}$C, $^{36}$Cl and $^{90}$Sr/$^{90}$Y, the latter three of which are not detected using this experimental arrangement, can be seen below:

$^{60}$Co, $^{133}$Ba, $^{134}$Cs, $^{137}$Cs, $^{152}$Eu, $^{154}$Eu, $^{155}$Eu and $^{241}$Am

Gamma spectrometry is a suitable technique for detection of these metallic radioisotopes, as opposed to liquid scintillation counting used for quantification of $^3$H and $^{14}$C which have no gamma radiation emissions and as such cannot be detected using gamma spectrometry. Autoradiography is another technique which can be used for detection of
radioisotopes in irradiated graphite, though this technique only measures the energy deposition in the phosphor storage screen and is indiscriminate between the sources of this energy. These two radioanalysis techniques have been applied to each sample both before and after thermal treatment, and any differences in the data produced may be indicative of radioactive releases during thermal treatment. Care should be taken interpreting autoradiography results due to the insensitivity of the technique to specific radioisotopes and the apparent degradation with time of either the screen or the detector, as described in Section 3.3.2.2. Since the pre- and post-treatment activity characterisations are conducted at different time periods, all quantified sample activities are normalised to the start date of this programme of research, the 18th September 2012.

A modelling paper included in the literature review, simulating high temperature treatment of irradiated graphite in excess air, suggests that all of the metallic radioisotopes of interest excluding caesium will exists in a solid phase for all treatment temperatures utilised irrespective of chlorine content in the gas phase, and therefore releases of these radioisotopes are not expected during thermal treatment\[98\]. It has been seen in the literature review that impurities are not evenly distributed through nuclear grade graphite, and thus the possibility exists that small ‘releases’ might be observed as clusters of activated metallic impurities fall from near the surfaces of the sample as the carbon surrounding them, binding to the bulk of the sample, is oxidised into the gas phase. Yang\[98\] also states that caesium will exist solely in a gaseous phase above 300°C, or 600°C in the presence of chlorine, and since this is the lowest treatment temperature utilised, some releases of \(^{134}\)Cs and \(^{137}\)Cs are to be expected.

### 7.2 Results

#### 7.2.1 Releases of Tritium

The releases of \(^{3}\)H observed with time following thermal treatment of multiple samples at 600, 650 and 700°C in a 1% oxygen environment is shown in Figure 95. As seen in Section 5, radioisotope release with time is not entirely reflective of the efficiency of the release behaviour because mass loss has not been taken to account. This graph, then, is a useful example of the difficulties encountered with quantitative analysis of \(^{3}\)H in irradiated graphite, as the magnitudes of uncertainty are relatively large and there is not a consistent trend with time between samples.
It is shown in Figure 95 that higher temperatures have resulted in a faster release of $^3$H, exhibiting higher fractional releases after a given treatment duration, though this does not take sample mass loss into account and so it cannot be definitively argued from this graph alone that temperature is the cause of this. There is no identifiable trend in the raw data between the original sample specific activity or sample mass and its $^3$H release behaviour, suggesting that $^3$H release characteristics are heavily dependent on the individual sample, possibly influenced by size effects, differing quantities and distributions of original activities or a consequence of the larger uncertainties associated with $^3$H quantification than other radioisotopes.

If the longer duration experiments in a 1% oxygen environment as conducted in Sections 5 and 6 are included in the plot, the fractional releases of $^3$H observed with time are as seen in Figure 96. Again, the mass loss incurred by thermal oxidation is neglected for this plot, though the response with time for longer durations of treatment of a single sample is noteworthy in that the release appears to become much more linear, with an $R^2$ coefficient of determination of 0.9998, as was similarly seen for the $^{14}$C data. This is unexpected if the mechanism of tritium release is by diffusion, as suggested in the literature, though the uncertainties associated with this data are significant and the poor relative sensitivity of this fractional release plot could mask a reducing release rate, as seen
for the $^{14}$C data. The green rhombus data points labelled ‘OMTT36’ are following multiple thermal treatments at 600°C to an accumulated 120 hours treatment. The uncertainty for the OMTT36 data points increases noticeably with time because the accumulative nature of this experiment, such that the uncertainty associated with each data point is dependent on the uncertainty preceding it.

![Graph](image.png)

Figure 96: Releases of $^3$H with Time during Treatment in a 1% Oxygen Environment, inclusive of longer treatment duration data

The positive y-axis intercept value in the linear trend line equation demonstrates mathematically that for sample OMTT36 a faster release of $^3$H occurred during earlier experiments. It should also be noted that the additional 600°C data from 12 to 32 hours shown in Figure 96 for longer duration treatment of separate samples is as variable and inconsistent as the shorter duration data highlighted in Figure 95, showing that the release rate between samples varies considerably and somewhat unpredictably.

The rate of $^3$H release with time, which is seen in Figure 97, can yield more sensitive information as to the release behaviour with increasing treatment duration, where the rate of $^3$H release from an irradiated graphite sample is reducing with time, particularly at earlier junctures of any treatment process. For sample OMTT36, which is treated multiple times, the rate of reduction slows at approximately 72 hours of accumulated treatment, following
which a more steady release rate appears to be reached, similarly to that seen for $^{14}$C release.

![Graph](image.png)

**Figure 97: The Release Rate of $^3$H against Time during Treatment in a 1% Oxygen Environment**

It is difficult to determine from Figure 97 whether this data is indicative of a diffusion process, though the eventual equilibration of the release rate supports the theory that not all of the $^3$H, if any, is released by a diffusion mechanism.

The fractional releases of $^3$H against sample mass loss are shown in Figure 98, which indicates that after a given time the $^3$H release rate stabilises and is directly proportional to the amount of oxidation inflicted to the sample. This is evidenced by the linear trend line passed through the latter 48 hours’ worth of treatment’s data points yielding an $R^2$ coefficient of determination of 0.9994. Although the calculated uncertainty indicated by the error bars is relatively large, when the linear trend line is extrapolated to 100% mass loss, a fractional release of $^3$H of 103.4% is projected, and thus unless an unexpected physical phenomenon presents itself between the 23% mass loss achieved and the final 100% mass loss then the $^3$H release profile will likely continue on this linear path until full sample destruction.
The linear relationship between $^3$H release from irradiated graphite during thermal treatment and sample mass loss has ramifications for the release mechanism of $^3$H because this suggests that a large proportion of the $^3$H is locked into the graphitic structure, approximately evenly distributed at this bulk scale, and at these treatment temperatures can only be released by oxidation of the surrounding carbon material, rather than by a diffusion mechanism.

The explanation as to why $^3$H exhibits similar thermal treatment release characteristics to $^{14}$C is not immediately apparent, particularly since the literature suggests these radioisotopes are released by fundamentally different mechanisms. Three speculative suggestions as to why this $^3$H release behaviour may have occurred are:

1) The first theory assumes that the $^3$H is diffusing out of the graphite, as the literature suggests. Diffusion is a partially concentration gradient driven process, and so as some of the $^3$H leaves the bulk material the hydrogen concentration gradient between the sample and the surrounding cover gas will reduce, resulting in a consequent reduction in the rate of removal, which can be seen in Figure 98 by the curve that is formed by all of the treatment data between 0 and approximately 5% mass loss. As the diffusion rate slows by this mechanism, it is possible that the oxidation of the graphite bulk by thermal
oxidation at 600°C in a 1% oxygen atmosphere becomes the dominant mechanism of $^3$H release, as surface material is chemically removed faster than the relatively evenly distributed $^3$H can diffuse from it, yielding a linear relationship with mass loss from this stage onwards.

2) The second theory is that the $^3$H in irradiated graphite is held in a variety of chemical bonds and forms, some of which are more thermodynamically stable than others. It is possible that there may exist a relatively mobile and diffusible fraction of $^3$H, which is released from graphite relatively easily on application of an elevated temperature, as seen by the initial faster release of $^3$H in Figure 98, but there is also a more strongly bound fraction of $^3$H which cannot be liberated until the graphite adjacent to where it resides is oxidised, yielding a linear 1:1 release relationship with mass loss, seen by extrapolation of the linear trend line to 100% mass loss.

3) The third and final theory is that, similarly to that believed for $^{14}$C, a surface accumulation of $^3$H is occurring, which is subsequently removed from the sample early in a treatment experiment because of its location near the surfaces in the graphitic structure, with the remainder of the $^3$H distributed through the bulk material. The mechanism for this accumulation at the graphite surfaces is not immediately obvious, and could be by diffusion during reactor operation, potentially over many years, effected by neutron damage or operational temperature. Thermal treatment exposes irradiated graphite samples to elevated temperatures in a hydrogen-deficient cover gas, which is a very similar environment to that found in a reactor core, and as such if $^3$H diffusion is suspected during thermal treatment experiments, then it is entirely plausible that this same phenomenon of $^3$H diffusion occurs during reactor operation, though at a slower rate. Black’s$^{[42]}$ work at the University of Manchester, modelling the production of radioisotopes including $^3$H in irradiated graphite, found that the models based on Magnox reactors consistently overpredict the $^3$H activity compared to experimentally determined values, sometimes by a factor of 70 or more, which is significantly larger than found for other radioisotopes. Acknowledging that there may be some uncertainties in the models, this disparity in activities could also be because a significant proportion of the $^3$H formed in the graphite is no longer in a sample by the time activity characterisation experiments are performed. This could be because of the concentration gradient of hydrogen between the graphite and the surrounding coolant gas which is causing diffusion of formed $^3$H towards the surfaces of the graphite during reactor operation, and then either further diffusion into the hydrogen-deficient coolant gas or undergoing radiolytic oxidation at the graphite surface, a
phenomenon thought to also remove $^{14}$C from the graphite as seen in the literature review. Elevated temperatures are likely to accelerate the rate of diffusion, and so despite the reactor operational temperatures being 200 to 250°C lower than those utilised for thermal treatment, the timescales for diffusion during reactor operation are of the order of tens of years, as opposed to a number of hours for treatment. It should be noted that an unknown quantity of $^3$H may also have been removed from graphite samples used for characterisation during sample machining processes. Tritium is difficult to detect because of its low atomic mass, which renders most experimental techniques ineffective for its detection, and the low energy of its beta radiation, which is difficult to analyse and generally requires destructive analysis by liquid scintillation counting. For these reasons, it is possible that a surface concentration of $^3$H has so far remained undetected in the literature.

The further and potentially more likely theory is that the $^3$H behaviour exhibited in Figure 98 can be explained by a combination of two or more of the theories outlined above, each contributing to the final $^3$H release profile from irradiated graphite. As stated previously, further research is required to determine the precise nature of the release of $^3$H during thermal treatment.

### 7.2.2 Releases of Metallic Radioisotopes

The metallic radioisotopes found in irradiated graphite have predominantly been analysed using high resolution gamma spectrometry, which has been conducted for a number of samples both before and after thermal treatment, to observe whether any release of these activated impurities is occurring during treatment. A total of 17 samples have been analysed both pre- and post-treatment, which is inclusive of five 650 and five 700°C treated samples, with the remaining 7 samples having been subjected to treatment at 600°C. Two additional samples, OMTT16 and OMTT17, have pre-treatment gamma spectra only.

An annotated gamma spectrum from an irradiated graphite sample, OMTT27, is seen in Figure 99. The features highlighted in Section 3.2.2.1 to be found in a gamma spectrum have been annotated, including two of the $^{60}$Co full energy photopeaks at 1173 and 1332 keV, the $^{137}$Cs peak at 661.6 keV, the characteristic Compton edges resultant of the two cobalt photopeaks, the Compton continuum and a double escape peak. The double
escape peak can be found at precisely 1022 keV below the higher 1332 keV energy cobalt peak, at 310 keV, indicative that pair production is occurring and gamma rays resultant from annihilation of positrons are escaping the detector crystal without detection, as described in detail in Section 3.2.2.1. The majority of unidentified peaks are summation peaks, caused by the detector recording multiple peaks at one instance. Figure 99 shows that the ‘real time’ of the scan was 7342.690 seconds, and the ‘live time’ of the scan was 7200 seconds, and so the dead time of the detector was approximately 0.02%, allowing confidence that the statistical representativeness of the peaks determined in the spectrum is good.

![Gamma Spectrum](image)

Figure 99: A Typical Gamma Spectrum from an Oldbury Magnox Reactor Graphite Sample, with annotated features

The prominent radioisotopes detected in these irradiated graphite samples are:

\[ ^{60}\text{Co}, ^{133}\text{Ba}, ^{134}\text{Cs}, ^{137}\text{Cs}, ^{154}\text{Eu}, ^{155}\text{Eu} \text{ and } ^{241}\text{Am} \]

It should be noted that this list is inclusive of all of those expected except for \(^{152}\text{Eu}\), which in this case has likely been mostly ‘burnt up’ earlier in the reactor lifetime, as
described in Section 2.2, with any small amounts of remaining $^{152}$Eu decaying to levels below that which can be detected. A number of lower activity radioisotopes will be present in these graphite samples, though the elevated Compton continuum brought about by Compton scattering from the relatively high activity of $^{60}$Co-derived gamma rays could be masking a number of lower activity radioisotopes which would be found below this continuum.

The average pre-treatment specific activities of each of the identified and quantified radioisotopes in the irradiated graphite sample analysed are seen in Table 18.

Table 18: Average Specific Activities of Quantified Prominent Radioisotopes in Oldbury Magnox Reactor Irradiated Graphite Samples

<table>
<thead>
<tr>
<th>Radioisotope</th>
<th>Average Specific Activity (Bq/g)</th>
<th>Uncertainty (2σ) (Bq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{60}$Co</td>
<td>6288/7146*</td>
<td>357/405*</td>
</tr>
<tr>
<td>$^{133}$Ba</td>
<td>551</td>
<td>37</td>
</tr>
<tr>
<td>$^{134}$Cs</td>
<td>109</td>
<td>10</td>
</tr>
<tr>
<td>$^{137}$Cs</td>
<td>178</td>
<td>22</td>
</tr>
<tr>
<td>$^{154}$Eu</td>
<td>292</td>
<td>15</td>
</tr>
<tr>
<td>$^{155}$Eu</td>
<td>237</td>
<td>32</td>
</tr>
<tr>
<td>$^{241}$Am</td>
<td>6.0</td>
<td>2.8</td>
</tr>
</tbody>
</table>

*The specific activity of $^{60}$Co in OMTT27 is not included in the first $^{60}$Co activity average determined in Table 18 because the activity of cobalt in this sample is 22590 ± 1279 Bq/g, which is a factor of three times more than other samples, almost singlehandedly influencing the average value to deviate from a representative value, as seen by the second $^{60}$Co average.

The uncertainty in the gamma spectrometry measurement is performed by a complex algorithm in the GENIE2K software, which combines factors such as the intensity of the peak, the nuclide identification confidence, which is dependent on peak position, spectrum calibration, number of counts and detector performance, the number of found peaks out of those expected for a given radioisotope, the dead time of the detector and the simulated efficiency determined from the sample geometry model. Therefore, radioisotopes which are lower in activity will inevitably have a higher fractional uncertainty associated with them, as there is less confidence in their quantified activity. The uncertainty associated with $^{137}$Cs is larger than other isotopes of similar magnitude activity because, as seen in Appendix C, quantification of this radioisotope is reliant on a single photopeak at 661.6 keV.
There is a limitation to the uncertainty determined by the software, which is the existence of an inhomogeneous distribution of radioactivity through the samples. This is shown in the pre-treatment radiographs of samples OMTT11 to OMTT20 in Figure 100, taken using autoradiography as described in Section 3.2.2.2.

The prominent sources of radioactivity are not evenly distributed through any sample, appearing as ‘hotspots’ in the sample, indicated by the darker regions in the radiographs of Figure 100. Furthermore, the number and intensity of these hotspots can be seen to vary between samples with OMTT11 exhibiting multiple localised regions of radioactivity, and OMTT19 showing barely any. The large hotspot seen at the edge of OMTT17 is the result of a high intensity of radioactivity, which is confirmed to be part of the sample as opposed to surface contamination on the screen by taking ‘blank’ radiographs of the screen using the same 22 hour exposure time. This cluster of radioisotopes is likely held in the graphitic structure a small distance from the screen so that its area of interaction with the screen is larger than if it were in contact, showing the importance of considering the effects of hotspots in three dimensions. Figure 101 schematically demonstrates the difficulties presented by hotspots for quantitative activity determination by gamma spectroscopy. There are two equally radioactive hotspots, named ‘A’ and ‘B’, in a graphite
sample placed in the centre of a gamma spectrometer end window. The gamma radiation emitting from these hotspots will be emitted in all directions, in a sphere of influence, and so three equal directions for each hotspot have been selected to illustrate the difficulty that hotspots present. The radiation emitted from hotspot A, located centrally along the sample and as close to the detector crystal as possible, has a greater total interaction path length through the detector crystal than hotspot B, which is located as far from the crystal as it is possible in this sample, with displacement from the end window in the x and z Cartesian directions. In reality, displacement in the y direction is also possible. This experimental arrangement would result in hotspot A registering a larger activity than hotspot B, despite their equal activities.

Figure 101: A Schematic Showing an Example Sample with Two Hotspots of Equal Activity, ‘A’ and ‘B’, atop a Gamma Spectrometer. Not drawn to scale.

As seen in Figure 57, the actual sample size is significantly smaller than the detector end window for this programme of research, though this effect could still have a small influence on the uncertainty in the quantified activities, particularly when comparing pre- and post-treatment activities of samples where a consistent sample position on the detector was maintained though the precise sample orientation relative to the previous scan was not noted.

Although this method of autoradiography cannot be used quantitatively for irradiated graphite samples, it can be used to complement the gamma spectrometry data and visually represent the differences in radioactivity between samples. Despite the
significant uncertainties associated with quantitative measurement of low activity radioisotopes, all of the radioisotopes excluding the relatively high energy beta- and gamma-radiation emitting $^{60}$Co have comparatively predictable specific activities between samples, as seen in Table 19.

<table>
<thead>
<tr>
<th>Radioisotope</th>
<th>Average Specific Activity (Bq/g)</th>
<th>Standard Deviation (σ)(Bq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{60}$Co</td>
<td>7146</td>
<td>4357</td>
</tr>
<tr>
<td>$^{133}$Ba</td>
<td>551</td>
<td>30.9</td>
</tr>
<tr>
<td>$^{134}$Cs</td>
<td>109</td>
<td>8.48</td>
</tr>
<tr>
<td>$^{137}$Cs</td>
<td>178</td>
<td>48.0</td>
</tr>
<tr>
<td>$^{154}$Eu</td>
<td>292</td>
<td>34.1</td>
</tr>
<tr>
<td>$^{155}$Eu</td>
<td>237</td>
<td>28.6</td>
</tr>
<tr>
<td>$^{241}$Am</td>
<td>6.0</td>
<td>1.07</td>
</tr>
</tbody>
</table>

The approximate $^{60}$Co activity between samples determined by gamma spectrometry, however, is found to be constant except for five samples showing significantly elevated levels of cobalt activity. These are samples OMTT16, 17, 25, 26 and 27. The pre-treatment radiographs of samples OMTT21 to OMTT30 are given in Figure 102. It is apparent from the radiographs seen in Figure 100 and Figure 102 that samples OMTT17, 25, 26 and 27 are qualitatively showing evidence of greater levels of radioactive emission than those samples around them, which correlates with their elevated $^{60}$Co inventory, with the finer details of their emission locations being blurred by the magnitude of energy deposition into the screen for the entire sample region. Visually, this trend is not represented in Figure 100 for sample OMTT16, also showing an elevated $^{60}$Co content.
Recalling that comparison between radiographs taken at different times are not quantitatively comparable due to screen or detector degradation with time, the average relative intensity determined for an arbitrary region of interest from each sample can be deduced from the radiographs. The region of interest has been defined as the approximately rectangular region of the phosphor storage screen most affected by radioactivity, and follows the approximate dimensions of the sample itself. The samples yielding the three highest average intensities returned from each screen shown are samples OMTT11, 13, 16 for Figure 100 and OMTT25, 26 and 27 for Figure 102. These intensities can be compared with the $^{60}\text{Co}$ activities, as seen in Table 20. Sample OMTT16 has also been included in the table because it has been identified by gamma spectrometry as containing a large activity of $^{60}\text{Co}$.

Table 20 shows that the uncertainty in the quantified autoradiography data for the average intensity taken over the area of a whole sample is large, and in one instance larger than the measurement itself, rendering this technique inappropriate for quantitative activity determinations.
Table 20: Comparison of Autoradiography and Gamma Spectrometry Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average Intensity</th>
<th>Intensity Standard Deviation (2σ)</th>
<th>$^{60}$Co Activity (kBq/g)</th>
<th>Activity Uncertainty (2σ)(kBq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Screen 1 (Figure 100)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OMTT17</td>
<td>5115</td>
<td>4323</td>
<td>10.85</td>
<td>0.61</td>
</tr>
<tr>
<td>OMTT13</td>
<td>4908</td>
<td>11939</td>
<td>4.60</td>
<td>0.26</td>
</tr>
<tr>
<td>OMTT11</td>
<td>4840</td>
<td>3211</td>
<td>4.67</td>
<td>0.26</td>
</tr>
<tr>
<td>OMTT16</td>
<td>4477</td>
<td>2183</td>
<td>11.73</td>
<td>0.66</td>
</tr>
<tr>
<td>Screen 2 (Figure 102)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OMTT26</td>
<td>10620</td>
<td>6531</td>
<td>21.21</td>
<td>1.20</td>
</tr>
<tr>
<td>OMTT27</td>
<td>9272</td>
<td>6558</td>
<td>22.59</td>
<td>1.28</td>
</tr>
<tr>
<td>OMTT25</td>
<td>6510</td>
<td>4398</td>
<td>9.76</td>
<td>0.55</td>
</tr>
</tbody>
</table>

The results for Screen 1 show a disjoint between the gamma spectrometry results and the average intensities taken from the autoradiography data, which for sample OMTT17 is likely a result of the large hotspot for this sample seen in Figure 100. The average intensity across this hotspot, if considered in isolation, is $11027 \pm 8805$, and so the average intensity of this sample is unduly elevated by this localised hotspot, which correlates positively with the gamma spectrometry. A direct positive correlation between sample activity and average intensity can also be seen for the samples of Screen 2, where elevated average intensities are supported by increased measured $^{60}$Co activities. These results demonstrate that there is a link between the autoradiography and $^{60}$Co activity determined by gamma spectrometry, suggesting strongly that the hotspots are likely to be localised regions of $^{60}$Co, as opposed to any of the alternative radioisotopes. The cause of the disparity between results for sample OMTT16 however is unclear, and as such autoradiography alone could be deemed unreliable for semi-quantitative $^{60}$Co activity determinations in irradiated graphite.

The pre- and post-treatment total activities determined by gamma spectrometry for each radioisotope separately can be seen in Figure 103 to Figure 109. The total activities of each radioisotope have been determined in this instance because the treatment causes mass loss to the sample, and so a constant activity of a given radioisotope will yield a higher specific activity post-treatment because the mass of the sample has been reduced.

All of the samples seen in Figure 103 to Figure 109 have been treated at temperatures from 600°C up to 700°C in a 1% oxygen environment, and as such distinctions between treatment regimes have not been made for each sample because the metallic impurities within them should all behave similarly irrespective of the treatment
temperature utilised. The literature suggests that all of the elements examined, excluding caesium, will exist in a solid state throughout these experiments, with caesium existing in an entirely gaseous state above 600°C with HCl present and 300°C without. It is found from Figure 103 to Figure 109 that in almost all instances the pre- and post-treatment activities are similar, and the uncertainties in their measurements overlap, indicating that if any form of radioactive release has occurred then it is within the margin of uncertainty and as such has not been detected using this apparatus. It is not even immediately apparent from these plots that a consistent small reduction in activity exists for these radioisotopes post-treatment, as there appear to be multiple instances where the measured pre-treatment activity is larger, and multiple instances where the opposite is also true.

*Figure 103: The Activity of $^{60}$Co in each Sample, Pre- and Post-Treatment*
**Figure 104: The Activity of $^{133}$Ba in each Sample, Pre- and Post-Treatment**

**Figure 105: The Activity of $^{134}$Cs in each Sample, Pre- and Post-Treatment**
Figure 106: The Activity of $^{137}$Cs in each Sample, Pre- and Post-Treatment

Figure 107: The Activity of $^{154}$Eu in each Sample, Pre- and Post-Treatment
Figure 108: The Activity of $^{155}$Eu in each Sample, Pre- and Post-Treatment

Figure 109: The Activity of $^{241}$Am in each Sample, Pre- and Post-Treatment
There are four instances where the uncertainties do not overlap, which are $^{133}$Ba analysis of OMTT22 and $^{154}$Eu analyses of samples OMTT12, OMTT22 and OMTT23. In the case of OMTT22, the sample appears to have gained a significant proportional activity of $^{133}$Ba and $^{154}$Eu between analyses. This result could be a consequence of the uncertainties aroused by inhomogeneous distributions of radioactivity, or hotspots, as described previously, which can yield more prominent effects for lower activity radioisotopes. Figure 100 shows that sample OMTT22 has few hotspots, and so inconsistent positioning of these on the detector could cause discrepancies in the results. For samples OMTT12 and OMTT23, the opposite has occurred, and europium has been lost between pre- and post-treatment characterisations, which given the consistency in the other samples and the chemically identical $^{155}$Eu data are potentially caused by hotspots or loss of material in the form of dust during other characterisation techniques, sample transfers and mass measurements.

It can be seen from these results that the $^{134,137}$Cs content, which is expected to be gaseous above $600^\circ$C, is consistently immobile, with the original activities determined in the sample before thermal treatment appearing to remain in the sample irrespective of treatment temperature. This holds true for samples OMTT24 to OMTT29, which were exposed to a temperature of $600^\circ$C for increasing durations up to 32 hours, showing that the caesium remains in the sample even following significant periods of time at elevated temperatures. This suggests that either the caesium exists in an unexpected stable form in the irradiated graphite, or that it becomes gaseous though is trapped by the graphite matrix surrounding it.

A clearer means of examining the release behaviour of the metallic radioisotopes during thermal treatment is to consider the percentage difference in activities between pre- and post-treatment gamma spectra, as seen in Figure 110 to Figure 116. It is apparent that the majority of samples exhibit no meaningful display of radioactive release during thermal treatment, with the change in radioactivity for each radioisotope occurring close to 0%, with the measurement uncertainties overlapping the 0% line in most instances.
Figure 110: The Percentage Change in Activity of $^{60}$Co in each Sample with Treatment

Figure 111: The Percentage Change in Activity of $^{133}$Ba in each Sample with Treatment
Figure 112: The Percentage Change in Activity of $^{134}$Cs in each Sample with Treatment

Figure 113: The Percentage Change in Activity of $^{137}$Cs in each Sample with Treatment
Figure 114: The Percentage Change in Activity of $^{154}$Eu in each Sample with Treatment

Figure 115: The Percentage Change in Activity of $^{155}$Eu in each Sample with Treatment
Figure 116: The Percentage Change in Activity of $^{241}$Am in each Sample with Treatment

Any data points above the 0% line, marked as a bold black line on each plot, have ‘gained’ relative radioactivity between measurements, and any data points below the zero line have ‘lost’ radioactivity between measurements. All sample activities have been normalised to the start date of this programme of research, and therefore any apparent losses in activity are not as a consequence of natural radioactive decay. There is an approximately even distribution between samples that have ‘gained’ and ‘lost’ radioactivity and so this can be attributed to natural scatter in the data, rather than a systematic error. Sample OMTT22 shows a consistently higher fractional gain in radioactivity than seen in the scatter in the data for other samples, across many radioisotopes, which is likely a consequence of hotspots, as highlighted previously. The additional uncertainties associated with these hotspots are not expressed in the error bars. Samples OMTT21 and OMTT23 appear to consistently return a larger radioactive ‘release’, signified by a negative percentage, though this is thought to be due to hotspots or loss of material in the form of dust during other characterisation techniques, sample transfers and mass measurements.

Analysis of the data in this form clearly shows that radioactive losses of radiocaesium, the only volatile radioisotope examined by gamma spectrometry, have not measurably occurred.
7.3 Conclusions Reached in Section 7

The main findings of this results section are:

- The release profile of $^3$H with time exhibits a faster rate of release earlier in the experiment, followed by a linear release profile, for these irradiated graphite samples.
- The release profile of $^3$H with mass loss exhibits a faster rate of release at smaller mass losses, followed by a linear release profile which equates to approximately 100% release at 100% mass loss if extrapolated, suggesting that this trend will continue.
- The release mechanism for $^3$H is inconclusive from this data, as discussed at length, with the predicted diffusion processes negated by a linear release profile with mass loss and time, and so further research is required.
- All of the expected prominent metallic radioisotopes can be detected in these irradiated graphite samples using high resolution gamma spectrometry, excluding $^{152}$Eu.
- The pre-treatment activities of most radioisotopes are relatively consistent between samples, excluding $^{60}$Co which can vary considerably.
- Radioactivity is not evenly distributed through a sample, as seen qualitatively in radiation hotspots identified by autoradiography.
- The uncertainty in gamma spectra caused by radiation hotspots is significant.
- There is a correlation between radiograph average intensity and sample $^{60}$Co activity, suggesting that hotspots seen by autoradiography are predominantly a consequence of $^{60}$Co derived radiation.
- There are no observable releases of metallic radioisotopes from these samples during treatment in a 1% oxygen atmosphere between 600 and 700°C.
- Contrary to the literature, the lack of observable release is inclusive of $^{134}$Cs and $^{137}$Cs, which are expected to be gaseous above 600°C, suggesting that these are either trapped in the graphitic structure or exist as an unpredicted stable form.
8. Conclusions and Future Work

8.1 Major Conclusions

A number of conclusions can be drawn from analysis of the experimental data collected over the course of this programme of research. The original aims and objectives for this research were to:

- Familiarise with and optimise the existing thermal treatment process, and investigate the sources of uncertainty
- Quantify the radioactivity of prominent radioisotopes in Oldbury Magnox reactor installed set graphite
- Determine whether a preferential release of $^{14}\text{C}$ can be achieved from Oldbury Magnox reactor-sourced graphite
- Investigate the selective release efficiency that can be achieved for $^{14}\text{C}$ from Oldbury Magnox reactor-sourced graphite
- Determine the maximum fraction of $^{14}\text{C}$ that could be released from irradiated graphite, whilst retaining sample structural integrity
- Use thermal treatment to estimate the fraction of $^{14}\text{N}$-derived $^{14}\text{C}$ compared to $^{13}\text{C}$-derived in UK graphite
- Investigate the effects of thermal treatment on $^{3}\text{H}$ and metallic radioisotopes

The major conclusions deduced from this programme of experimental research, which fulfil the aims and objectives, are:

**Preferential removal of $^{14}\text{C}$-enriched graphite can be achieved:**

Comparison of the activity of $^{14}\text{C}$ released during thermal treatment experiments and the proportion of $^{14}\text{C}$ in the remaining irradiated graphite material has shown that under controlled environments preferential removal of a fraction of $^{14}\text{C}$ from the bulk material of Oldbury Magnox reactor installed set graphite can be achieved.
Between 600 and 700°C the $^{14}$C release profiles are unaffected by the treatment temperature:

The rate of oxidation of graphite is heavily influenced by the sample temperature, with the rate of oxidation at 700°C in a 1% oxygen atmosphere occurring an order of magnitude faster than at 600°C. Thermal treatment experiments conducted at temperatures of 600, 650 and 700°C demonstrate however that the selective removal efficiency of $^{14}$C per unit mass loss for this source of Oldbury Magnox reactor graphite is not influenced by the treatment temperature in this temperature range. This has been confirmed by observing $^{14}$C releases after equivalent sample mass losses using differing treatment temperatures.

**Preferential releases of $^{14}$C are derived from near surface regions:**

It has been determined by mensuration that the fractional mass loss during thermal treatment at 600°C is significantly larger than the geometric volume loss of a cylindrical sample, indicating that the mass loss must have occurred predominantly from exposed surfaces within the sample. This is consistent with expected first regime oxidation behaviour from the literature. Consequently, the corresponding preferential releases of $^{14}$C observed must arise from oxidised graphite at or near surfaces throughout the internal of the sample.

**The selective release efficiency of $^{14}$C reduces with mass loss:**

There is a negative correlation between the selective release efficiency of $^{14}$C and increasing mass loss from Oldbury Magnox reactor installed set irradiated graphite. The specific activity of the oxidised graphite reduces quickly with mass loss, approximately as a power law, which is indicative of exhaustion of a $^{14}$C-enriched surface layer. The observed preferential release of $^{14}$C is not continuous with increasing sample mass loss and as such there is a limit to the effective $^{14}$C release that can be achieved.
The $^{14}$C release profile from irradiated graphite is predictable:

The overall $^{14}$C release profile from Oldbury Magnox reactor irradiated graphite samples can be approximated as a combination of linear and power law components, indicative of $^{13}$C and $^{14}$N-derived $^{14}$C respectively. Power law release behaviour is exhibited at low sample mass losses, tending towards linear behaviour at higher mass losses when the $^{14}$C-enriched surface region is exhausted and randomly distributed $^{13}$C-derived $^{14}$C remains. Despite variation of $^{14}$C inventories between samples, this behaviour is consistent across all thermal treatment experiments conducted.

An estimated minimum 8% of the $^{14}$C in these samples is derived from nitrogen:

The transition from the power law component to the linear component of the $^{14}$C release profile for this irradiated graphite source is difficult to quantitatively determine, and thus analysis of the first and second derivatives of the release profile has allowed an estimate to be drawn as to when this transition occurs. This corresponds to approximately 8% of the $^{14}$C inventory found in these irradiated graphite samples. This is a ‘minimum’ estimate of the $^{14}$N-derived surface region $^{14}$C because unquantified losses of surface region $^{14}$C will have occurred prior to thermal treatment as a consequence of radiolytic oxidation at graphite surfaces during normal reactor operation.

The $^3$H release behaviour is comparable in profile to that of $^{14}$C:

The release profile of $^3$H from Oldbury Magnox reactor installed set graphite during thermal treatment is comparable to that found for $^{14}$C, though there is a larger degree of scatter and uncertainty in the data. The rate of release of $^3$H falls approximately as a power law with increasing weight loss, until a linear relationship between $^3$H release and mass loss is observed. When the linear portion of the release profile is extrapolated to 100% mass loss it corresponds to approximately 103% $^3$H release, indicating that this linear release rate is unlikely to change with increasing mass loss. The release mechanism for $^3$H is inconclusive from this data, as discussed at length, and thus further research is required.
Hotspots of $^{60}$Co are inhomogeneously distributed across a sample:

Radiographs of Oldbury Magnox reactor irradiated graphite samples show the radioactive inventory within a sample is not evenly distributed, as there are localised regions of high energy radiation emission. There is a positive correlation between the average intensity of the radiographs and the $^{60}$Co activities determined for each sample by germanium gamma spectrometry, indicating that the identified hotspots are likely to be localised concentrations of $^{60}$Co.

There are no observable releases of metallic radioisotopes during thermal treatment:

Quantitative gamma spectrometry has been performed on each thermally treated sample, both before and after thermal treatment. There are no observable releases of metallic radioisotopes from irradiated graphite samples during this procedure, irrespective of treatment time or temperature. This is inclusive of $^{134}$Cs and $^{137}$Cs, which the literature states will be gaseous at all temperatures exceeding 600°C, demonstrating that the radiocaesium may exist in a previously unexpected form in irradiated graphite.

8.2 Future Work

There are a number of avenues of scientific research that could be explored to either compliment or develop from this programme of experimental research. These are outlined below, in no particular order.

Accurately determine location of $^{14}$C release:

For this research, the location of $^{14}$C release from the irradiated graphite samples have been deduced from comparison of the literature and metrology of the samples, demonstrating that where a large mass loss occurs with a relatively small geometric volume change, the mass loss must have occurred from internal surfaces of the sample. X-ray
Computer Tomography, a 3-dimensional visualisation technique, could be used to identify the precise locations of mass loss.

**Investigate the release behaviour of $^3$H for Magnox samples:**

The mechanism for $^3$H release is inconclusive from the data presented in this programme of research, with a diffusion mechanism suspected from preliminary data. Long duration experiments at high temperatures in an inert environment, which should exhibit diminishing releases of $^3$H with time, with no significant mass loss or release of $^{14}$C, would prove that the mechanism for tritium release is by diffusion from the bulk material. There may be a temperature dependency if this is the case, with higher temperatures causing larger fractional releases of $^3$H more quickly.

**Determine the chemical form of the radiocaesium inventory:**

It has been seen that the radiocaesium in these irradiated graphite samples has not been liberated from the samples during thermal treatment as the literature suggests it might. There is some evidence that the caesium inventory has not volatilised, at least not entirely, despite temperatures of 1000°C and full oxidation of the carbon. Experimental techniques such as X-ray Photoelectron Spectroscopy (XPS) could be used to identify the chemical form of caesium in irradiated graphite.

**Application of thermal treatment to alternative sources of irradiated graphite:**

The low temperature thermal treatment process explored in this programme of experimental research has investigated a single source of irradiated graphite, which is from an installed set retrieved from Oldbury Reactor 2 in which an accelerated rate of radiolytic oxidation has been induced. The thermal treatment process should be applied to trepanned reactor core samples from Oldbury and alternative sources of Magnox reactor graphite, such as one of the Wylfa reactors, and AGR-derived graphite to confirm that the radioisotope release behaviour is representative of the remainder of the UK irradiated graphite waste inventory. This technique could also be applied to international sources of
graphite, such as RBMK reactor graphite, to compare the effectiveness of decontamination for alternative reactor design graphites.
References

[22] Jensen, S., *Description of the Magnox type of gas cooled reactor (MAGNOX).*


[61] von Lensa, W., Treatment and Disposal of Irradiated Graphite and Other Carbonaceous Waste.


OECD, NEA (2015) JANIS software, ENDF/B-VII.1 Library.


Appendix A – UK Graphite Reactors

The UK nuclear industry, aside from a single PWR, has been largely reliant on graphite-moderated reactors, and consequently a significant volume of irradiated graphite waste has accumulated over many generations and types of reactor.

Figure 117: GLEEP Test Reactor\textsuperscript{[128]}

Figure 118: BEPO Test Reactor\textsuperscript{[129]}

Nuclear energy started to develop in the UK in the 1940s when two low energy experimental air-cooled, graphite-moderated reactors, known as Graphite Low Energy Experimental Pile (GLEEP), seen in Figure 117, and its successor British Experimental Pile
Zero (BEPO), Figure 118, were constructed as test reactors; these early reactors were used to investigate reactor operation and design, and for a time were also used for commercial isotope production\textsuperscript{[130]}. GLEEP, containing 505 tonnes of graphite\textsuperscript{[131]}, has been completely dismantled, whilst BEPO, containing 766 tonnes of graphite, is yet to be fully decommissioned.

These experimental reactors were followed in the early ‘50s by the pair of Windscale Piles (Figure 119) constructed in Cumbria, notorious for the fire that occurred in the reactor core of Unit 1. These were large air-cooled, graphite-moderated reactor units, designed for plutonium production, and later adapted for tritium production, as part of the UK’s atomic weapons program. Each unit housed approximately 1966 tonnes of graphite moderator\textsuperscript{[133]}. 

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{windscale_piles_facility}\caption{Windscale Piles Facility\textsuperscript{[132]}}
\end{figure}
Three further test reactors, known as DIDO (Figure 120), PLUTO and DMTR (Figure 121), were commissioned in 1956, 1957 and 1958 respectively; these were designed for material testing as part of the UK’s civil nuclear research program, allowing simulation of many years neutron irradiation in a matter of months. Although these reactors used heavy water instead of graphite as a moderator material, they had graphite neutron reflectors around the core, contributing a relatively small 17 tonnes each to the UK inventory of waste graphite\textsuperscript{131}. 

\textit{Figure 120:} DIDO Test Reactor\textsuperscript{133} 

\textit{Figure 121:} DMTR Test Reactor, 2006\textsuperscript{134}
In the late ‘50s, the Dounreay Fast Reactor (DFR) was constructed in Scotland as a testing platform for the fast reactor concept, shown in Figure 122. Fast reactors do not require materials such as graphite for neutron moderation, using instead the energy of fast neutrons to maintain a reaction, though in this design a borated graphite jacket was used to surround the reactor core as both a neutron reflector and shield; this equates to approximately 200 tonnes of borated graphite waste. Following the experience with this
fast reactor, a Prototype Fast Reactor (PFR) was also built at Dounreay, the core of which is seen in Figure 123, starting operation in 1974, which also used graphite shielding. The amount of graphite used in this prototype reactor is unknown to the author.

![Figure 124: The Largest Magnox Reactors Built, Wylfa](image)

The first fleet of commercial nuclear reactors in the UK designated for electricity production, dating from 1956, are known as ‘Magnox’ reactors, referring to the magnesium oxide alloy fuel cladding used. It should be noted that the first Magnox power station, at Calder Hall, was a dual-purpose plutonium and energy production site for a number of years. A total of 26 of these large carbon dioxide-cooled and graphite-moderated reactors were built in the UK, with the largest having cores containing up to 3470 tonnes of graphite[^41], all of which will be designated as waste upon closure making these reactors a significant contributor to the UK irradiated graphite inventory. All Magnox power stations in the UK, except one of the newest and largest, Wylfa on Anglesey (Figure 124), have ceased operation; the remaining Wylfa reactor 1 is due to close in December 2015[^138].
Another prototype reactor, known as the Dragon prototype High Temperature Reactor (HTR) and seen in Figure 125, was constructed at Winfrith as part of an international project. Dragon was operational by 1976, utilising a graphite core and helium coolant. This prototype was designed for materials testing for future European high temperature reactor development, and contained approximately 40 tonnes of graphite\textsuperscript{[41]}, and so is a somewhat minor contributor to the UK irradiated graphite waste inventory.

\textit{Figure 125: Dragon HTR Prototype During Decommissioning\textsuperscript{[129]}}
The second generation of commercial energy production reactors in the UK are the Advanced Gas Reactors (AGR), which are a development of the carbon dioxide-cooled, graphite-moderated Magnox design, operating at an increased temperature for improved efficiency. Before full implementation of this design could take place, the prototype Windscale Advanced Gas Reactor (WAGR) seen in Figure 126 was constructed and operational in 1962, to test this higher temperature design for development of fuel and other components. This prototype reactor contained approximately 210 tonnes of
graphite\textsuperscript{[131]}. A full fleet of 14 AGR reactors followed between 1976 and 1989, with the larger reactor cores containing of the order of 1500 tonnes graphite\textsuperscript{[41]}, all of which are still operational today. The Heysham AGR reactor buildings can be seen in Figure 127. An AGR reactor at Hinkley Point B contains 1248 tonnes of graphite\textsuperscript{[141]}. Coupled with the Magnox fleet, these reactors will be the largest contributor to the UK irradiated graphite waste inventory.
## Appendix B – Data from the UK 2010 Radioactive Waste Inventory\[^{23}\]

Table B1: A Compilation of Contributors to the UK Irradiated Graphite Waste Inventory, as per the 2010 Radioactive Waste Inventory\[^{23}\]

<table>
<thead>
<tr>
<th>Site</th>
<th>Stream Identifier</th>
<th>Waste</th>
<th>Waste Type</th>
<th>Volume (m(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calder Hall</td>
<td>2A303</td>
<td>Graphite LLW</td>
<td>LLW</td>
<td>7.8</td>
</tr>
<tr>
<td>Calder Hall</td>
<td>2A310</td>
<td>Graphite ILW</td>
<td>ILW</td>
<td>7750</td>
</tr>
<tr>
<td>Chapelcross</td>
<td>2C204</td>
<td>Graphite LLW</td>
<td>LLW</td>
<td>7.4</td>
</tr>
<tr>
<td>Chapelcross</td>
<td>2C311</td>
<td>Graphite ILW</td>
<td>ILW</td>
<td>4510</td>
</tr>
<tr>
<td>Sellafield</td>
<td>2F07</td>
<td>AGR Graphite Fuel Assembly Components</td>
<td>ILW</td>
<td>13900</td>
</tr>
<tr>
<td>Windscale</td>
<td>2S10/C</td>
<td>WAGR Stringer Graphite Debris</td>
<td>ILW</td>
<td>59</td>
</tr>
<tr>
<td>Dungeness B</td>
<td>3J313</td>
<td>Graphite ILW</td>
<td>ILW</td>
<td>4720</td>
</tr>
<tr>
<td>Dungeness B</td>
<td>3J317</td>
<td>Graphite LLW</td>
<td>LLW</td>
<td>2260</td>
</tr>
<tr>
<td>Hartlepool</td>
<td>3K25</td>
<td>Fuel Stringer Debris - Graphite &amp; assoc. Metals</td>
<td>ILW</td>
<td>337</td>
</tr>
<tr>
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<td>LLW</td>
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<tr>
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<td>LLW</td>
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<tr>
<td>Heysham 2</td>
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<td>Fuel Stringer Debris - Graphite</td>
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<td>5130</td>
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<td>LLW</td>
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<td>Graphite ILW</td>
<td>ILW</td>
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<td>LLW</td>
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<td>Graphite LLW</td>
<td>LLW</td>
<td>873</td>
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<td>Dounreay</td>
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<td>Graphite/THTR Waste</td>
<td>ILW</td>
<td>202</td>
</tr>
<tr>
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<td>9A31</td>
<td>Fuel Element Debris Graphite</td>
<td>ILW</td>
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<td>LLW</td>
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<td>ILW</td>
<td>3740</td>
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<td>LLW</td>
<td>266</td>
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<td>ILW</td>
<td>4390</td>
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<td>Graphite LLW</td>
<td>LLW</td>
<td>58.1</td>
</tr>
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<td>ILW</td>
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<td>4080</td>
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<td>ILW</td>
<td>4460</td>
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<td>ILW</td>
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<td>Graphite LLW</td>
<td>LLW</td>
<td>59.3</td>
</tr>
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<td>Wylfa</td>
<td>9H311</td>
<td>Graphite ILW</td>
<td>ILW</td>
<td>6790</td>
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</tbody>
</table>
Table B1: A Compilation of Contributors to the UK Irradiated Graphite Waste Inventory, as per the 2010 Radioactive Waste Inventory\textsuperscript{[23]} (continued)

<table>
<thead>
<tr>
<th>Location</th>
<th>Code</th>
<th>Description</th>
<th>Category</th>
<th>Volume (m\textsuperscript{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wylfa</td>
<td>9H315</td>
<td>Graphite LLW</td>
<td>LLW</td>
<td>4,110</td>
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<td>ILW</td>
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<td>ILW</td>
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<td>Fuel Element Debris Graphite</td>
<td>ILW</td>
<td>569</td>
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<td>Fuel Element Debris Graphite</td>
<td>ILW</td>
<td>552</td>
</tr>
<tr>
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<td>Fuel Element Debris Graphite</td>
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<td>Hunterston A</td>
<td>9J313</td>
<td>Graphite LLW</td>
<td>LLW</td>
<td>8.7</td>
</tr>
</tbody>
</table>

Estimated Total Volume Nuclear Waste in the UK: \(4,720,000\) m\textsuperscript{3}

- Total Volume ILW in UK: \(287,000\) m\textsuperscript{3}
- Total Volume LLW in UK: \(4,430,000\) m\textsuperscript{3}

Estimated Total Irradiated Graphite Waste in the UK: \(119,858.8\) m\textsuperscript{3}

- Volume of Graphite ILW in UK: \(104,758.7\) m\textsuperscript{3}
- Volume of Graphite LLW in UK: \(15,100.1\) m\textsuperscript{3}

Percentage of Total UK ILW Contributable to Graphite: 36.5%

Percentage of Graphite Waste that is designated ILW: 87.4%
Appendix C – Radioisotope Production Pathways and Significance

The radioisotopes listed in Section 2.2.2 are produced from different source impurities, and are significant to irradiated graphite waste management for different reasons. In this section, the individual isotopes will be discussed in terms of their likely source impurity and the consequences of the resultant activation for radioactive waste management.

Tritium, $^3\text{H}$: Tritium is an unstable beta-particle emitting isotope of hydrogen, with two extra neutrons in the nucleus. This isotope has a half life of 12.32 years, and decays into $^3\text{He}$, which is stable, as seen in Figure 128. The beta particle ejected will have a maximum energy of 18.59 keV, with the average beta-particle energy being around 5.69 keV\cite{45}. This is considered a very low energy emission, with the maximum range of a $^3\text{H}$ beta-particle in air of approximately 6mm\cite{142}, and so the risk of receiving an external dose from tritium exposure is relatively small. The hazards associated with tritium are largely attributed to its high mobility, since chemically it behaves as hydrogen, is often in the form of tritiated water vapour, and can easily be taken up into biological organisms including plants, animals and people\cite{142}. Tritium is also the highest activity radioisotope found in irradiated graphite immediately after closure of the reactor, with activities orders of magnitudes higher than many other radioisotopes, as seen in Table 6.

![Tritium Decay Scheme](image)

\[
^3\text{H} (\tau_{1/2} 12.32\text{y}) \quad 100\% \beta^- (18.59 \text{ keV}) \quad ^3\text{He} (\text{stable})
\]

Figure 128: Decay Scheme for the Radioactive Decay of Tritium, data from NuDat 2.6\cite{45}

Black's\cite{42} research, including modelling activation in irradiated graphite from both Oldbury and Wylfa Magnox reactor power stations, demonstrates that the dominant production route for $^3\text{H}$ in graphite is through neutron activation of the $^6\text{Li}$ impurity.
Lithium-6 is approximately 7.59% abundant in natural lithium\[^{47}\]. Black’s models strongly suggest that the production of \(^{3}\)H peaks early in the operational lifetime of a graphite moderated reactor, as the parent isotope \(^{6}\)Li is effectively burnt out. A cyclic reactivation process then occurs whereby the produced tritium naturally decays by beta emission into \(^{3}\)He and then is activated by a neutron-proton reaction into tritium again, as seen in Equation (25)\[^{42}\].

\[
^{6}\text{Li}(n,\alpha)^{3}\text{H}(\beta^{-})^{3}\text{He}(n,p)^{3}\text{H}
\] (25)

This means that the final tritium inventory is largely independent of total neutron fluence\[^{42}\], and plateaus. Black notes that the actual final inventory in a reactor system is difficult to predict because of the high mobility of the \(^{3}\)H isotope.

Tritium could also be sourced from neutron absorption of hydrogen to deuterium, and then further neutron absorption and activation to tritium, as seen in Equation (26), which is an issue for heavy water moderated reactors such as the Canadian CANDU design\[^{143}\].

\[
^{1}\text{H}(n,\gamma)^{2}\text{H}(n,\gamma)^{3}\text{H}
\] (26)

It should be noted that the hydrogen impurity in graphite is not given in Table 5, though it is thought that some hydrocarbons in the raw materials could contribute traces of hydrogen impurity in the manufactured graphite article\[^{9}\], and in material graphitised to 3000°C this is “probably less than 50ppm” \[^{9}\], suggesting that there may be some uncertainty surrounding this. Hydrogen can also be introduced to the reactor system in the form of water, as a direct ingress of water into the reactor or exposure to a humid atmosphere such as during a reactor outage\[^{9}\]. This ‘probable’ impurity content is somewhat higher than that of lithium, given in Table 5.

If the neutron absorption cross sections for the initial hydrogen to deuterium, and then the secondary deuterium to tritium reaction are compared to that of the lithium to tritium reaction, as seen in Figure 129, they are orders of magnitude lower across the entire energy spectrum, and require more than a single reaction, supporting Black’s model which shows that tritium production from the lithium impurity dominates.
Figure 129: Comparison of Neutron Absorption Cross Sections for Tritium Production from Hydrogen and Lithium, data from JANIS\(^{40}\)

Another potential source of tritium in irradiated graphite, described in an IAEA technical document, is through a neutron absorption reaction with nitrogen-\(^{14}\)\(^{41}\), as seen in Equation (27).

\[
^{14}\text{N}(n,^{3}\text{H})^{12}\text{C}
\]  

(27)

The cross section for this tritium production reaction does not become significant until around 5 MeV\(^{40}\), however, and since the maximum energy of neutrons found in a thermal reactor is of the order of 10 MeV, with an average energy of 2 MeV\(^{35}\), and given that the \(^{14}\text{N}(n,p)^{14}\text{C}\) reaction cross section is almost consistently larger across the neutron energy spectrum, as seen in Figure 130, it could be suggested that this production route for tritium is less probable in graphite.
Carbon-14, $^{14}$C: Carbon-14 is a naturally occurring unstable isotope of carbon, with two additional neutrons in the nucleus, and a half life of 5730 years. This isotope decays into stable $^{14}$N by emission of a beta-particle of maximum energy 156.48 keV and average energy 49.47 keV\[^{45}\]. The decay scheme for $^{14}$C can be seen in Figure 131. Similarly to tritium, this is generally considered a low energy emission, though the beta particles can travel up to approximately 24cm in air\[^{144}\]. Carbon-14 is the second highest activity radioisotope found in irradiated graphite after a Magnox reactor shutdown\[^{44}\], though as shown in Figure 11 it takes only a short amount of time for the tritium content to decay and the carbon-14 to become the dominant radioisotope in irradiated graphite. The major hazard associated with carbon-14 in the context of irradiated graphite waste is the possibility of wide scale uptake into biological organisms and the food chain\[^{41}\] due to the large activities produced over an entire reactor core, the long half life spanning many future generations, and its mobility in the geo- and biosphere.
The production of carbon-14 in a graphite-moderated nuclear reactor environment is a topic of some controversy, with many sources disagreeing as to the prominence of precursor isotopes and consequences for the resultant $^{14}\text{C}$ location within the graphitic lattice. Consequently, this topic of $^{14}\text{C}$ production in neutron irradiated graphite, which has potential relevance to the efficiency of any thermal treatment process to remove it from graphite, has been discussed at length in Section 2.3.

*Chlorine-36, $^{36}\text{Cl}$:* Chlorine-36 is a radioactive isotope of chlorine which decays almost exclusively by beta-particle emission$^{[45]}$, as demonstrated by the decay scheme in Figure 132. This beta particle has a relatively high maximum energy of 709.55 keV, though the half life of this isotope is 301,000 years, and so a relatively large amount of chlorine must be accrued and activated before a significant activity can be detected. It can be deduced from Table 6 that the expected $^{36}\text{Cl}$ inventory is two orders of magnitude lower than that of both $^{1}\text{H}$ and $^{14}\text{C}$, though Figure 11 demonstrates that because of the long half life this activity is expected to persist for many years, similarly to $^{14}\text{C}$.

---

**Figure 131: Decay Scheme for the Radioactive Decay of Carbon-14, data from NuDat 2.6$^{[45]}$**

\[ ^{14}\text{C} (\tau_{1/2} \text{ 5730y}) \]

100% $\beta^{-}$ (156.48 keV)

\[ ^{14}\text{N} \text{ (stable)} \]

---

**Figure 132: Decay Scheme for the Radioactive Decay of Chlorine-36, data from NuDat 2.6$^{[45]}$**

\[ ^{36}\text{Cl} (\tau_{1/2} \text{ 301000y}) \]

100% $\beta^{-}$ (709.55 keV)

\[ ^{35}\text{Cl} \text{ (stable)} \]
Chlorine is known to be highly mobile, with sources such as Rahmani\cite{145} noting that measurements on their graphite, especially in powder form, suggested that additional chlorine had been acquired from the air. As such, this is another isotope of concern for release to the environment through transport to the biosphere by groundwater and uptake into the food chain\cite{146}, with NIREX identifying it as a long-term threat particularly because of its long half life, implying that in practical terms it will ‘never’ decay away\cite{147}.

It is plausible that the chlorine impurity found in unirradiated graphite is largely sourced from the raw materials, though another potential identified source of the relatively high reaction cross section chlorine impurity, for gas-purified graphite, is as a remainder of halogen salts from the purification stage of the manufacturing process\cite{9}. Although typical impurity values of between 2 and 5.7 ppm are given in Table 5, work by EdF-France remarks that the chlorine impurity studied in the French Uranium Naturel Graphite Gaz (UNGG) reactors, which are similar in design to UK Magnox reactors, is inhomogeneously distributed and can vary by a factor of 10 times in some cases, across just a few centimetres of graphite\cite{148}. The high mobility and non-uniform distribution of this radioactive isotope make $^{36}$Cl inventory predictions difficult to produce\cite{42}.

Cobalt-60, $^{60}$Co: This isotope of cobalt is the third highest activity radioisotope in irradiated graphite 10 years after a reactor closure\cite{44}, though has a half life of 5.27 years and so will decay to more reasonable levels for dismantling within a reasonable timeframe of the order of tens of years, as demonstrated in Figure 11\cite{42}. Cobalt-60 is specifically noted in an ASTM for new grades of HTR-designated graphites as a problem isotope for future disposal\cite{43}, which could be due to its tendency to almost always decay by beta-particle emission, of up to 317.05 keV, followed by two characteristic high energy gamma rays of 1173.23 and 1332.49 keV, as seen schematically in Figure 133.
There are multiple precursor impurity isotopes that, following a series of activation or decay events, can become cobalt-60 including nickel and iron, both of which feature in Table 5. The work by Black strongly suggests that the dominant route for production of cobalt-60 in irradiated graphite in the Oldbury Magnox reactor environment, irrespective of the input impurity data utilised, is neutron activation of the cobalt-59 isotope\textsuperscript{(42)}, as per Equation (28).

$$^{59}\text{Co}(n,\gamma)^{60}\text{Co}$$

\textit{Strontium-90, $^{90}\text{Sr}$}: Data for this isotope of strontium is often presented in conjunction with its daughter isotope, $^{90}\text{Y}$, as seen in White’s report\textsuperscript{(44)}. This is because $^{90}\text{Sr}$ decays by beta-particle emission of maximum energy 546 keV, with a half life of approximately 28.79 years, to $^{90}\text{Y}$ which itself has a relatively short half life of only 64 hours and thus decays quickly by a further beta emission to stable zirconium-90, as shown schematically in Figure 134. The beta-particle emitted by the daughter isotope, $^{90}\text{Y}$, has a significant maximum energy of 2280.1 keV\textsuperscript{(45)} and an average energy of 933.7 keV, and so represents a reasonable hazard for external dose. The US health physics society recommends storage of $^{90}\text{Sr}$ behind a minimum thickness of 12mm of Plexiglas to reduce the dose rate, a measure deemed unnecessary for storage of other lower energy beta-particle emitters such as $^{14}\text{C}$\textsuperscript{(144, 149)}. 

\begin{center}
\textbf{Figure 133: Decay Scheme for the Radioactive Decay of Cobalt-60, data from NuDat 2.6\textsuperscript{(45)}}
\end{center}
Strontium-90 is an isotope of significant concern in irradiated graphite waste because of the health effects that can result from ingestion or inhalation; chemically this isotope behaves similarly to calcium, and consequently has a natural tendency to be a bone seeker, meaning that it can harbour and accumulate in bones and bone marrow\textsuperscript{[150]}.

The literature consensus is that strontium-90 is a fission product from uranium\textsuperscript{[44]} or thorium\textsuperscript{[53]}, and as such could exist in irradiated graphite as a product of the fission of the natural uranium impurity content, measured at 0.07 ppm during an NDA Characterisation Study\textsuperscript{[42]}, or introduced to the graphite as contamination from fuel failures or traces of uranium carried into the core on fuel-element surfaces\textsuperscript{[41]}.  

\textit{Barium-133, $^{133}$Ba:} Barium-133 is a metallic synthetic radioisotope, such that it is not found in nature, though it can be found in irradiated graphite. It has a half life of 10.551 years and decays exclusively by electron capture, whereby an electron from one of the inner shells is captured into the nucleus resulting in the release of low energy Auger electrons from the atom, as well as frequent gamma rays. The prominent gamma ray emissions are of 356.01, 81.00 and 302.85 keV energy with 62.05, 32.9 and 18.34\% probability of occurrence respectively, though in reality there are many gamma emissions of differing energies\textsuperscript{[45]}. This results in a relatively complex decay scheme, as seen in Figure 135, the gamma energy emissions for which are found in Table 21.
Figure 135: Decay Scheme for the Radioactive Decay of Barium-133, data from NuDat 2.6\cite{45}

Table 21: Gamma Emission Energies Associated with Barium-133, numbered as per Figure 135, and their Relative Intensities\cite{45}

<table>
<thead>
<tr>
<th>Gamma Emission</th>
<th>Energy (keV)</th>
<th>Intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_1$</td>
<td>53.16</td>
<td>2.14</td>
</tr>
<tr>
<td>$\gamma_2$</td>
<td>79.61</td>
<td>2.65</td>
</tr>
<tr>
<td>$\gamma_3$</td>
<td>81.00</td>
<td>32.90</td>
</tr>
<tr>
<td>$\gamma_4$</td>
<td>160.61</td>
<td>0.64</td>
</tr>
<tr>
<td>$\gamma_5$</td>
<td>223.24</td>
<td>0.45</td>
</tr>
<tr>
<td>$\gamma_6$</td>
<td>276.40</td>
<td>7.16</td>
</tr>
<tr>
<td>$\gamma_7$</td>
<td>302.85</td>
<td>18.34</td>
</tr>
<tr>
<td>$\gamma_8$</td>
<td>356.01</td>
<td>62.05</td>
</tr>
<tr>
<td>$\gamma_9$</td>
<td>383.85</td>
<td>8.94</td>
</tr>
</tbody>
</table>

Black's\cite{42} work suggests that the dominant production pathway for barium-133 is through neutron activation of the barium-132 impurity isotope, though it is noted that some of the barium-133 inventory could be derived from unknown fission products, which are not included in the model. Barium-133 is an isotope that features in White's analysis of the fission products produced from 0.1 ppm uranium impurity in a 'typical' Magnox reactor over an operational lifetime\cite{44}, and so this is a distinct possibility.

Caesium-134, $^{134}$Cs: This isotope of caesium is one of the caesium radioisotopes associated with irradiated graphite waste. It always decays by beta particle and multiple gamma ray emissions, with a half life of 2.0652 years\cite{45}, and becomes a stable atom of
barium-134. The highest energy beta emission, with a probability of 70.17% occurrence, has a maximum energy of 658.1 keV which is approximately 4 times that of $^{14}\text{C}$, yet more than a factor of 3 less energetic than the beta emission from $^{90}\text{Y}$. Twelve different gamma rays appear in the decay scheme, seen in Figure 136, with the most probable 604.721 keV emission occurring 97.62% of radioactive decays.

\[
\begin{align*}
^{134}\text{Cs} \ (\tau_{1/2} \ 2.0652\text{y}) & \quad 27.27\% \beta^- \ (88.8 \text{ keV}) \\
2.50\% \beta^- \ (415.4 \text{ keV}) & \quad 70.17\% \beta^- \ (658.1 \text{ keV}) \\
\gamma_1 & \quad \gamma_2 \quad \gamma_3 \quad \gamma_4 \quad \gamma_5 \\
\gamma_6 \quad \gamma_7 \quad \gamma_8 \quad \gamma_9 \quad \gamma_{10} \quad \gamma_{11} \quad \gamma_{12} \\
134\text{Ba} \ (\text{stable})
\end{align*}
\]

*Figure 136: The Decay Scheme for Radioactive Isotope Caesium-134, data from NuDat 2.6[45]*

<table>
<thead>
<tr>
<th>Gamma Emission</th>
<th>Energy (keV)</th>
<th>Intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_1$</td>
<td>232.60</td>
<td>$5 \times 10^{-3}$</td>
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<tr>
<td>$\gamma_2$</td>
<td>242.74</td>
<td>0.03</td>
</tr>
<tr>
<td>$\gamma_3$</td>
<td>326.59</td>
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<tr>
<td>$\gamma_4$</td>
<td>475.37</td>
<td>1.48</td>
</tr>
<tr>
<td>$\gamma_5$</td>
<td>563.25</td>
<td>8.34</td>
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<td>$\gamma_6$</td>
<td>569.33</td>
<td>15.37</td>
</tr>
<tr>
<td>$\gamma_7$</td>
<td>604.72</td>
<td>97.62</td>
</tr>
<tr>
<td>$\gamma_8$</td>
<td>795.86</td>
<td>85.46</td>
</tr>
<tr>
<td>$\gamma_9$</td>
<td>801.95</td>
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</tr>
<tr>
<td>$\gamma_{10}$</td>
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</tr>
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<td>$\gamma_{11}$</td>
<td>1167.97</td>
<td>1.79</td>
</tr>
<tr>
<td>$\gamma_{12}$</td>
<td>1365.19</td>
<td>3.02</td>
</tr>
</tbody>
</table>

Caesium-134 is predominantly produced from caesium and barium impurities in a reactor environment[42], with a potential contribution from fission products[44], and is an isotope of concern for irradiated graphite waste because of the noticeable activities
predicted to be in the final inventory\textsuperscript{44} and the ease with which caesium can move through the environment due to its chemical nature.

\textit{Caesium-137, }$^{137}$\textit{Cs:} Caesium-137 is the other caesium radioisotope of note found in irradiated graphite waste, with three more neutrons in its nucleus than $^{134}$Cs. Similarly to $^{90}$Sr and $^{90}$Y, $^{137}$Cs is not the only isotope in its immediate decay chain to command concern as a radiological hazard. Approximately 5.3\% of occurrences, $^{137}$Cs will decay by emission of a high energy beta particle of maximum energy 1175.63 keV. However, this isotope more often decays by a lower energy beta particle emission, with a half life of 30.08 years and maximum energy 513.97 keV, to a metastable form of barium-137. This metastable isotope, designated $^{137m}$Ba, has a half life of just 2.552 minutes before it undergoes an internal transition and decays by a characteristic gamma ray emission of 661.66 keV to the ground state of barium-137. This is seen schematically in Figure 137.

\textbf{Figure 137: The Decay Scheme for Radioactive Isotope Caesium-137, data from NuDat 2.6}\textsuperscript{45}

It is thought that caesium-137 in irradiated graphite is predominantly sourced from fission of uranium\textsuperscript{42, 53} or thorium\textsuperscript{53}, and features strongly in White's\textsuperscript{44} analysis of the fission products resulting from irradiation of 0.1 ppm uranium impurity in the unirradiated graphite, as the second highest activity resultant radioisotope.

\textit{Europium-152, -154 and -155, }$^{152,154,155}$\textit{Eu:} The isotopes europium-152, -154 and -155 will be discussed together, as the final relative activities of each are intertwined somewhat. The radioactive half lives of these are 13.517, 8.601 and 4.753 years respectively\textsuperscript{45}, and they each have complex decay schemes with multiple beta particles and gamma rays of varying energies. The most hazardous beta particles expected to arise
occur during 10% of the decays of $^{154}$Eu and have a maximum energy of 1845.7 keV\[43\], exposure to which could inflict a significant radiological dose. In relative terms, the radioactive emissions from $^{154}$Eu are somewhat less energetic than those of the other isotopes of europium, with the highest energy beta particle carrying energy of 252.7 keV and the highest energy gamma ray emission being 105.3 keV.

Black\[42\] finds that there are a variety of production pathways for the radioactive europium isotopes found in irradiated graphite, predominantly through activation of europium and samarium impurity isotopes. Nightingale\[9\] notes that the concentrations of europium and samarium in purified graphites is found to be approximately 1% of that in typical unpurified graphites, demonstrating the value of this purification process to graphite for nuclear application. Black also finds that the final inventory and relative ratio of each europium isotope is flux dependent, as is demonstrated for $^{154}$Eu in Figure 138, which is postulated by Black to be because of precursor burnup early in the reactor lifetime; the relatively high cross section\[40\] and ‘short’ half life of 8.601 years means that a good proportion of the $^{154}$Eu may have been produced early in the reactor operation, followed by radioactive decay\[42\] or potentially further activation by neutron absorption to radioisotopes such as $^{155}$Eu over the following years. Black further notes that this effect could lead to high flux reactors having a smaller $^{154}$Eu inventory\[42\], which is supported by an IAEA technical document which states that $^{152}$Eu is mostly found at the outer regions of a graphite moderated reactor because of burnup in regions of higher flux\[41\].

![Figure 138: Comparison of Production Rate of Radionuclides with Flux\[42\]](image-url)
**Americium-241, $^{241}\text{Am}$**: Americium is one of the many high atomic mass alpha emitters that are thought to be in graphite\textsuperscript{[41]}, in low levels, which is thought to arise from either fission of the natural uranium impurity found in graphite\textsuperscript{[44]}, from fuel failures during operation or fission of traces of uranium carried into the reactor circuit on fuel element surfaces\textsuperscript{[41]}.

This heavy isotope has a half life of 432.6 years and decays exclusively by emission of an high energy alpha particle of typical order 5 MeV to the long-lived $^{237}\text{Np}$, followed by release of an array of potential electrons, X-rays and gamma rays. The most frequent gamma emission is at 59.54 keV energy with an occurrence of 35.9\%\textsuperscript{[45]}, which is often utilised for calibration of gamma spectrometers and to determine the activity of $^{241}\text{Am}$ in a sample\textsuperscript{[151]}. 
Appendix D – Mass Balance Test Data

Table B1: 4d.p. Mass Balance Test Results

<table>
<thead>
<tr>
<th>Vial</th>
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<th>3</th>
<th>4</th>
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<th>6</th>
<th>7</th>
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</table>
Appendix E – Specific Activity of Carbon-14

If

\[ 1 \text{ mol } ^{12}\text{C} = 12\text{g} = 6.022 \times 10^{23} \text{ atoms} = N_A \]

and

\[ 1 \text{ mol } ^{14}\text{C} = 14\text{g} = 6.022 \times 10^{23} \text{ atoms} = N_A \]

then

\[ 12\text{g} \ ^{14}\text{C} = \frac{12}{14} \times N_A = 5.162 \times 10^{23} \text{ atoms} = N_{12\text{g} \ ^{14}\text{C}} \]

where \( N_A \) is Avogadro’s number.

Using the radioactive decay equations,

\[ \lambda = \frac{\ln(2)}{T_{1/2}} \quad \text{(E1)} \]

\[ A = \lambda N \quad \text{(E2)} \]

where \( \lambda \) is the decay constant, \( T_{1/2} \) is half life, \( A \) is activity and \( N \) is number of particles.

If

\[ T_{1/2 \ ^{14}\text{C}} = 5730 \text{ y} = 1.807 \times 10^{11} \text{ s} \]

Then using Equation (E1) it follows that,

\[ \lambda_{^{14}\text{C}} = \frac{\ln(2)}{T_{1/2 \ ^{14}\text{C}}} = 3.836 \times 10^{-12} \text{ s}^{-1} \]

And therefore using Equation (E2),

\[ A_{12\text{g} \ ^{14}\text{C}} = \lambda_{^{14}\text{C}} \times N_{12\text{g} \ ^{14}\text{C}} = 1.98 \times 10^{12} \text{ Bq} \]
This can be expressed as Bq/g of $^{14}$C, such that

$$\text{Bq/g}_{^{14}\text{C}} = \frac{A_{^{12}\text{g}^{14}\text{C}}}{12} = 1.65 \times 10^{11} \text{ Bq/g} = 165 \text{ GBq/g}$$

This calculated value correlates with the specific activity for $^{14}$C of 4460 mCi/g stated in a safety sheet from Michigan State University$^{(6)}$. 