Carbon-14 Release from Oldbury Graphite

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Abstract

The release and migration of carbon-14 has been identified as an important issue for the geological disposal of higher activity radioactive waste in the UK. Carbon-14 has a sufficiently long half-life for its release in gaseous form to be of relevance in the post-closure safety case. The majority of the carbon-14 in the UK radioactive waste inventory is present in irradiated graphite. Therefore an understanding of the rate and speciation of releases of carbon-14 from irradiated graphite under disposal conditions is of importance to the post-closure safety case for a geological disposal facility (GDF).

This report describes results of a study to measure gaseous carbon-14 releases from irradiated Magnox graphite from Oldbury Reactor 2. Single segments of graphite were immersed in a high-pH solution under anoxic conditions, at ambient temperature to simulate disposal conditions in a GDF (referred to as baseline conditions). In addition, the effects of near-neutral pH, oxic conditions, higher temperature and reduced particle size (powdered) graphite on the rates and speciation of gaseous releases have been investigated in variant experiments; a separate one-year experiment was performed to measure radionuclide releases to solution under baseline conditions.

Under baseline conditions the predominant releases of carbon-14 were to the solution phase, with about 0.07% of the carbon-14 inventory being released to solution in one year. About 1% of the carbon-14 release was to the gas phase as a mixture of $^{14}$C-containing hydrocarbon/organic species and $^{14}$CO at a ratio of approximately 2:1. The rates of release decreased with time but detectable quantities of carbon-14 were found in all gas-phase samples, including that for the final cumulative sampling period which ran from three to twelve months.

A revised model for carbon-14 release from graphite has been proposed based on the experimental data.
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Building 587  
Curie Avenue  
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Didcot  
Oxfordshire OX11 0RH  
email rwmfeedback@nda.gov.uk
Executive Summary

The release and migration of carbon-14 has been identified as an important issue for the geological disposal of higher activity radioactive waste in the UK. Carbon-14 has a sufficiently long half-life for its release in gaseous form to be of relevance in the post-closure safety case. There is potential for some gaseous species containing carbon-14 to migrate to the biosphere with bulk gas or dissolved in groundwater. The majority of the carbon-14 in the UK radioactive waste inventory is derived from irradiated graphite. This graphite has the potential to be a source of gases containing carbon-14 if it underwent degradation or reaction in a repository environment. Recent scoping calculations have shown that, if it is assumed that the carbon-14 in graphite reacts to form carbon-14-bearing methane ($^{14}$CH₄) and that this migrates as a free gas to the biosphere, there could be a significant impact on the calculated risk from the gas pathway. Therefore an understanding of the rates and chemical form of carbon-14 release from irradiated graphite under disposal conditions is of importance to the post-closure safety case for a geological disposal facility (GDF).

In previous studies, gaseous releases of carbon-14 were measured from WAGR and BEP0 graphite during leaching in strongly alkaline solutions under oxic conditions. This study builds on the previous work with the aim of improving understanding of the longer-term release rate of gaseous carbon-14 from irradiated Magnox graphite using a sample from Oldbury power station. The main objectives of the programme were to:

1. determine the speciation and rate of gaseous release of carbon-14 from irradiated Oldbury graphite when in contact with alkaline solution under anoxic conditions and compare this to the release under oxic conditions;
2. scope the effects of changes in pH, particle size and temperature on carbon-14 speciation and rate of release under anoxic conditions; and
3. provide data and understanding for a possible update to the treatment of the releases of carbon-14 from irradiated graphite in assessment models.

In addition, tests were undertaken to build confidence in the analytical methodology.

Eight segments (each about 30g in weight) of irradiated Magnox graphite were obtained for use in this study. The segments had been cut from a cylindrical spacer piece obtained from an installed set that was removed from Oldbury Reactor 2 in 2005, some 38 years after installation. Powdered sub-samples of the outer and inner (i.e. cut) surfaces of two of the segments were analysed for their radionuclide content to provide an estimate of the radionuclide inventory in each experiment.

Seven leaching experiments were performed, each using a single segment of irradiated graphite. Six experiments were designed to measure gaseous releases (with solution analysis on termination in some cases) and one to measure solution phase releases (only) with time for up to about one year after immersing the graphite in solution. Duplicate gas-release experiments and the solution release experiment were performed under anoxic, pH 13 conditions (in 0.1mol dm$^{-1}$ NaOH solution) at ambient temperature (‘baseline’ conditions) to simulate the post-closure conditions for disposal of graphite wastes in a cement-based GDF. The effects of oxic conditions, near-neutral pH, higher temperature (50°C) and reduced particle size (powdered sample) on the rates and speciation of gas-phase releases were investigated in variant experiments.

The speciation of gaseous carbon-releases was investigated using sampling apparatus capable of separating carbon dioxide, carbon monoxide and volatile hydrocarbons / organic compounds. Although the main focus of this programme was carbon-14 release, the speciation of tritium released in the gas phase was also examined in one baseline experiment, with separation of HTO, HT and tritiated hydrocarbons.

The main conclusions from this work are as follows.

- Under baseline conditions (anoxic, under pH 13 solution, ambient temperature), the predominant carbon-14 release was to the solution phase, with about 0.07% of the carbon-14 inventory being released into solution in one year. About 1% of the released carbon-14 was released to the gas phase.
In all five of the gas-phase release experiments under high-pH conditions, broadly similar levels of total carbon-14 release were observed to the gas phase from each of the five graphite segments on comparable timescales.

In all seven experiments, for both gaseous and solution-phase release, an initial phase of rapid carbon-14 release was observed, which was followed (beyond about 28 days) by a longer-term phase of slower release.

Under baseline conditions (anoxic, under pH 13 solution, ambient temperature, single piece graphite sample):
- an initial rapid release of \( \sim 3 \text{ Bq} \) of carbon-14 to the gas phase was observed in the first week, which represents \( \sim 10^{-6} \) of the carbon-14 in the graphite;
- the rates of release decreased with time but detectable quantities of carbon-14 were found in all gas samples. For the final cumulative sampling period, which ran from three to twelve months, a release of \( \sim 2 \text{ Bq} \) was measured;
- the gaseous carbon-14 was predominantly in the form of hydrocarbons and other volatile organic compounds and CO. The ratio of carbon-14 in hydrocarbons / organic compounds to CO was approximately 2:1. Less than 2% of the gas-phase release was in the form of \( ^{14}\text{CO}_2 \).

When the graphite was powdered, the rapidly releasable fraction of carbon-14 to the gas phase was found to be lower (by a factor of \( \sim 2 \)) than from leaching intact segments, whereas the total solution phase release after 91 days was higher (by about 65%). This contrasting behaviour is most likely due to a loss of loosely-bound volatile carbon-14 species during the powdering process and an overall increase in release rate, primarily to solution, due to the increased surface area of the sample.

At pH 7, levels of \( ^{14}\text{CO} \) and carbon-14-bearing volatile organic compounds were similar to the baseline values. However, the overall gaseous carbon-14 release was at least an order of magnitude higher than the baseline, due to significantly more \( ^{14}\text{CO}_2 \) being released as gas from solution rather than being retained as dissolved carbonate.

There is some evidence that increased temperature increases the release rate of carbon-14, but this observation is from a limited set of data.

Under oxic conditions the total carbon-14 gaseous release rate was similar to the baseline condition values but the ratio of organic compounds to CO was closer to 1:1. The rates of carbon-14 release from Oldbury graphite were significantly lower than those measured previously from irradiated BEP0 graphite under oxic conditions, but the ratio of hydrocarbon / organic species to CO was higher.

The differences between the fractional releases of carbon-14 from Oldbury and BEP0 graphites are likely to be due to differences between the original graphites, their irradiation histories, operating temperatures and coolant gases. The results of this study do not allow us to determine whether any one of these differences is a dominant effect although a wider comparison of irradiated graphites might.

Based on these experimental observations, an updated conceptual model for carbon-14 release from graphite has been proposed and a mathematical model representation formulated. The data obtained in this study for leaching of Oldbury Magnox graphite under anoxic, high-pH conditions have been fitted to illustrate how the model may be parameterised.

Gaseous tritium releases were measured in one of the baseline condition experiments. A very rapid initial release of predominantly HT and organic-bound tritium was observed which represented \( \sim 0.1\% \) of the tritium inventory in the graphite. After one week the rate decreased rapidly, and the subsequent gaseous release was primarily in the form of HTO (released from the solution phase by evaporation).

Gamma spectrometry of the leachate solutions showed cobalt-60 and caesium-137 to be the other significant isotopes leached from the Oldbury graphite. Cobalt-60, which appears to be relatively homogeneously distributed through the graphite, was found to be significantly more readily solubilised than carbon-14; about 5-6% of the cobalt-60 inventory was released in one year and its
release was still continuing at this point. The leaching behaviour of caesium-137 is more typical of that of a surface contaminant; a high proportion of the caesium-137 was released into solution within the first two days of leaching. However, the solution concentration was observed to decrease steadily thereafter and had dropped by about 25% after one year. A possible explanation for this behaviour is that dissolved caesium-137 (originally concentrated on the external surfaces) had diffused into the porosity of the graphite where it may have been sorbed to pore surfaces.
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1. Introduction

The release and migration of gaseous carbon-14-containing species has been identified as a key issue for geological disposal of intermediate-level radioactive wastes in the UK. There are 9,987 TBq of carbon-14 in the 2010 UK baseline inventory [1]. It has been calculated that if carbon-14 is released to the biosphere in the form of methane, then risk guidance levels may be exceeded if the release rate is greater than ~6 x 10^4 TBq/year. The majority of the carbon-14 in the UK radioactive waste inventory is present in irradiated graphite and this graphite has the potential to be a source of gases containing carbon-14 if it undergoes degradation or reaction in a repository environment. Recent scoping calculations have shown that, if it is assumed that the carbon-14 in graphite reacts to form carbon-14-bearing methane (14CH₄) and that this migrates as a free gas to the biosphere, there could be a significant impact on the calculated risk from the gas pathway [2]. Therefore an understanding of the release of carbon-14 from irradiated graphite under disposal conditions is of importance to the post-closure safety case for a geological disposal facility (GDF).

The current baseline for the disposal of irradiated graphite wastes envisages packaging in waste containers that will be emplaced in disposal vaults, which will be backfilled with a cement-based material designed to maintain a high-pH environment in the vaults following their resaturation with groundwater. Conditions in a GDF are expected to become anoxic in the post-closure period as a result of the consumption of available oxygen by metal corrosion processes.

In previous experimental work, small releases of gaseous carbon-14 were measured from samples of irradiated graphites (from the Windscale Advanced Gas-cooled Reactor (WAGR)[3, 4] and the British Experimental Pile 0 reactor (BEP0) [5, 6]) on immersion in alkaline solutions. The majority of the carbon-14 remained in the graphite although there was also some release of carbon-14 in a form that was retained in the liquid phase (possibly as the aqueous species 14CO₃²⁻ resulting from the release of 14CO₂). In the measurements on BEP0 graphite, gaseous 13CO and 14CO₂ were not distinguished, but the fraction of CO₂ in the gas phases was assumed to be negligible, due to its high solubility in alkaline solution. All of these studies were performed under oxic conditions and the impact of anoxic conditions on the speciation of released carbon-14 was not known.

This report describes measurements of carbon-14 releases from samples of irradiated graphite from the Oldbury Magnox Reactor 2 during leaching. The main objectives of the programme were to:

1. determine the speciation and rate of gaseous release of carbon-14 from irradiated Oldbury graphite when in contact with alkaline solution under anoxic conditions and compare this to the release under oxic conditions;
2. scoping the effects of changes in pH, particle size and temperature on carbon-14 speciation and rate of release under anoxic conditions; and
3. provide data and understanding for a possible update to the treatment of the releases of carbon-14 from irradiated graphite in assessment models.

In addition, tests were undertaken to build confidence in the analytical methodology.

Seven leaching experiments were performed on samples of irradiated graphite, six measuring gaseous releases and one measuring releases to solution with time. The solution release experiment was performed independently from the gas release experiments, to avoid the possibility of disturbing the conditions in the reaction vessels in the gas-sampling experiments. Details of the seven experiments are summarised in Table 1. The two baseline gas release experiments and the solution experiment were run for 12 months to investigate the longer-term release, under conditions most relevant to disposal in a cement-based GDF. The conditions chosen for the baseline experiments were to submerge a single piece of graphite in a pH 13 solution at ambient temperature, with anoxic conditions maintained by a nitrogen atmosphere and the presence of iron metal. The other four experiments were run for 3 months only, changing one of the conditions from the baseline. The aim of the three-month experiments was to give an indication of which conditions are most important in controlling release rates.
Gaseous tritium measurements were also made for one of the baseline experiments under anoxic alkaline conditions at room temperature (Run 2).

A tool commonly used in gas generation calculations for UK waste is SMOGG (Simplified model of gas generation) [7]. SMOGG models the generation of bulk and radioactive gases from waste packages or groups of waste packages. It is predominantly used to model gas generation during GDF operations and for many thousands of years post-closure. SMOGG includes a model for the generation of carbon-14 from irradiated graphite, which was developed on the basis of only limited data on gaseous carbon-14 releases from the sources available at the time. The experimental study described in this report was designed to provide additional data and understanding of gaseous carbon-14 releases from irradiated Magnox graphite, to reduce the uncertainties in the treatment of carbon-14 gas generation in SMOGG. As a result of this study and other recent work [8], an updated conceptual model for carbon-14 releases from irradiated graphite has been proposed, a revised mathematical model has been formulated and the data obtained for Oldbury Magnox graphite have been fitted to illustrate how the proposed model may be parameterised.

Table 1. Summary of experimental conditions for graphite leaching.

<table>
<thead>
<tr>
<th>Code</th>
<th>Name</th>
<th>Solution pH</th>
<th>Atmosphere</th>
<th>Temperature</th>
<th>Graphite form</th>
<th>Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1</td>
<td>Oxic</td>
<td>13</td>
<td>Air</td>
<td>Ambient</td>
<td>Intact</td>
<td>3 months</td>
</tr>
<tr>
<td>Run 2</td>
<td>Baseline 1</td>
<td>13</td>
<td>Nitrogen</td>
<td>Ambient</td>
<td>Intact</td>
<td>12 months</td>
</tr>
<tr>
<td>Run 3</td>
<td>Baseline 2</td>
<td>13</td>
<td>Nitrogen</td>
<td>Ambient</td>
<td>Intact</td>
<td>12 months</td>
</tr>
<tr>
<td>Run 3b</td>
<td>Solution sampling</td>
<td>13</td>
<td>Nitrogen</td>
<td>Ambient</td>
<td>Intact</td>
<td>12 months</td>
</tr>
<tr>
<td>Run 4</td>
<td>Neutral pH</td>
<td>7</td>
<td>Nitrogen</td>
<td>Ambient</td>
<td>Intact</td>
<td>3 months</td>
</tr>
<tr>
<td>Run 5</td>
<td>Powdered graphite</td>
<td>13</td>
<td>Nitrogen</td>
<td>Ambient</td>
<td>Powder</td>
<td>3 months</td>
</tr>
<tr>
<td>Run 6</td>
<td>Higher temperature</td>
<td>13</td>
<td>Nitrogen</td>
<td>50 °C</td>
<td>Intact</td>
<td>3 months</td>
</tr>
</tbody>
</table>

This report is structured as follows:

- Section 2 contains details of the preparation and characterisation of the Oldbury graphite samples;
- Section 3 contains details of the experimental apparatus and the analytical techniques used in this study;
- in Section 4 the experimental conditions for the measurements of radionuclide release from Oldbury graphite are described;
- the experimental results are presented in Section 5;
- the results are compared and discussed and a revised model for the release of carbon-14 from irradiated graphite is proposed in Section 6;
- the conclusions are summarised in Section 7;
- tests to measure the recovery efficiency of the analytical techniques used for carbon-14 analysis were also performed and are described in Appendix 1 and Appendix 2 for gas-phase and solution-phase methods respectively.
2. Preparation and Assay of Graphite Samples

2.1 Description of graphite

Eight pieces of irradiated graphite from one of the Magnox reactors at Oldbury were made available for this study. The graphite samples were cut from a cylindrical spacer piece from an installed set removed from Reactor 2 at Oldbury in 2005. The set was installed in Channel S77 of the reactor at the time of its construction and remained in place for approximately 38 years. The spacer piece was a hollow cylinder weighing about 300g, approximately 90mm in length and 70mm in diameter with a central hole approximately 10mm in diameter.

The cylindrical sample (code 635) was first sliced into three at right-angles to its axis and then each slice was quartered as shown in Figure 1. The segments were given codes of the form: 635-BLOCK-x-y-z, where: x is the block number, y is the slice number and z is the quadrant number. Sample masses are given in Table 2. The cylindrical block had a radius of approximately 37mm and each slice a thickness of about 30mm. The size and physical appearance of a typical segment are shown in Figure 2.

Table 2. Masses of graphite samples as received.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Sample mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>635-BLOCK-1-2-1</td>
<td>26.0412</td>
</tr>
<tr>
<td>635-BLOCK-1-2-2</td>
<td>28.9431</td>
</tr>
<tr>
<td>635-BLOCK-1-2-3</td>
<td>32.4467</td>
</tr>
<tr>
<td>635-BLOCK-1-2-4</td>
<td>32.9710</td>
</tr>
<tr>
<td>635-BLOCK-1-3-1</td>
<td>32.4950</td>
</tr>
<tr>
<td>635-BLOCK-1-3-2</td>
<td>30.0996</td>
</tr>
<tr>
<td>635-BLOCK-1-3-3</td>
<td>32.0017</td>
</tr>
<tr>
<td>635-BLOCK-1-3-4</td>
<td>31.2368</td>
</tr>
</tbody>
</table>

Based on measurements of the geometric volume of the graphite samples and the masses in Table 2, the bulk density of the graphite was estimated to be 0.9 g cm$^{-3}$. The density of a pure graphite crystal is ~2.3 g cm$^{-3}$, giving an estimated porosity of 0.6 for the irradiated Oldbury graphite. This compares a typical density for virgin graphite of 1.75 g cm$^{-3}$ [9] and so a porosity of ~0.3.

2.2 Graphite Analysis

Samples of graphite powder (masses 3.6g to 4.6g) were taken from quadrants 635-BLOCK-1-2-3 and 635-BLOCK-1-3-1, one from the outer surface and one from the side in each case, as
illustrated in Figure 1. Samples of powder were removed by hand using a file and mixed by shaking.

Figure 1. Schematic diagram of graphite sample locations.

Figure 2. Graphite quadrant 635-BLOCK-1-2-2.

2.2.1 Carbon-14 and tritium analysis

Carbon-14 and tritium analyses of the graphite were carried out by Inutec Ltd, Winfrith. Three sub-samples, of mass 1g to 2g were taken from each of the samples of graphite powder. The sub-samples were combusted in a flowing oxygen-rich atmosphere at 950°C in the presence of a copper catalyst to convert carbon and hydrogen species into carbon dioxide and water respectively. The combustion gas flow was directed through a series of bubblers - two acidic (0.1 mol dm⁻³ HNO₃ solution) and two alkaline (methoxypropylamine, trade name CarboSorb®) to selectively trap H₂O and CO₂ respectively. Combustion was continued until all material was combusted and verification weighings were made to confirm completion of combustion.
The resulting bubbler solutions were assayed for activity by liquid scintillation counting on a Hidex 300 SL instrument. A pseudocumene-based scintillation cocktail (trade name Hi-Safe®) was used for tritium and a trimethylbenzene-based scintillant (trade name Permafluor®) for carbon-14. The analytical yield was assessed by combustion of a known quantity of certified, $[^3\text{H}]$glucose and $[^14\text{C}]$glucose standards, traceable to national laboratory standards, in the presence of 1 g graphite, to simulate sample loading. Before and after the analysis of the samples, two blank graphite samples were combusted and analysed to ensure no cross-over and to provide background measurements. Separate quality control samples (spiked graphite) were run to test the performance of the method. These samples showed that the method was bias free (method performance was 100%) with a precision of ±2%.

2.2.2 Gamma spectrometry

Gamma spectrometry of the graphite was carried out by AMEC Analytical Services, Birchwood Park. Counting vials were filled with graphite powder, up to a calibration line, to produce a standard counting geometry. High-resolution gamma spectrometry was carried out using Ortec high-purity germanium detectors, coupled to computerised multi-channel analysers. Ortec’s GammaVision software incorporating peak search and peak shape functions and a validated radionuclide library was used for peak identification and quantification. System calibration was undertaken for the standardised geometry using a nationally traceable “mixed gamma” reference solution, in the energy range 60 keV - 1836 keV.

2.2.3 Results – radionuclide content of graphite

The complete set of results from the carbon-14 and tritium analyses is given in Table 3; the mean values have been calculated for the three sub-samples. The results show good consistency in the triplicate sub-samples. Table 4 gives the mean carbon-14 and tritium results, along with activities for all gamma-emitters above the limit of detection. For carbon-14 and tritium, the uncertainty on the mean is given by the variance on the triplicate results. Activities for gamma-emitters are from a single measurement and the errors given are the two sigma (2σ) uncertainties for the analysis method. It can be seen that the activities of tritium, carbon-14 and cobalt-60 are relatively uniform across the four sampling locations, although carbon-14 activities appear to be slightly higher (by about 25%) at the outer surfaces of the cylindrical spacer piece compared to the cut ‘side’ surfaces.

Table 5 shows the mean specific activities for each radionuclide in the graphite block. These values were used to calculate the radionuclide inventories in the samples used for the leaching experiments. It is notable from Table 3 and Table 4 that isotopes derived from activation of the graphite and its trace impurities, such as carbon-14 and cobalt-60, appear to have a more homogenous distribution than isotopes derived from contamination such as americium-241 and caesium-137. The latter are not evenly distributed and so there is a high degree of uncertainty in the inventory of these isotopes in the leaching experiments.
Table 3. Carbon-14 and tritium analysis of graphite sub-samples. Uncertainty on individual measurements given as $2\sigma$. Overall uncertainty on mean values $2\sigma$. Reference date is 19 December 2011.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Sub-sample no.</th>
<th>Tritium (kBq g$^{-1}$)</th>
<th>Carbon-14 (kBq g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>635 Block 1-2-3 Side</td>
<td>1</td>
<td>379 ± 9</td>
<td>71 ± 2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>344 ± 8</td>
<td>72 ± 2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>352 ± 8</td>
<td>77 ± 2</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>360 ± 50</td>
<td>73 ± 9</td>
</tr>
<tr>
<td>635 Block 1-2-3 Outer</td>
<td>1</td>
<td>406 ± 13</td>
<td>90 ± 3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>366 ± 11</td>
<td>96 ± 3</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>341 ± 11</td>
<td>97 ± 3</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>370 ± 80</td>
<td>94 ± 10</td>
</tr>
<tr>
<td>635 Block 1-3-1 Side</td>
<td>1</td>
<td>361 ± 8</td>
<td>76 ± 2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>335 ± 7</td>
<td>74 ± 2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>331 ± 7</td>
<td>78 ± 2</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>340 ± 40</td>
<td>76 ± 5</td>
</tr>
<tr>
<td>635 Block 1-3-1 Outer</td>
<td>1</td>
<td>419 ± 9</td>
<td>91 ± 2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>369 ± 8</td>
<td>94 ± 2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>379 ± 8</td>
<td>97 ± 2</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>390 ± 70</td>
<td>94 ± 7</td>
</tr>
</tbody>
</table>

Table 4. Specific activities of measured radionuclides in four samples taken from the irradiated graphite block 635.

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Specific activity (Bq g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1-2-3 Side</td>
</tr>
<tr>
<td>Am-241</td>
<td>26 ± 17</td>
</tr>
<tr>
<td>Ba-133</td>
<td>652 ± 31</td>
</tr>
<tr>
<td>Co-60</td>
<td>$8.5 \times 10^4$ ± $0.3 \times 10^4$</td>
</tr>
<tr>
<td>Cs-134</td>
<td>495 ± 25</td>
</tr>
<tr>
<td>Cs-137</td>
<td>6310 ± 250</td>
</tr>
<tr>
<td>Eu-154</td>
<td>192 ± 34</td>
</tr>
<tr>
<td>Eu-155</td>
<td>127 ± 29</td>
</tr>
<tr>
<td>H-3$^\dagger$</td>
<td>$3.6 \times 10^5$ ± $0.5 \times 10^5$</td>
</tr>
<tr>
<td>C-14$^\dagger$</td>
<td>$7.3 \times 10^4$ ± $0.9 \times 10^4$</td>
</tr>
</tbody>
</table>

$^\dagger$ Mean of results on three sub-samples given in Table 3.
Table 5. Mean specific activities of measured radionuclides in irradiated graphite block 635 based on the four results given in Table 4; the uncertainties are one standard deviation of the calculated mean.

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Mean specific activity (Bq g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Am-241</td>
<td>70 ± 50</td>
</tr>
<tr>
<td>Ba-133</td>
<td>646 ± 22</td>
</tr>
<tr>
<td>Co-60</td>
<td>8.3 x 10(^4) ± 0.3 x 10(^4)</td>
</tr>
<tr>
<td>Cs-134</td>
<td>541 ± 205</td>
</tr>
<tr>
<td>Cs-137</td>
<td>6.9 x 10(^3) ± 4.5 x 10(^3)</td>
</tr>
<tr>
<td>Eu-154</td>
<td>216 ± 51</td>
</tr>
<tr>
<td>Eu-155</td>
<td>136 ± 28</td>
</tr>
<tr>
<td>H-3</td>
<td>3.7 x 10(^5) ± 0.2 x 10(^5)</td>
</tr>
<tr>
<td>C-14</td>
<td>8.4 x 10(^4) ± 1.1 x 10(^5)</td>
</tr>
</tbody>
</table>
3. Experimental Methodology

A set of experiments was carried out to measure releases of radionuclides from irradiated graphite immersed in aqueous solutions. The main focus of the programme was the measurement of gaseous carbon-14 releases to the gas phase, but tritium releases to the gas phase were also measured in one experiment and the solution concentrations of carbon-14, tritium, and major gamma-emitting isotopes were also determined under the baseline conditions (anoxic, pH 13, ambient temperature).

In this section the methods used for the measurement of carbon-14 and tritium releases to the gas phase and the determination of radionuclide concentrations in graphite leachates are described.

A number of tests were performed to determine the efficiency of the methods used for selective carbon-14 capture, separation and analysis. These tests are described in Appendix 1 and Appendix 2 for gas-phase and solution-phase analysis methods respectively.

3.1 Measurement of gaseous releases

3.1.1 Overview

A schematic diagram of the apparatus used for the gaseous release experiments is shown in Figure 3. The main components are:

- scrubber units, comprising of soda lime and silica gel columns to remove CO\textsubscript{2} and H\textsubscript{2}O from the incoming gas stream (either nitrogen or air);
- a leaching vessel in which the graphite is leached;
- three gas sampling units in series, for the selective capture of volatile releases of carbon-14 and tritium.

The final sampling unit also contained a pump to draw gas through the leaching vessel and then through the three sampling units.

![Figure 3. Schematic diagram of experimental apparatus.](image)

The inlet gas to the leaching vessel was either nitrogen, for the anoxic experiments, or air, for the oxic experiment. In the case of anoxic experiments, an additional input of air was required after the leaching vessel to provide oxygen for catalytic combustion in the last two of the three sampling
units. These input gases were first drawn through soda lime columns to remove CO$_2$ and then silica gel columns to remove water, thereby also ensuring that the background levels of carbon-14 and tritium (present as $^{14}$CO$_2$ and HTO) were minimised.

The graphite was immersed in 250 cm$^3$ of either 0.1 mol dm$^{-3}$ NaOH solution (pH 13 experiments) or 0.1 mol dm$^{-3}$ NaCl solution (pH 7 experiment). During periods of gas-phase sampling, the inlet gas was drawn through the leaching vessel (Figure 4) over the surface of the solution (rather than being bubbled through it, to minimise evaporation) and then through the three gas-sampling units. Details of the design and operation of the gas samplers are given in Section 3.1.2.

![Figure 4. Scrubber unit and reaction vessel.](image)

### 3.1.2 Gas sampling apparatus

The gas samplers were designed and manufactured by Radiocarbon Dating, Lockinge (RCD) Limited and are based on dry-bed absorber systems. Soda lime columns are used for the capture of CO$_2$ and silica gel columns for the capture of H$_2$O. At the first sampling unit $^{14}$CO$_2$ and HTO are collected. The second sampler allows the selective oxidation and capture of $^{14}$CO/HT and then the third the oxidation and capture of carbon-14/tritium-containing hydrocarbon and any volatile organic carbon (VOC) species$^{[1]}$.

The incorporation of the $^{14}$CO$_2$/HTO sampler unit was an addition to the apparatus used in the previous study [5, 6]. In the previous experiment, the graphite sample was immersed in 0.1 mol dm$^{-3}$ NaOH solution and it was assumed that any CO$_2$ released would be retained in the alkaline solution as $^{14}$C-carbonate. Sampling of $^{14}$CO$_2$ in the gas phase was incorporated in these studies to discriminate its release from $^{14}$CO. In addition, this study included a leaching experiment at near-neutral pH, in which a significant proportion of any $^{14}$CO$_2$ released would be expected to partition to the gas phase.

The sequence of columns and their function in the CO$_2$/HTO sampler is shown in Figure 5.

After the CO$_2$/HTO sampler the gas then passed to the CO/HT sampler shown in Figure 6. The first silica gel column was designed for collection of HTO, when the sampler was used as the initial sampling unit. However, when used in series with the CO$_2$/HTO sampler this column is redundant and so is not usually analysed.

$^{[1]}$ The possibility of the oxidation of small volatile organic species other than hydrocarbons (such as formaldehyde) at the CuO furnace has not been investigated in this study. It is thus possible that the ‘CO’ fraction could have a contribution from species other than carbon monoxide.
Figure 5. CO\textsubscript{2}/HTO sampler.

Figure 6. CO/HT sampler.

Figure 7. Hydrocarbon / volatile organic compounds sampler.
The gas was then drawn through the hydrocarbon/volatile organic compounds sampler shown in Figure 7. The first silica gel column was designed for collection of HTO, when the sampler was used as a ‘stand alone’ unit. However, when used in series with the CO/HT sampler this column is redundant and so is not usually analysed.

The sampling units were manufactured to vacuum equipment engineering standards and run at slightly less than atmospheric pressure. Air was drawn through the system by a pump situated near to the outlet port of the hydrocarbon/volatile organic compounds sampler unit. Before the pump, the gas flow rate through the columns was balanced with a ballast gas flow, by means of a valve. This flow control method enabled the pump motor to be operated at a regulated voltage, and hence speed, producing a reliable, steady flow through the instrument over extended exposure times, with the total flow through the pump maintained at around 1 dm$^3$ min$^{-1}$ with only a proportion (~200 cm$^3$ min$^{-1}$) drawn through the catalysts and columns.

The individual columns were designed to be handled as closed units, being supplied with valved, quick-release fittings that self seal on removal from the panel, allowing the columns to be replaced while maintaining the integrity of the system. The columns were removed from the sampling units at the end of each collection period and replaced with fresh columns.

### 3.1.3 Analysis of gas-phase components

After use, columns were returned to RCD for analysis. Absorbed water was extracted from the silica gel by distillation in a vacuum vessel for two hours at 105°C. The distilled water was collected in a double trap system cooled to -78°C with a solid carbon dioxide/acetone mixture. Absorbed CO$_2$ was extracted from the soda lime by acidification. The CO$_2$ gas collected was then reacted with lithium to produce lithium carbide. The carbide was then hydrolysed to produce acetylene, and then converted to benzene by trimerisation on a catalyst. The benzene produced was mixed with a proprietary scintillant (Opti-Fluor). Tritium and carbon-14 activities were determined by liquid scintillation counting (LSC) using a Wallac Quantulus instrument calibrated against standard samples. Counting times of two to three weeks allowed the detection of down to 0.03 to 0.01 Bq of carbon-14 per sample.

### 3.1.4 Test of gas analysis methodology

Appendix 1 gives details of a series of tests designed to measure the efficiency of components of the gas sampling method. These tests made use of the two sampling units used in the previous study before their use in the current study. In summary, the tests results showed:

- the efficiency of the soda lime columns in extracting CO$_2$ from gas is >95%.
- the efficiency of the CuO catalyst column to selectively oxidise CO to CO$_2$ is >90%, with <2% oxidation of CH$_4$; and
- the efficiency of the Pd catalyst in oxidising CH$_4$ to CO$_2$ is > 97%.

Overall, the results give confidence in the RCD techniques for the assessment of the trace quantities of carbon-14 emanating from irradiated graphite on leaching. The least confident result is that for the conversion of CO to CO$_2$ over the CuO catalyst (90% efficiency), which was derived from only one test with a low concentration CO sample. A poorer efficiency of ~60% was measured for old CuO catalyst prior to regeneration, suggesting that there may be some drop in its efficiency with time. However, the results from tests with methane show that there was no significant oxidation of methane over the CuO catalyst but essentially quantitative oxidation at the Pd catalyst. Thus, any CO not oxidised over CuO catalyst would be oxidised over the Pd catalyst and thereby included in the total inventory of gas-phase carbon-14.

### 3.1.5 Background measurements

No measurements of background carbon-14 or tritium concentrations were carried out as part of this set of experiments. However, a background measurement was made previously [3]. In that measurement, air was drawn continuously through the soda lime and silica gel columns of the scrubber unit (removing CO$_2$ and water from the inlet gas, Figure 4) and then through the hydrocarbon/VOC sampler to collect the total backgrounds of carbon-14 and tritium that had passed through the scrubber unit. After two weeks’ continuous operation, background levels were
found to be below the limits of detection of 0.03 Bq and 0.2 Bq per sample for carbon-14 and tritium, respectively.

In this study the longest gas-sampling period was about nine months during which the gas samplers were operated for about eight hours each week, giving a total running time of approximately 320 hours (13 days). This was equivalent to the period over which the background was measured previously. Therefore, in this study, it has been assumed that any contribution from background activity was negligible in terms of the overall release and no background corrections have been made.

3.2 Measurement of releases to solution

In experiments measuring gaseous releases, a sample of the solution was taken only at the end of the experiment, to avoid the possibility of disturbing the conditions in the reaction vessels. However, for the baseline conditions a parallel graphite leaching experiment was set up (Run 3b), in which the solution was sampled at 2 days, 7 days, 28 days, 3 months and 12 months, to coincide with the gas sampling periods.

10 cm$^3$ volumes of solution were taken for analysis. Tritium and carbon-14 and were determined by separation followed by liquid scintillation counting. High resolution gamma spectrometry (HRGS) was used to determine the concentration of gamma-emitting isotopes present. All solution analyses were carried out by AMEC Analytical Services, Birchwood Park. Prior to analysis all solutions were passed through a preconditioned 0.45 µm filter. Preconditioning was carried out by first washing with 10 cm$^3$ of deionised water, followed by 10 cm$^3$ of the sample solution, both discarded to waste.

Carbon-14 and tritium in solution were analysed by taking a known mass of sample and combusting in a two-stage catalytic pyrolyser. The pyrolyser consists of several independently controlled furnaces, through which a silica tube was inserted. The latter half of the silica tube carries an alumina/platinum catalyst, which was maintained in the furnace at 850°C. The sample was heated in a stream of air and oxygen in the presence of the catalyst to convert carbon to carbon dioxide, which was collected in a bubbler containing Carbon-Trap®. An aliquot was then measured in a liquid scintillation counter to determine the carbon-14 content. Carbon-14 of known activity concentration was used to determine the counting efficiency. The heated catalyst oxidises all forms of tritium to HTO with high efficiency. The outlet was passed into a system of water bubblers where the HTO vapour condensed and the tritium exchanged with the water in the bubblers. An aliquot of the bubbler solution was made alkaline and sodium thiosulphate added. The water was then distilled at low temperature to remove both radioactive and non-radioactive interferences. An aliquot of the distillate was then measured in a liquid scintillation counter to determine the tritium content. Tritiated water standards were used to produce a quench curve to determine the counting efficiency. This method was intended to measure the total tritium in solution, which is HTO and organically-bound tritium combined. For carbon-14 and tritium analysis, the instrument used was a Perkin Elmer Quantulus 1220 and the scintillation cocktail was Meridian Technologies’ Goldstar.

For gamma analysis an aliquot of the sample solution was transferred to a vessel of standard geometry. HRGS was undertaken using a number of Ortec high-purity germanium detectors linked via signal processing electronics to a computerised multi-channel analyser. Industry standard software was used for peak search, radionuclide identification and determination. Spectrometry calibration was undertaken over an energy range from 60 keV to 2000 keV for a range of densities and geometries using a nationally traceable “mixed gamma” reference solution.
4. Leaching Experiments

Seven leaching experiments were performed on samples of irradiated graphite, as outlined in Table 1. Six of these measured gaseous releases and one measured releases to solution with time. The solution release experiment was performed independently, rather than periodically sampling one of the gas sampling experiments, to avoid the possibility of disturbing the conditions in the leaching vessels during the experiment.

The two baseline gas experiments and the solution release experiment were run for 12 months to investigate the longer-term release under anoxic, high-pH conditions. The other four experiments, in which one of the conditions was changed from the baseline case, were run for three months only. The aim of these three-month variant case experiments was to give an indication of which conditions are the most important in controlling the rates of carbon-14 release to the gas phase.

4.1 Anoxic conditions – Baseline experiments

Experiment Code: Run 2 and Run 3
Graphite samples: 635-BLOCK-1-2-4 and 635-BLOCK-1-3-2 respectively
Graphite masses: 33.0 and 30.1g respectively
Flushing gas: nitrogen
Solution pH: 13
Temperature: ambient.
Solution volume: 250 cm$^3$
Duration: 12 months

To ensure that these experiments were run under anoxic conditions the following steps were taken:

- solutions were deoxygenated before use;
- iron foils were placed in the reaction vessel;
- all handling of solutions and sampling of the reaction vessel was performed under nitrogen;
- the vessel was regularly flushed with nitrogen gas during sampling.

Deoxygenated water was prepared by first boiling, then sparging with nitrogen, followed by equilibration with iron powder in a nitrogen-atmosphere glovebox. Iron powder was supplied by Goodfellow Cambridge Ltd and was high purity, >99.99%. The Eh (against the standard hydrogen electrode, SHE) of the water contacted with iron powder was measured routinely to monitor the approach to equilibrium and results are given in Table 6. The water was then used to prepare solutions of 0.1 mol dm$^{-3}$ NaOH solution.

### Table 6. Equilibration of deionised water with iron.

<table>
<thead>
<tr>
<th>Days</th>
<th>Eh vs. SHE (mV)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-177</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>-289</td>
<td>Under nitrogen within a glove box.</td>
</tr>
<tr>
<td>14</td>
<td>-345</td>
<td>Solution contacted with Fe powder</td>
</tr>
<tr>
<td>16</td>
<td>-325</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>-321</td>
<td></td>
</tr>
</tbody>
</table>

A graphite segment was placed a reaction vessel and transferred to a nitrogen atmosphere glovebox. A strip of iron foil (high purity, > 99.99% supplied by Goodfellow Cambridge Ltd) approximately 25 x 50 mm, was placed in each reaction vessel to maintain reducing conditions. The 250 cm$^3$ of the deoxygenated 0.1 mol dm$^{-3}$ NaOH solution was added to the vessel, via a
dropping funnel and the vessel was sealed. The vessels were removed from the glovebox and connected to the experimental apparatus as shown schematically in Figure 3, using nitrogen as the flushing gas. The vessel was flushed continuously for the first 7 days, then once per week for a period of 6 to 8 hours. During periods between flushing inlet and outlet valves to the reaction vessel were closed to retain the nitrogen atmosphere. Columns of the gas samplers were changed and analysed at 3 days, 7 days, 28 days, and 3 months. The experiment was terminated after a total duration of 12 months and the final columns (9 months' cumulative gas collection) analysed.

Samples of the leachate solutions were also taken at termination. Solution samples were passed through Millipore Millex-HV 0.45µm filters and analysed for carbon-14, tritium and major γ-emitting isotopes by the methods described in Section 3.2.

4.2 Oxic conditions

Experiment Code: Run 1
Graphite sample: 635-BLOCK-1-2-2
Graphite mass: 28.9g
Flushing gas: air
Solution pH: 13
Temperature: ambient.
Solution volume: 250 cm$^3$
Duration: 2.5 months

The conditions are the same as those used in a previous experiment with BEP0 graphite [5]. The graphite segment was placed in a reaction vessel under air and 250 cm$^3$ of 0.1 mol dm$^{-3}$ NaOH solution was added, via a dropping funnel. The vessel was immediately sealed, then connected to the gas-sampling apparatus as shown schematically in Figure 3. The reaction vessel was sampled continuously for the first seven days, by flushing with air. After seven days the headspace of the vessel was flushed for sampling once per week, for 6 to 8 hours per day, with the vessel sealed for the remainder of the time. The columns were changed at 7 days and 28 days and the experiment was terminated at 72 days. Soda lime columns for each of the three sampling periods were analysed for carbon-14.

4.3 Neutral pH

Experiment Code: Run 4
Graphite sample: 635-BLOCK-1-3-4
Graphite mass: 31.2g
Flushing gas: nitrogen
Solution pH: 7.5 (initial), 6.8 (final)
Temperature: ambient.
Solution volume: 250 cm$^3$
Duration: 3 months

The procedure was the same as that used for the baseline experiments except that the leaching solution was 0.1 mol dm$^{-3}$ NaCl solution. The vessel was flushed continuously for the first 7 days, then once per week for a period of 6 to 8 hours. Columns were changed at 7 days and 28 days and the experiment was terminated after 3 months. Soda lime columns for each of the three sampling periods were analysed for carbon-14.

4.4 Powdered graphite

Experiment Code: Run 5
Graphite sample: 635-BLOCK-1-3-3
Graphite mass: 25.3g
Flushing gas: nitrogen
Solution pH: 13
Temperature: ambient.
Solution volume: 250 cm$^3$
Duration: 3 months

Graphite was powdered by removing pieces from segment 635-BLOCK-1-3-3 with a file and crushing to a fine powder. Otherwise the procedure was the same as that used for the baseline experiments. Columns were changed at 7 days and 28 days and the experiment was terminated after 3 months. Soda lime columns for each of the three sampling periods were analysed for carbon-14. In addition, solution samples were taken for analysis on termination. Solution samples were passed through Millipore Millex-HV 0.45µm filters and analysed for carbon-14, tritium and major γ-emitting isotopes by the methods described in section 3.2.

4.5 Higher temperature

Experiment Code: Run 6
Graphite sample: 635-BLOCK-1-2-3
Graphite mass: 32.5g
Flushing gas: nitrogen
Solution pH: 13
Temperature: 50°C.
Solution volume: 250 cm$^3$
Duration: 3 months

The procedure was the same as that used for the baseline experiments except that the vessel was heated to 50°C. A condenser was placed in the gas circuit, just after the reaction vessel to reduce the loss of water by evaporation. The reaction vessel was maintained at 50°C for the course of the experiment by use of a silicone rubber insulated heating element placed around the outside of the reaction vessel. The columns were changed after 7 days and 28 days and the experiment was terminated after 3 months. Soda lime columns for each of the three sampling periods were analysed for carbon-14.

4.6 Solution sampling experiment

Experiment Code: Run 3b
Graphite sample: 635-BLOCK-1-3-1
Graphite mass: 22.6g
Atmosphere: nitrogen
Solution pH: 13
Temperature: ambient.
Solution volume: 250 cm$^3$
Duration: 12 months

A graphite segment was placed in a glass jar of similar dimensions to the reaction vessel used in the gas-monitoring experiments. The jar was fitted with a plastic screw top with a PTFE seal. The jar was transferred to a nitrogen atmosphere glovebox and a strip of iron foil (high purity, > 99.99% supplied by Goodfellow Cambridge Ltd) approximately 25 x 50 mm, was placed in the jar. 250 cm$^3$ of deoxygenated 0.1 mol dm$^{-3}$ NaOH solution was added to the jar which was then sealed. After leaching durations of approximately 2 days, 7 days, 1 month, 3 months and 12 months, 10 cm$^3$ samples of the solution were removed for analysis. The solution samples were passed through Millipore Millex-HV 0.45µm filters and analysed for carbon-14, tritium and gamma-emitting isotopes using the methods described in Section 3.2.
5. Results

5.1 Gas phase release of carbon-14

Measured carbon-14 activities released to the gas phase on leaching irradiated graphite are presented in Table 7. The activities of carbon-14 captured in each sampling unit during each sampling period are shown in the first set of results columns in Table 7. From these results, the cumulative releases for each carbon-14 species measured to the end of each sampling period have been calculated and are then shown in the right hand set of results columns. The activity results in Table 7 have been converted into cumulative fractional releases by normalisation against the carbon-14 inventory of the experiment based on the mass of graphite and the mean specific activity for carbon-14 of 8.4 ± 1.1 x 10^4 Bq g^-1 measured in block 635 (Table 5). The cumulative fractional releases for each species are presented in Table 8.

Plots of the cumulative releases and speciation of carbon-14 in the six gas-phase experiments are shown in Figure 8 to Figure 11. In common with previous work [4, 5, 6], carbon-14 release rates to the gas phase were highest over the first few weeks of leaching and decreased with time.

5.1.1 Anoxic conditions - baseline experiments

The gas phase releases of carbon-14 in the duplicate baseline experiments (anoxic, pH13, single piece specimen of graphite, ambient temperature) are reasonably consistent (Figure 8). In the first seven days the total carbon-14 releases to the gas phase were about 3 Bq. The rate decreased with time and was ~2 Bq over the 9 months duration of the final sampling periods. The baseline experiments ran for ~12 months in total, over which time a total of ~7 Bq of carbon-14 was released to the gas phase in each experiment, which represents a fraction of 2.7 x 10^-6 of the inventory of the graphite. The ratio of activity associated with CO to that with volatile hydrocarbon/organic compounds was 1:2 at all sampling periods. Only a small fraction of the gaseous release (0.12 Bq) was in the form of $^{14}$CO$_2$.

5.1.2 Oxic conditions

Under oxic conditions the total carbon-14 release to the gas phase was similar to the baseline experiments with ~3 Bq released in the first week and a cumulative total of 5 Bq in the 3 months that the experiment was run. However, the proportion of $^{14}$CO to organic compounds was higher (~1:1), possibly reflecting the increased availability of oxygen (Figure 9). The $^{14}$CO$_2$ activities constituted only a small proportion of the release to the gas phase.

5.1.3 Neutral pH

In the experiment with graphite immersed in a near-neutral-pH solution an initial carbon-14 release of 36 Bq to the gas phase was observed over the first 7 days. The total release in the three months of the experiment was 130 Bq. It can be seen from the data plotted in Figure 10(a) that the gas release was predominantly in the form of $^{10}$CO$_2$ and is considerably higher than the baseline experiments. In Figure 10(b) the same data are plotted on an expanded ordinate scale to illustrate that the concentrations of $^{14}$CO and carbon-14-bearing volatile organic compounds in the gas phase were similar to the baseline values. The pH of the solution is expected to affect gaseous release of carbon owing to the decreasing solubility of CO$_2$ with decreasing pH [10].

5.1.4 Powdered graphite

The experiment with powdered graphite gave the lowest initial release of carbon-14 to the gas phase (Table 7 and Figure 11(a)) of ~1.4 Bq in the first 7 days. However, over the final sampling period (30 to 93 days) the activity released was ~0.8 Bq, which is closer to activities measured in the baseline experiments for the same period, but there is a higher proportion of the release as $^{14}$CO$_2$. The total gaseous carbon-14 release over the 3 month experiment was ~2.9 Bq, equivalent to a fraction of 1.4 x 10^-6 of the total inventory in the experiment. Given the far higher surface area of powdered graphite compared to the intact samples, a higher release may have been expected. It is possible that the process of crushing released some of the carbon-14, prior to the use of the
powdered graphite in the experiment. The same effect has been noted in previous graphite leaching experiments [4].

5.1.5 Higher temperature

Graphite immersed in a solution at 50°C produced total carbon-14 gas-phase releases of 7 Bq in the first week and 9 Bq in the first month. These releases are approximately twice those seen in the baseline experiments. However, there was a notable decrease in the carbon-14 release rate during the final two months of the experiment; the total carbon-14 release during the last sampling period was closer to the baseline values. After three months the total carbon-14 release was 10 Bq (~3.6 x10^-6 of the activity in the graphite). The ratio of $^{14}$CO to volatile organic compounds was 1:2 over all sampling periods, similar to the ambient temperature experiments. The $^{14}$CO$_2$ activity in the gas phase (0.39 Bq) was higher than in the baseline experiments, but contributed only a small fraction (~4%) of the gas-phase release (Figure 11(b)).
Table 7. Gaseous release of carbon-14 from irradiated Oldbury graphite.

<table>
<thead>
<tr>
<th>Run</th>
<th>Conditions</th>
<th>Days</th>
<th>(^{14}\text{C}) measured in gas phase over sampling period (Bq)</th>
<th>(^{14}\text{C}) cumulative release to the gas phase to end of sampling period (Bq)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(\text{CO}_2)</td>
<td>(\text{CO})</td>
</tr>
<tr>
<td>1</td>
<td>Oxic Single piece of graphite pH 13, 20°C</td>
<td>7.0</td>
<td>0.04 ± 0.001</td>
<td>1.73 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28.8</td>
<td>0.01 ± 0.001</td>
<td>0.4 ± 0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70.9</td>
<td>0.02 ± 0.002</td>
<td>0.38 ± 0.02</td>
</tr>
<tr>
<td>2</td>
<td>Anoxic Single piece of graphite pH 13, 20°C</td>
<td>2.9</td>
<td>0.01 ± 0.001</td>
<td>0.44 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.0</td>
<td>0.02 ± 0.001</td>
<td>0.56 ± 0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>31.0</td>
<td>0.01 ± 0.001</td>
<td>0.47 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>94.0</td>
<td>0.01 ± 0.001</td>
<td>0.42 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>365.0</td>
<td>0.07 ± 0.004</td>
<td>0.53 ± 0.03</td>
</tr>
<tr>
<td>3</td>
<td>Anoxic Single piece of graphite pH 13, 20°C</td>
<td>2.3</td>
<td>&lt; ± 0.01</td>
<td>0.54 ± 0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.3</td>
<td>&lt; ± 0.01</td>
<td>0.32 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>31.2</td>
<td>&lt; ± 0.01</td>
<td>0.21 ± 0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>99.2</td>
<td>0.08 ± 0.04</td>
<td>0.30 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>366.0</td>
<td>0.21 ± 0.01</td>
<td>0.66 ± 0.03</td>
</tr>
<tr>
<td>4</td>
<td>Anoxic Single piece of graphite pH 7, 20°C</td>
<td>7.1</td>
<td>30.7 ± 1.6</td>
<td>1.43 ± 0.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30.1</td>
<td>19.05 ± 0.5</td>
<td>0.27 ± 0.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>93.1</td>
<td>72.1 ± 3.6</td>
<td>0.71 ± 0.04</td>
</tr>
</tbody>
</table>
Table 7. Gaseous release of carbon-14 from irradiated Oldbury graphite. (Continued)

<table>
<thead>
<tr>
<th>Run</th>
<th>Conditions</th>
<th>Days</th>
<th>$^{14}$C measured in gas phase over sampling period (Bq)</th>
<th>$^{14}$C cumulative release to the gas phase to end of sampling period (Bq)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO$_2$</td>
<td>CO</td>
</tr>
<tr>
<td>5</td>
<td>Anoxic Graphite powder pH 13, 20$^\circ$C</td>
<td>7.0</td>
<td>0.09 ± 0.01</td>
<td>0.39 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28.0</td>
<td>0.01 ± 0.001</td>
<td>0.29 ± 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>91.0</td>
<td>0.42 ± 0.02</td>
<td>0.2 ± 0.01</td>
</tr>
<tr>
<td>6</td>
<td>Anoxic Single piece of graphite pH 13, 50$^\circ$C</td>
<td>6.9</td>
<td>0.10 ± 0.01</td>
<td>2.05 ± 0.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28.0</td>
<td>0.21 ± 0.02</td>
<td>0.67 ± 0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>94.2</td>
<td>0.08 ± 0.01</td>
<td>0.2 ± 0.02</td>
</tr>
</tbody>
</table>
Table 8. Fractional gaseous release of carbon-14 from irradiated Oldbury graphite.

<table>
<thead>
<tr>
<th>Run</th>
<th>Conditions</th>
<th>Time (days)</th>
<th>Fraction of inventory as $^{14}$CO$_2$</th>
<th>Fraction of inventory as $^{14}$CO</th>
<th>Fraction of inventory as $^{14}$C-bearing volatile hydrocarbon / organic compounds</th>
<th>Total $^{14}$C gaseous release</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Oxic</td>
<td>7.0</td>
<td>$1.64 \times 10^{-8} \pm 0.04 \times 10^{-8}$</td>
<td>$7.11 \times 10^{-7} \pm 0.08 \times 10^{-7}$</td>
<td>$6.86 \times 10^{-7} \pm 0.04 \times 10^{-7}$</td>
<td>$1.41 \times 10^{-6} \pm 0.01 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28.8</td>
<td>$2.05 \times 10^{-8} \pm 0.06 \times 10^{-8}$</td>
<td>$8.75 \times 10^{-7} \pm 0.09 \times 10^{-7}$</td>
<td>$8.17 \times 10^{-7} \pm 0.06 \times 10^{-7}$</td>
<td>$1.71 \times 10^{-6} \pm 0.01 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70.9</td>
<td>$2.87 \times 10^{-8} \pm 0.10 \times 10^{-8}$</td>
<td>$1.03 \times 10^{-6} \pm 0.01 \times 10^{-6}$</td>
<td>$9.77 \times 10^{-7} \pm 0.10 \times 10^{-7}$</td>
<td>$2.04 \times 10^{-6} \pm 0.02 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>Anoxic</td>
<td>2.9</td>
<td>$3.6 \times 10^{-9} \pm 0.16 \times 10^{-9}$</td>
<td>$1.58 \times 10^{-7} \pm 0.08 \times 10^{-7}$</td>
<td>$5.11 \times 10^{-7} \pm 0.20 \times 10^{-7}$</td>
<td>$6.73 \times 10^{-7} \pm 0.26 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.0</td>
<td>$1.08 \times 10^{-8} \pm 0.04 \times 10^{-8}$</td>
<td>$3.60 \times 10^{-7} \pm 0.13 \times 10^{-7}$</td>
<td>$8.82 \times 10^{-7} \pm 0.23 \times 10^{-7}$</td>
<td>$1.25 \times 10^{-6} \pm 0.03 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>31.0</td>
<td>$1.44 \times 10^{-8} \pm 0.04 \times 10^{-8}$</td>
<td>$5.29 \times 10^{-7} \pm 0.16 \times 10^{-7}$</td>
<td>$1.12 \times 10^{-6} \pm 0.02 \times 10^{-6}$</td>
<td>$1.66 \times 10^{-6} \pm 0.04 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>94.0</td>
<td>$1.80 \times 10^{-9} \pm 0.04 \times 10^{-9}$</td>
<td>$6.80 \times 10^{-7} \pm 0.17 \times 10^{-7}$</td>
<td>$1.40 \times 10^{-6} \pm 0.03 \times 10^{-6}$</td>
<td>$2.1 \times 10^{-6} \pm 0.04 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>365.0</td>
<td>$4.32 \times 10^{-9} \pm 0.10 \times 10^{-9}$</td>
<td>$8.71 \times 10^{-7} \pm 0.20 \times 10^{-7}$</td>
<td>$1.83 \times 10^{-6} \pm 0.03 \times 10^{-6}$</td>
<td>$2.74 \times 10^{-6} \pm 0.05 \times 10^{-6}$</td>
</tr>
<tr>
<td>2</td>
<td>Anoxic</td>
<td>2.3</td>
<td>$&lt; 4 \times 10^{-9}$</td>
<td>$2.13 \times 10^{-7} \pm 0.12 \times 10^{-7}$</td>
<td>$3.71 \times 10^{-7} \pm 0.20 \times 10^{-7}$</td>
<td>$5.84 \times 10^{-7} \pm 0.23 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.3</td>
<td>$&lt; 8 \times 10^{-9}$</td>
<td>$3.39 \times 10^{-7} \pm 0.14 \times 10^{-7}$</td>
<td>$7.73 \times 10^{-7} \pm 0.28 \times 10^{-7}$</td>
<td>$1.11 \times 10^{-6} \pm 0.03 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>31.2</td>
<td>$&lt; 1 \times 10^{-8}$</td>
<td>$4.22 \times 10^{-7} \pm 0.15 \times 10^{-7}$</td>
<td>$9.23 \times 10^{-7} \pm 0.29 \times 10^{-7}$</td>
<td>$1.34 \times 10^{-6} \pm 0.03 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>99.2</td>
<td>$3.15 \times 10^{-9} \pm 1.63 \times 10^{-9}$</td>
<td>$5.40 \times 10^{-7} \pm 0.17 \times 10^{-7}$</td>
<td>$1.19 \times 10^{-6} \pm 0.04 \times 10^{-6}$</td>
<td>$1.76 \times 10^{-6} \pm 0.04 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>366.0</td>
<td>$1.14 \times 10^{-7} \pm 0.17 \times 10^{-7}$</td>
<td>$8.00 \times 10^{-7} \pm 0.20 \times 10^{-7}$</td>
<td>$1.76 \times 10^{-6} \pm 0.05 \times 10^{-6}$</td>
<td>$2.67 \times 10^{-6} \pm 0.05 \times 10^{-6}$</td>
</tr>
<tr>
<td>3</td>
<td>Anoxic</td>
<td>7.1</td>
<td>$1.17 \times 10^{-5} \pm 0.06 \times 10^{-5}$</td>
<td>$5.44 \times 10^{-7} \pm 0.27 \times 10^{-7}$</td>
<td>$1.31 \times 10^{-6} \pm 0.07 \times 10^{-6}$</td>
<td>$1.35 \times 10^{-5} \pm 0.06 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30.1</td>
<td>$1.89 \times 10^{-5} \pm 0.06 \times 10^{-5}$</td>
<td>$6.47 \times 10^{-7} \pm 0.38 \times 10^{-7}$</td>
<td>$1.7 \times 10^{-6} \pm 0.07 \times 10^{-6}$</td>
<td>$2.13 \times 10^{-5} \pm 0.06 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>93.1</td>
<td>$4.64 \times 10^{-5} \pm 0.15 \times 10^{-5}$</td>
<td>$9.17 \times 10^{-7} \pm 1.57 \times 10^{-7}$</td>
<td>$2.07 \times 10^{-6} \pm 0.07 \times 10^{-6}$</td>
<td>$4.93 \times 10^{-5} \pm 0.15 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

| 4   | Anoxic     | 7.1        | $1.17 \times 10^{-5} \pm 0.06 \times 10^{-5}$ | $5.44 \times 10^{-7} \pm 0.27 \times 10^{-7}$ | $1.31 \times 10^{-6} \pm 0.07 \times 10^{-6}$ | $1.35 \times 10^{-5} \pm 0.06 \times 10^{-5}$ |
|     |             | 30.1       | $1.89 \times 10^{-5} \pm 0.06 \times 10^{-5}$ | $6.47 \times 10^{-7} \pm 0.38 \times 10^{-7}$ | $1.7 \times 10^{-6} \pm 0.07 \times 10^{-6}$ | $2.13 \times 10^{-5} \pm 0.06 \times 10^{-5}$ |
|     |             | 93.1       | $4.64 \times 10^{-5} \pm 0.15 \times 10^{-5}$ | $9.17 \times 10^{-7} \pm 1.57 \times 10^{-7}$ | $2.07 \times 10^{-6} \pm 0.07 \times 10^{-6}$ | $4.93 \times 10^{-5} \pm 0.15 \times 10^{-5}$ |
### Table 8. Fractional gaseous release of carbon-14 from irradiated Oldbury graphite. (Continued)

<table>
<thead>
<tr>
<th>Run</th>
<th>Conditions</th>
<th>Time (days)</th>
<th>Fraction of inventory as $^{14}$CO$_2$</th>
<th>Fraction of inventory as $^{14}$CO</th>
<th>Fraction of inventory as $^{14}$C-bearing volatile hydrocarbon / organic compounds</th>
<th>Total $^{14}$C gaseous release</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Anoxic Graphite powder</td>
<td>7.0</td>
<td>$4.22 \times 10^{-8} \pm 0.47 \times 10^{-8}$</td>
<td>$1.83 \times 10^{-7} \pm 0.09 \times 10^{-7}$</td>
<td>$4.27 \times 10^{-7} \pm 0.23 \times 10^{-7}$</td>
<td>$6.52 \times 10^{-7} \pm 0.26 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>pH 13, 20°C</td>
<td>28.0</td>
<td>$4.69 \times 10^{-8} \pm 0.66 \times 10^{-8}$</td>
<td>$3.19 \times 10^{-7} \pm 0.13 \times 10^{-7}$</td>
<td>$6.15 \times 10^{-7} \pm 0.25 \times 10^{-7}$</td>
<td>$9.81 \times 10^{-7} \pm 0.29 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>91.0</td>
<td>$2.44 \times 10^{-7} \pm 0.11 \times 10^{-7}$</td>
<td>$4.13 \times 10^{-7} \pm 0.14 \times 10^{-7}$</td>
<td>$7.13 \times 10^{-7} \pm 0.26 \times 10^{-7}$</td>
<td>$1.37 \times 10^{-6} \pm 0.03 \times 10^{-6}$</td>
</tr>
<tr>
<td>6</td>
<td>Anoxic Single piece of graphite</td>
<td>6.9</td>
<td>$3.65 \times 10^{-8} \pm 0.37 \times 10^{-8}$</td>
<td>$7.49 \times 10^{-7} \pm 0.40 \times 10^{-7}$</td>
<td>$1.92 \times 10^{-6} \pm 0.08 \times 10^{-6}$</td>
<td>$2.71 \times 10^{-6} \pm 0.09 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>pH 13, 50°C</td>
<td>28.0</td>
<td>$1.13 \times 10^{-7} \pm 0.08 \times 10^{-7}$</td>
<td>$9.93 \times 10^{-7} \pm 0.43 \times 10^{-7}$</td>
<td>$2.26 \times 10^{-6} \pm 0.09 \times 10^{-6}$</td>
<td>$3.36 \times 10^{-6} \pm 0.1 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>94.2</td>
<td>$1.42 \times 10^{-7} \pm 0.09 \times 10^{-7}$</td>
<td>$1.07 \times 10^{-6} \pm 0.04 \times 10^{-6}$</td>
<td>$2.41 \times 10^{-6} \pm 0.09 \times 10^{-6}$</td>
<td>$3.62 \times 10^{-6} \pm 0.1 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

The uncertainties given are based on 2$\sigma$ counting uncertainties on gas phase measurements only. The uncertainty on the graphite inventory is ~13% (2. s.d.), but is not included because this is a systematic uncertainty. i.e. error in the carbon-14 inventory of the graphite would shift all values by the same degree.
Figure 8. Fractional releases and speciation of gaseous carbon-14 from irradiated Oldbury graphite in the baseline experiments under anoxic, pH 13, ambient temperature conditions.
Figure 9. Run 1. Fractional release and speciation of gaseous carbon-14 from irradiated Oldbury graphite under oxic conditions, at pH 13 and ambient temperature.
Figure 10. Fractional release and speciation of gaseous carbon-14 from irradiated Oldbury graphite under anoxic conditions, at pH 7 and ambient temperature, Run 4: (a) the upper plot is at large scale to show $^{14}$CO$_2$ release; (b) the lower plot is on an expanded ordinate scale to show the CO and volatile organic compounds.
Figure 11. Fractional release and speciation of gaseous carbon-14 from irradiated Oldbury graphite under anoxic conditions at pH 13: (a) Run 5, powdered graphite at ambient temperature; and (b) Run 6, single piece of graphite at 50 °C.
5.2 Gas phase release of tritium

Tritium measurements were made only for Run 2 (baseline experiment, anoxic, ambient temperature, single piece of graphite). Measured activities and cumulative activities with time for HTO, HT and tritiated hydrocarbon/VOC releases are given in Table 9; cumulative fractional releases with time are presented in Table 10 and are plotted in Figure 12.

There was a very high initial release of tritium over the first week of the experiment, which was composed mainly of 3.2 kBq of HT and 7.1 kBq of tritiated hydrocarbons / VOCs. Thereafter the releases of tritium species reached a near plateau. Over the one year experiment, the total tritium activity detected in the gas phase had risen to ~12 kBq, approximately 0.1% of the initial tritium in the graphite.

To confirm that the high initial results for HT and volatile organic species were genuine, the silica gel columns at the inlet side of the CO/HT sampler (Figure 6, column 1) and the hydrocarbon/ volatile organics compounds sampler (Figure 7, column 1) were analysed for tritium. As explained in Section 3.1.2, these columns are a feature from when the units were used in a ‘stand alone mode’ and so are redundant and not normally analysed. Both of the columns showed low levels of tritium captured as HTO. This demonstrated that HTO captured at column 3 of both the CO/HT and the hydrocarbon/ VOC units came from oxidation of HT and volatile organic compounds at the catalysts and not from HTO ‘spilling over’ from the previous (14CO2/HTO) sampling unit. The gradual release of HTO is attributed to evaporation from the liquid phase during gas-phase sampling.

![Figure 12. Fractional and speciation of tritium gas-phase release from Oldbury graphite. Run 2.](image-url)
### Table 9. Gaseous release of $^3$H from irradiated Oldbury graphite (Run 2).

<table>
<thead>
<tr>
<th>Run</th>
<th>Conditions</th>
<th>Days</th>
<th>Tritium measured in gas phase over sampling period (Bq)*</th>
<th>Tritium cumulative release to end of sampling period (Bq)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>HTO</td>
<td>HT</td>
</tr>
<tr>
<td>2</td>
<td>Anoxic</td>
<td>2.9</td>
<td>35.2 ± 0.1</td>
<td>1002 ± 58</td>
</tr>
<tr>
<td></td>
<td>Single piece of graphite</td>
<td>7.0</td>
<td>423 ± 25</td>
<td>2232 ± 131</td>
</tr>
<tr>
<td></td>
<td>pH 13, 20°C</td>
<td>31.0</td>
<td>156 ± 9</td>
<td>29 ± 2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>94.0</td>
<td>245 ± 14</td>
<td>1.1 ± 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>365.0</td>
<td>398 ± 24</td>
<td>2.7 ± 0.2</td>
</tr>
</tbody>
</table>

* Decay corrected to start of experiment

### Table 10. Fractional gaseous release of $^3$H from irradiated Oldbury graphite (Run 2).

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Fraction of inventory as HTO</th>
<th>Fraction of inventory as HT</th>
<th>Fraction of inventory as tritium-bearing organic compounds</th>
<th>Total tritium gaseous release</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.9</td>
<td>2.92 x 10^4 ± 0.17 x 10^4</td>
<td>8.33 x 10^5 ± 0.5 x 10^5</td>
<td>2.11 x 10^4 ± 0.10 x 10^4</td>
<td>2.97 x 10^4 ± 0.11 x 10^4</td>
</tr>
<tr>
<td>7.0</td>
<td>3.81 x 10^5 ± 0.17 x 10^5</td>
<td>2.69 x 10^4 ± 0.12 x 10^4</td>
<td>5.93 x 10^4 ± 0.19 x 10^4</td>
<td>9.00 x 10^4 ± 0.22 x 10^4</td>
</tr>
<tr>
<td>31.0</td>
<td>5.10 x 10^5 ± 0.22 x 10^5</td>
<td>2.71 x 10^4 ± 0.11 x 10^4</td>
<td>6.14 x 10^4 ± 0.19 x 10^4</td>
<td>9.36 x 10^4 ± 0.22 x 10^4</td>
</tr>
<tr>
<td>94.0</td>
<td>7.14 x 10^5 ± 0.31 x 10^5</td>
<td>2.71 x 10^4 ± 0.11 x 10^4</td>
<td>6.18 x 10^4 ± 0.18 x 10^4</td>
<td>9.60 x 10^4 ± 0.22 x 10^4</td>
</tr>
<tr>
<td>365.0</td>
<td>1.04 x 10^4 ± 0.05 x 10^4</td>
<td>2.72 x 10^4 ± 0.11 x 10^4</td>
<td>6.20 x 10^4 ± 0.18 x 10^4</td>
<td>9.96 x 10^4 ± 0.22 x 10^4</td>
</tr>
</tbody>
</table>
5.3 Solution phase releases

A single leaching experiment (Run 3b) was performed to monitor releases of carbon-14, tritium and significant y-emitting isotopes to solution with time. Releases to solution with time are given in Table 11. These values have been adjusted for removal of solution in sampling and decay corrected to the start date of the experiment. The values were divided by the initial graphite inventories to calculate fractional releases which are presented in Table 12 and plotted in Figure 13 and Figure 14. The solution concentrations in the gas monitoring experiments were measured only at the end, to avoid breaking the integrity of the system during the experiments and are given in Table 13.

The errors given in both tables represent only the 2σ counting uncertainty on the solution activities. An additional source of uncertainty in the calculated fractional release comes from the uncertainty in the total inventory of the graphite (given in Table 5), but this is a systematic uncertainty on the fractional release, i.e. this error will be the same for each measurement. To illustrate this, the plots of solution concentration with time given in Figure 13 and Figure 14 show the uncertainty on the solution measurements as error bars, with the errors introduced by the uncertainty on the graphite inventory shown as the pink and blue lines (these are the upper and lower bound on fractional release based uncertainty in the graphite inventory and do not include uncertainties in solution concentration). Due to the uneven distribution of caesium-137 within the graphite the activity in the sample has a large uncertainty and the upper bound on the fractional release is 100%.

In the solution release experiment (Run 3b), 0.06% of the carbon-14 (1.6 kBq) was leached into solution in one year and appeared to still be rising. Solution phase measurements at the end of the baseline gas monitoring experiments (see Table 13) showed similar fractional releases of carbon-14 in the range 0.06 to 0.08% at 12 months. Powdered graphite (also Table 13) released 0.04% of the carbon-14 present into solution in 3 months. This is twice that found in the leachate from the single piece specimen at the same duration of leaching.

Tritium releases were around 0.2% of the inventory after 12 months leaching in both the solution experiment and at the end of baseline gas-sampling experiments. The tritium plot in Figure 13 shows an anomalous drop in concentration at 97 days, but the concentrations appears to be still rising at 12 months. Powdered graphite gave a higher fractional release rate of 0.3% in 3 months.

An initial release of ~3% of the cobalt-60 was measured in solution after 7 days. This continued to rise to 5% over 12 months. In the gas sampling experiments fractional releases of 5% to 6% were found in the baseline experiments after 12 months and 5% from the powdered graphite after 3 months.

Release fractions have been calculated for caesium-137 and are given in Table 12 and Table 13. However there is a great deal of uncertainty in these values because the uneven distribution of the isotope in the graphite makes it difficult to estimate the total amount present. However caesium does appear to be readily leached from the graphite with estimated release fractions between 6% and 47%. The behaviour of caesium with time, appears to show an almost instant release of a large fractions of the activity on contact with the solution, followed by a drop in concentration with time. This may be interpreted as a fast dissolution of caesium contamination on the graphite surface, then a gradual re-sorption of some caesium onto the graphite with time.
Table 11. Solution releases with time from a single piece specimen of irradiated Oldbury graphite.

<table>
<thead>
<tr>
<th>Days</th>
<th>$^{14}$C (Bq)</th>
<th>$^{3}$H (Bq)</th>
<th>$^{60}$Co (Bq)</th>
<th>$^{137}$Cs (Bq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$1.0 \times 10^2 \pm 0.1 \times 10^2$</td>
<td>$4.9 \times 10^2 \pm 0.6 \times 10^2$</td>
<td>$4.7 \times 10^4 \pm 0.2 \times 10^4$</td>
<td>$7.2 \times 10^5 \pm 0.3 \times 10^5$</td>
</tr>
<tr>
<td>7</td>
<td>$1.6 \times 10^2 \pm 0.2 \times 10^2$</td>
<td>$1.2 \times 10^4 \pm 0.1 \times 10^4$</td>
<td>$5.5 \times 10^4 \pm 0.2 \times 10^4$</td>
<td>$6.8 \times 10^5 \pm 0.3 \times 10^5$</td>
</tr>
<tr>
<td>31</td>
<td>$3.4 \times 10^2 \pm 0.3 \times 10^2$</td>
<td>$1.2 \times 10^4 \pm 0.1 \times 10^4$</td>
<td>$5.7 \times 10^4 \pm 0.2 \times 10^4$</td>
<td>$6.4 \times 10^5 \pm 0.3 \times 10^5$</td>
</tr>
<tr>
<td>97</td>
<td>$4.3 \times 10^2 \pm 0.3 \times 10^2$</td>
<td>$9 \times 10^3 \pm 0.9 \times 10^3$</td>
<td>$6.6 \times 10^4 \pm 0.2 \times 10^4$</td>
<td>$6.1 \times 10^5 \pm 0.2 \times 10^5$</td>
</tr>
<tr>
<td>372</td>
<td>$1.1 \times 10^3 \pm 0.1 \times 10^3$</td>
<td>$2 \times 10^4 \pm 0.2 \times 10^4$</td>
<td>$9.6 \times 10^4 \pm 0.3 \times 10^4$</td>
<td>$5.4 \times 10^5 \pm 0.2 \times 10^5$</td>
</tr>
</tbody>
</table>

Table 12. Fractional solution releases with time from a single piece specimen of irradiated Oldbury graphite.

<table>
<thead>
<tr>
<th>Days</th>
<th>$^{14}$C Fraction (10$^{-5}$)</th>
<th>$^{3}$H Fraction (10$^{-4}$)</th>
<th>$^{60}$Co Fraction (10$^{-2}$)</th>
<th>$^{137}$Cs Fraction (10$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$5.4 \times 10^{-5} \pm 0.6 \times 10^{-5}$</td>
<td>$5.9 \times 10^{-4} \pm 0.7 \times 10^{-4}$</td>
<td>$2.5 \times 10^{-2} \pm 0.1 \times 10^{-2}$</td>
<td>$4.7 \times 10^{-1} \pm 0.2 \times 10^{-1}$</td>
</tr>
<tr>
<td>7</td>
<td>$8.3 \times 10^{-5} \pm 0.8 \times 10^{-5}$</td>
<td>$1.4 \times 10^{-3} \pm 0.2 \times 10^{-3}$</td>
<td>$2.9 \times 10^{-2} \pm 0.1 \times 10^{-2}$</td>
<td>$4.4 \times 10^{-1} \pm 0.2 \times 10^{-1}$</td>
</tr>
<tr>
<td>31</td>
<td>$1.8 \times 10^{-4} \pm 0.1 \times 10^{-4}$</td>
<td>$1.5 \times 10^{-3} \pm 0.2 \times 10^{-3}$</td>
<td>$3.0 \times 10^{-2} \pm 0.1 \times 10^{-2}$</td>
<td>$4.1 \times 10^{-1} \pm 0.2 \times 10^{-1}$</td>
</tr>
<tr>
<td>97</td>
<td>$2.3 \times 10^{-4} \pm 0.2 \times 10^{-4}$</td>
<td>$1.1 \times 10^{-3} \pm 0.1 \times 10^{-3}$</td>
<td>$3.5 \times 10^{-2} \pm 0.1 \times 10^{-2}$</td>
<td>$4.0 \times 10^{-1} \pm 0.1 \times 10^{-1}$</td>
</tr>
<tr>
<td>372</td>
<td>$6.0 \times 10^{-4} \pm 0.4 \times 10^{-4}$</td>
<td>$2.4 \times 10^{-3} \pm 0.2 \times 10^{-3}$</td>
<td>$5.1 \times 10^{-2} \pm 0.1 \times 10^{-2}$</td>
<td>$3.5 \times 10^{-1} \pm 0.1 \times 10^{-1}$</td>
</tr>
</tbody>
</table>
Table 13. Final fractional releases to solution in gas monitoring experiments. Uncertainties in the fractional release reflect only that on the solution concentration (±2σ). Uncertainties on the inventory of the graphite are show separately.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Duration (Days)</th>
<th>Fraction of graphite inventory released into solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(^{14}\text{C})</td>
</tr>
<tr>
<td>Run 2 Anoxic, pH 13, Single piece of graphite</td>
<td>372</td>
<td>(5.8 \times 10^{-4} \pm 0.4 \times 10^{-4})</td>
</tr>
<tr>
<td>Run 3 Anoxic, pH 13, Single piece of graphite</td>
<td>366</td>
<td>(7.8 \times 10^{-4} \pm 0.6 \times 10^{-4})</td>
</tr>
<tr>
<td>Run 5 Anoxic, pH 13, powdered graphite</td>
<td>91</td>
<td>(3.8 \times 10^{-4} \pm 0.3 \times 10^{-4})</td>
</tr>
<tr>
<td>2 (\sigma) uncertainty on graphite inventory</td>
<td></td>
<td>(\pm 15%)</td>
</tr>
</tbody>
</table>
Figure 13. Fractional releases to solution in Oldbury graphite leaching experiment under anoxic conditions at pH 13 and ambient temperature: (a) carbon-14 and (b) tritium; error bars show the uncertainties on solution concentration measurements; pink and blue lines show systematic errors based on the uncertainty in the graphite inventory.
Figure 14. Fractional releases to solution in Oldbury graphite leaching experiment under anoxic conditions at pH 13 and ambient temperature: a) cobalt-60 and b) caesium-137; error bars show the uncertainties on solution concentration measurements; pink and blue lines show systematic errors based on the uncertainty in the graphite inventory.
6. Discussion

6.1 Carbon-14 release

Under all experimental conditions, the gaseous releases of carbon-14 exhibited an initial phase of relatively rapid release. This was followed by a second phase where, in most cases, the rate was significantly lower. The only exception was for graphite immersed in a solution at pH 7 (Figure 10), where the rate of gas-phase release remained fairly high throughout the experiment and was associated mainly with $^{14}\text{CO}_2$. Rates for the release of $^{14}\text{CO}$ and $^{14}\text{C}$-bearing hydrocarbons/VOCs showed little pH dependency; but $^{14}\text{CO}_2$ release was negligible at pH 13.

6.1.1 Baseline conditions (anoxic, high-pH and ambient temperature)

In the baseline experiments a single piece specimen of graphite was immersed in 0.1 mol dm$^{-3}$ NaOH solution, at ambient temperature under a nitrogen atmosphere to maintain anoxic conditions. The sodium hydroxide solution simulates the high-pH conditions that will occur in a GDF with a cementitious backfill. Anoxic conditions will be established relatively quickly after closure in a GDF due to the consumption of oxygen by the corrosion of metals (present as wastes and waste container materials).

Cumulative fractional releases of carbon-14 from graphite with time to both solution and gas phases under baseline conditions are plotted together in Figure 15. It can be seen that releases to both solution and gas phases show an initial rapid release over to the first 7 days. The release rate settles at a significantly lower value after ~28 days. The rapid release fraction is estimated to be $~2 \times 10^{-4}$ to solution and $~2 \times 10^{-6}$ to the gas phase. The ratio of solution to gaseous release was ~100 at most sampling points, but was higher for the final samples.

Gaseous releases under baseline conditions were mostly in the form of volatile organic compounds and $^{14}\text{CO}$ in the ratio 2:1. Both of these gases could migrate with any bulk gas phase such as hydrogen formed from corrosion of metallic wastes and containers in a GDF. However, the form of gaseous carbon-14 may be important in determining its potential pathways in the biosphere. The form of carbon-14 in the solution phase was not determined in the experiments, but is assumed to comprise both dissolved carbonate and non-volatile organic compounds. Work on BEP0 graphite investigated this issue by acidifying a pH 13 leachate and analysing the off-gas and residual solution [5]. This suggested that both organic and inorganic forms of carbon-14 were present, but the proportions were uncertain as a mass balance was not achieved. In the present study, the observation that $^{14}\text{CO}_2$ is released to the gas phase in the pH 7 experiment provides supporting evidence that a significant proportion of the release from the Oldbury graphite is likely to be as $^{14}\text{CO}_2$, which would be retained in the high-pH solution as carbonate.
6.1.2 Variant conditions

Four variant experiments were carried out in which one condition was altered from those in the baseline experiments. These were run for a shorter time than the baseline experiments with the aim of scoping the sensitivity of gaseous release rates to changes in the conditions.

Under oxic conditions, the total carbon-14 gas released in the initial rapid release phase and the longer-term rate showed no differences to the baseline within the experimental uncertainties. The only effect seen of changing to oxic conditions was a higher proportion of $^{14}$CO in the gas released (see Figure 8 and Figure 9). Under oxic conditions the ratio of carbon-14 activity associated with CO to that with organic compounds was ~1:1, compared to 2:1 under baseline conditions. Previous experiments with BEP0 graphite under oxic conditions gave an even higher proportion of CO, with one part volatile organic compounds to 4 parts CO.

At a temperature of 50°C, the total gaseous release of carbon-14 over the first 7 days of leaching was twice that of the baseline experiments, but thereafter, the longer-term release was similar to that measured at ambient temperature over comparable times. The temperatures experienced by waste packages are not expected to exceed 50°C, although curing of backfill may give rise to higher temperatures for a short period post-closure [11]. Therefore variations in release rate due to temperature effects may not be significant in the context of other uncertainties.

Using powdered graphite gave an initial gaseous release rate that was lower than in the baseline experiments. This is possibly due to some of the easily releasable carbon-14 being lost in the process of powdering the graphite. However, gaseous release rates from 7 to 91 days appear to be similar to those measured for the intact specimens over comparable sampling intervals. In contrast, the fractional release of carbon-14 to solution at the end of the three-month experiment was 0.038%, compared to 0.023% in the intact experiment, an increase of about 65%. Similar increases in the extent of release to solution from the powdered sample were observed also for cobalt-60 and tritium (compare Run 5 data in Table 13 with Table 12). This increase in the extent of release is most likely due to the larger surface area of the powdered sample.
In the baseline experiments and under the three variant conditions discussed above, $^{14}$CO$_2$ in the gas phase was only a small fraction of the total gaseous release, due to the pH 13 NaOH solution being effective in retaining carbon dioxide in solution as carbonate. In the pH 7 experiment (Run 4), the amounts of carbon-14 associated with CO and with volatile organic compounds were similar to the baseline cases, but the overall gaseous release was significantly higher due to the CO$_2$ component. About 122 Bq of $^{14}$CO$_2$ was released to the gas phase, compared to only 8Bq as other gaseous components. This represents a fraction of $5 \times 10^{-5}$ of the total graphite inventory released to the gas phase as CO$_2$. Unfortunately, no measurement was made of the solution phase in the pH 7 experiment, but at pH 13 the cumulative fractional release of carbon-14 to solution was $\sim 2 \times 10^{-4}$ after 3 months (Table 12). If similar total amounts were leached from the graphite at pH 7, this would suggest that a significant proportion of the carbon-14 remained in solution. At pH 7 the solubility of carbon dioxide at pH 7 is fairly low\(^\text{[9]}\), so that some of the carbon-14 in solution at this pH may be associated with other chemical forms such as non-volatile organic compounds. Carbon-14 associated with non-volatile organic compounds is likely to remain in solution over the range of pH values occurring in a GDF unless the compounds undergo degradation to lower molecular weight species, which may be more volatile. An analysis of the quantity and forms of organic carbon-14 in graphite leachate solutions would allow a better understanding of the sensitivity of gaseous releases to changes in pH.

### 6.1.3 Comparison with other data sets

The total carbon-14 releases to the gas phase (i.e. the sum of $^{14}$CO$_2$, $^{14}$CO and $^{14}$C-organic species) in each of the six gas-release experiments are compared in Figure 16. Also plotted in Figure 16 are measurements from two previous studies of gas-phase releases from WAGR graphite \([3]\) and BEP0 graphite \([5]\). Other than the effect of alkaline pH compared to neutral pH, it is apparent that the greatest difference in fractional release is seen between different sources of graphite rather than the different experimental conditions. BEP0 was a 6 MWth (MW thermal output) air-cooled experimental reactor, which was commissioned in 1948 and ceased operation in 1968; the graphite sample used in the study reported in reference \([5]\) had thus seen 20 years of operation. Oldbury Reactor 2 was a 434 MWe (MW electrical output) carbon dioxide-cooled Magnox design, commissioned in 1967-68, that continued operation until 2011 (from reference in \(8\)). The Oldbury graphite used in this study was removed in 2005 after 37 years of operation.

It is considered likely that differences between manufactured graphites and their subsequent irradiation history and operating environment (e.g. coolant and operating temperature) could lead to differences in the ratio of the releasable and non-releasable fractions of carbon-14 and possibly in the species present. Radiolytic and general oxidation of graphite is significant in Magnox reactors over their operating lifetimes and is responsible for a decrease in density and an increase in porosity compared to virgin graphite \([14]\). In contrast, BEP0 operated at a much lower temperature and dose rate so that oxidation of graphite would have been much less (from reference in \(14\)).

It has been established through studies of the thermal treatment of irradiated graphites \([15,16,17]\) that carbon-14 is present at higher concentrations on the surfaces of irradiated graphites than in the bulk and as a result it can be selectively removed by heating in an inert atmosphere, air or steam at elevated temperatures (significantly above 400°C). It is possible that carbon-14 on the pore surfaces of reactor graphites would also be removed by processes such as radiolytic oxidation during reactor operation. This would lead to a reduction in the proportion of the carbon-14 on the surfaces of irradiated graphite, compared to that in the graphite matrix, and it is carbon-14 on the surface that is expected to be more readily releasable. Thus differences in the thermal history and

\[ \text{[i]} \] The solubility of carbon dioxide in water with a partial pressure of 1 atmosphere of the gas is $3.4 \times 10^{-5}$ mol dm$^{-3}$ equivalent to a value of Henry's constant $k_{h,cc} = C(\text{aqueous})/ C(\text{gas}) = 0.83$ \([12]\). Henry's constant holds for a lower partial pressure of gas, so at a typical atmospheric CO$_2$ concentration of 400ppm ($= 1.6 \times 10^{-4}$ mol dm$^{-3}$ at 25°C), the solubility of CO$_2$ in water is $1.5 \times 10^{-5}$ mol dm$^{-3}$. In a GDF located 500m below surface, the hydrostatic pressure would be around $5 \times 10^{-5}$ MPa ($\sim$50 atm) \([13]\). A reasonable approximation of CO$_2$ solubility at this pressure can be made by assuming the Henry’s law constant is independent of pressure, i.e. that there will be a 50-fold increase in solubility relative to atmospheric pressure. However, higher temperature and higher ionic strength of the solution will reduce the solubility of CO$_2$. The solubility of carbon dioxide quoted includes its reaction products with water such as HCO$_3$. \[ \text{[ii]} \]
extent of oxidation during reactor operation may affect the fraction of releasable carbon-14 and, together with the difference in coolant, provide a possible explanation for the higher fractional carbon-14 release observed in the experiment with BEPO graphite compared to that in the experiments with Oldbury Magnox graphite.

There is only a limited amount of data available in the literature on the leaching of carbon-14 into solution from irradiated graphite with which to compare the results from the Oldbury graphite, and all of these studies were performed at near-neutral rather than high pH, and under oxic conditions. The leaching of samples from the Hanford C Reactor at temperatures between 25°C and 90°C is reported by Gray and Morgan [18]. Further work by the same authors measured leaching of samples from the French G-2 reactor at Marcoule (samples identified as BA, Sup Nord and Nord Sub graphite) [19]. White et al. provide leaching data for Magnox graphite samples in de-ionised water and a simulated groundwater [20]. The solution leaching data from the Oldbury graphite are co-plotted with these selected data from the literature in Figure 17. In common with the gas release data, the largest variation in leaching rates is between different sources of graphite although effects of temperature and solution composition are also evident.

Figure 16. Total cumulative releases of carbon-14 from Oldbury graphite to the gas phase compared with data for BEP0 and WAGR graphites; error bars show combined uncertainty of carbon-14 content of the graphite and the measurement in the gas phase.
Figure 17. Comparison of carbon-14 solution leaching data for Oldbury graphite with literature data; values for the Magnox graphite presented by White et al. [20] were estimated from their figures.

6.2 Model of carbon-14 release from graphite

6.2.1 Previous mathematical model

Calculations of gas generation in a GDF, have previously been performed with SMOGG v5.1 [21]. This tool uses a simple empirical model for the release of carbon-14 from graphite into the gas phase. The release rate is calculated as [7]:

\[
q_c = k_c A_c(0) M_g e^{-(k_c + \lambda_c) t}
\]  

(1)

where

- \( q_c \) is the release rate of carbon-14 from the graphite [TBq a\(^{-1}\)];
- \( k_c \) is a rate constant for the release of carbon-14 from the graphite [a\(^{-1}\)];
- \( A_c(0) \) is the initial specific activity of the carbon-14 in the graphite [TBq kg\(^{-1}\)];
- \( M_g \) is the mass of graphite present [kg];
- \( \lambda_c \) is the radioactive decay constant for carbon-14 [a\(^{-1}\)];
- \( t \) is the time [a].

The model also allows the carbon-14 release to be divided into two fractions; that released as CO\(_2\) and that released as volatile organic compounds (nominally represented as CH\(_4\)). The SMOGG model provides an option to specify whether CO\(_2\) generated is subsequently released as a gas or retained as carbonate. This model results in a carbon-14 release rate that reduces over time (in proportion to the amount remaining in the graphite), and in eventual release of all carbon-14 in the graphite.

The model requires the following input parameters:

- the initial specific activity of carbon-14 in the graphite;
- the graphite mass;
- the release rate constant; and
- the fraction of carbon-14 released as CO\(_2\) (the remainder is assumed to be released as CH\(_4\)).
As discussed in reference [2], the model was parameterised using very limited data from graphite leaching experiments [4] available at the time and assuming conservatively that 1% of carbon-14 released is in the form of CH$_4$.

6.2.2 Conceptual model based on current work

Examining the data for the cumulative fractional releases (plotted for baseline conditions in Figure 15), we can see that the majority of the carbon-14 release is to the solution phase rather than to the gas phase, broadly in agreement with the parameterisation of the previous model. Where the data differ from the previous model, however, is that, for both gaseous and dissolved releases, there appears to be an initial phase of rapid release followed by a longer-term phase of slower release beyond 28 days. These two phases of release are difficult to fit satisfactorily to a single exponential expression of the form described by Equation (1). An approximate fit could be obtained by setting the parameter $A_c(0)$ in Equation (1) to a small fraction of the initial activity in the graphite, at a value close to the total cumulative release at the end of the experiment. However, this parameterisation of the model assumes that the maximum carbon-14 release, even over timescales of thousands of years, is not significantly higher than the release seen in the one-year experiments, which cannot be justified by the experimental data. The data are better represented as a model with a small fraction of the carbon-14 in a form that is released very rapidly and a larger fraction that is released at a lower rate. The initial release is not of direct relevance to carbon-14 behaviour in a GDF, as it occurs over the first few days. However, it is important in the interpretation of experimental results, in that it needs to be distinguished from the longer-term behaviour in order to derive a release rate for the fraction that is slowly releasable.

The slowly releasable fraction may be the remainder of the carbon-14, but it is also possible that part of the carbon-14 will remain in a stable form that will not be released over timescales before carbon-14 will be reduced to insignificant levels by radioactive decay. Recent work on irradiated graphite from the BEP0 and Magnox Wylfa reactors shows that even under extremely aggressive conditions, such as leaching with a 1 mol dm$^{-3}$ phosphoric acid solution or 1.5 mol dm$^{-3}$ hydrogen peroxide, less than 30% of the carbon-14 could be leached into solution [8]. This suggests that even over the long timescales considered in geological disposal, a significant fraction of the carbon-14 could remain associated with the graphite and so is not releasable.

The experimental data also gave information on the speciation of carbon-14 released to the gas phase and the distribution between the solution and gas phases. This can be represented in the model by allocating fractions of the calculated release to CO, volatile organic compounds, and CO$_2$ and possibly non-volatile organic species. CO$_2$ could be further split into gas and aqueous fractions dependent on pH.

These observations lead to a conceptual model of carbon-14 in graphite in potentially 3 fractions:

1. a rapidly releasable fraction loosely bound to the graphite surface;
2. a slowly releasable fraction that will diffuse with time from the graphite porosity;
3. an essential unreleasable fraction that is bound in the graphite structure.

Carbon-14 released may be in the form of CO or volatile organics which could migrate with a bulk gas phase. Carbon-14 may also be released in the form of CO$_2$ that, depending on the local pH, may dissolve in the cement pore water and may then react with the grout components to precipitate as carbonate. This conceptual model is illustrated in Figure 18.
6.2.3 Revised mathematical model

To accommodate the conceptual model described above in future calculations, the simplest extension to the current model is to split the release rate, \( q_{cc} \), between two terms with the same form as Equation (1), to represent the fractions of carbon-14 undergoing initial fast release and longer-term, slow release, respectively. The following revised mathematical model is proposed:

\[
q_c = \left[ k_{ca} F_{ca} e^{-k_{ca}t} + k_{cc} F_{cc} e^{-k_{cc}t} \right] A_C(0) M_g e^{-A_{L,t}}
\]  

(2)

where

- \( k_{ca} \) is a rate constant for the rapid release of carbon-14 from the graphite \([\text{a}^{-1}]\);
- \( k_{cc} \) is a rate constant for the slower release of carbon-14 from the graphite \([\text{a}^{-1}]\);
- \( F_{ca} \) is the rapidly releasable fraction of carbon-14 in the graphite \([\text{TBq}]\);
- \( F_{cc} \) is the slowly releasable fraction of carbon-14 in the graphite \([\text{TBq}]\).

Note that in this revised model, the rapidly and slowly releasable fractions, \( F_{ca} \) and \( F_{cc} \), may add up to less than one, the remainder representing the non-releasable fraction.

The inputs required for this model would be:

- the initial specific activity of carbon-14 in the graphite;
- the graphite mass;
- the fractions of the carbon-14 activity in the graphite that are available for rapid and slower releases (any remaining fraction will not be releasable);
- rate constants for the rapid release of carbon-14 under the relevant conditions; and
- rate constants for the slower release of carbon-14 under the relevant conditions.

In addition, the releases can be divided between fractions released to the gas and solution phases respectively, and can be divided further between species in each of these phases.

Equation (2) can be integrated, over the time interval \( t = 0 \) to \( t \) giving:

\[
A(t) = \left[ F_{ca} (1 - e^{-k_{ca}t}) + F_{cc} (1 - e^{-k_{cc}t}) \right] A_C(0) M_g e^{-A_{L,t}}
\]

(3)

where \( A(t) \) is the total activity that has been released at time \( t \).

6.2.4 Parameterisation of the model

To provide an illustrative example of parameterisation, the revised model has been fitted to data for Oldbury graphite under baseline conditions.

The value of \( F_{cc} \) (the slowly-releasable fraction) cannot be fitted from the experimental data for Oldbury graphite because, under the conditions used, the timescale for the slow release to approach its maximum value is much longer than the duration of the experiments. However, as discussed above, a maximum leachable fraction can be estimated based on accelerated leaching tests. Reference [8] reported leachable fractions of carbon-14 from powdered irradiated graphite of

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**Figure 18. Schematic diagram of the revised mathematical model.**
up to 27% in 1 mol dm$^{-3}$ HCl solution. However, these conditions are far outside those that may be expected in a GDF and are only achieved in the presence of an oxidant. Leachable fractions from powdered graphite in near-neutral to pH 13 solutions were less than 5% and hence a value of 0.05 has been assigned to $F_{cc}$ for this illustrative parameterisation of the model.

Other model parameters, $k_{ca}$, $k_{cc}$ and $F_{ca}$ have been fitted to the data for solution phase releases from the Oldbury graphite baseline experiments (Run 3b). In all of the experiments, the slowest rates of carbon-14 release were measured during the final sampling period, and therefore $k_{cc}$ was fitted to the release rate in the solution experiment between three months and one year’s leaching. Extrapolation of this fitted release rate to zero time, gave the fraction of total carbon-14 release available for rapid release, $F_{ca}$. The rate of rapid release, $k_{ca}$, was then obtained by fitting to the experimental data. Finally, the fraction of carbon-14 released as volatile species, $f$, was set as 0.01, based on the ratio of total gas phase to solution phase releases (with the dissolved fraction as 0.99 by difference). These fitted parameters are given in Table 14 and the parameterised model for the total gaseous phase release is compared with both the experimental data and the current SMOGG model in Figure 19.

It is stressed here, that the derivation of a set of parameters for use in gas generation codes such as SMOGG [7] needs to take into account the uncertainties in the leaching behaviour of irradiated graphite wastes from different sources and under varying conditions. Therefore, it is envisaged that in a formal parameterisation of a revised model, consideration would be given to a variety of graphite types and leaching conditions and that parameters would be assigned a range of values. Data fitting of the type illustrated here could potentially be applied to the available data sets to provide parameter values for specific graphite types under specific conditions to inform the range of parameter values.

### Table 14. Parameters for the revised model of carbon-14 release from graphite obtained by fitting release data for Oldbury graphite under anoxic, pH 13 conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{ca}$ rate constant for the rapid release</td>
<td>50 a$^{-1}$</td>
</tr>
<tr>
<td>$F_{ca}$ initial rapidly releasable fraction</td>
<td>$1.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>$k_{cc}$ rate constant for the slower release</td>
<td>$2.5 \times 10^{-3}$ a$^{-1}$</td>
</tr>
<tr>
<td>$F_{cc}$ slowly releasable fraction</td>
<td>0.05</td>
</tr>
<tr>
<td>$f$ fraction of carbon-14 released as volatile compounds</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Figure 19. Experimental data and fitted model for gaseous carbon-14 releases from Oldbury graphite under anoxic, high-pH conditions; the current model for carbon-14 release from graphite as parameterised for the recent NDA gas assessment is shown for comparison [21].

6.3 Release of other radionuclides

6.3.1 Tritium

Tritium releases were measured for both the gaseous (Run 2) and aqueous phases (Run 3b). Approximately 0.2% of the tritium inventory was measured in solution after one year and the concentrations still appeared to be increasing at that time (Figure 10(b)). Tritium measurements show a high initial release of HT and volatile tritiated organic compounds, which represents almost 0.1% of the total inventory. After 28 days only low levels of HT and volatile tritiated organic compounds were measured in the gas phase. Lower levels of HTO were also detected. The high levels of HT and volatile tritiated organic compounds measured here were not observed in a similar previous experiment using BEP0 graphite [5, 6], where the majority of tritium in the gas phase was in the form of HTO.

6.3.2 Cobalt-60 and caesium-137

The major isotopes measured in solution by gamma spectrometry were cobalt-60 and caesium-137. Cobalt-60 is derived from activation of stable cobalt-59 present in the original graphite, whereas caesium-137 is a fission product that may be released into the reactor cooling gas by breaches in fuel cladding and be deposited on the surfaces of graphite as a contaminant. These different sources are evident in the differences in homogeneity of the two radionuclides in the graphite (Table 4). Whereas the measured specific activities of cobalt-60 in the four sub-samples of graphite block 635 were similar, those for caesium-137 varied by up to a factor of four.
In common with carbon-14 and tritium, cobalt-60 showed an initial fast release over the first seven days on immersion in water followed by a more gradual release over leaching times of up to one year. About 5-6% of the cobalt-60 content of the graphite was leached into solution over the one year timescale of the three baseline experiments (Table 12 and Table 13). This much higher fractional release of cobalt-60 than for carbon-14 (~0.06% over one year) is broadly consistent with the previous observations of radionuclide leaching from monolith samples of Magnox graphite in water (at 25°C) by White et al. [20], who observed about 2% cobalt-60 release to solution over about 150 days, compared to about 0.1% carbon-14 release over the same period. These findings imply that a higher proportion of the cobalt-60 inventory is readily leachable from the graphite than carbon-14.

Evaluation of the fractional release values for caesium-137 is complicated by the uncertainty in the inventory of caesium-137 in the graphite spacer piece. However, the graphite sample used for the solution release experiment (635 Block 1-3-1) was one of the two from which sub-samples were taken for radionuclide assay (Table 4). If the mean of the two assays for this segment is used, the caesium release is estimated to be about 81% in the first two days of leaching (as opposed to 47% if the mean for all four measurements is used, the case in Figure 14(b)). Clearly, whichever inventory is used, caesium-137 is readily leachable from the graphite. This is consistent with caesium-137 being concentrated on the surface of the graphite block.

After its fast initial release from the graphite in the first two days of leaching, the solution phase activity of caesium-137 was observed to steadily decrease with time and had dropped by about 25% after one year. The decreases observed are significantly greater than the estimated measurement uncertainties. A possible explanation for these observations is that caesium-137 (a soluble cation), located principally on the external surface of the irradiated graphite, is readily dissolved on immersion in water. Subsequently, dissolved caesium-137 diffuses into the porosity of the graphite in the porewater where some of it may be sorbed to the pore surfaces; the net effect is a drop in concentration of caesium-137 in the bulk solution.
7. Conclusions

A set of experiments were carried out principally to measure the rate and speciation of gaseous carbon-14 releases from irradiated Magnox graphite from the Oldbury Reactor 2, immersed in solutions. Some measurements were also made of gaseous tritium release and of the leaching of radionuclides into solution. The main conclusions from this work are as follows.

- Under baseline conditions typical of a cement-based GDF concept (anoxic, under pH 13 solution, ambient temperature), the predominant carbon-14 release was to the solution phase, with about 0.07% of the carbon-14 inventory being released into solution in one year. About 1% of the released carbon-14 was released to the gas phase. The speciation in solution was not determined, but is thought to comprise a mixture of $^{14}$C-carbonate and $^{14}$C-containing organic compounds.

- In all five of the gas-phase release experiments under high-pH conditions, broadly similar levels of total carbon-14 release were observed to the gas phase from each of the five graphite segments on comparable timescales.

- In all seven experiments, for both gaseous and solution-phase release, an initial phase of rapid carbon-14 release was observed, which was followed (beyond about 28 days) by a longer-term phase of slower release.

- Under baseline conditions:
  - an initial rapid release of carbon-14 to the gas phase was observed of ~3 Bq in the first week, which represents ~ $10^{-6}$ of the carbon-14 inventory of the graphite samples;
  - the rates of release decreased with time but detectable quantities of carbon-14 were found in all samples; for the final cumulative sampling period which ran from three to twelve months a release of ~2 Bq was measured;
  - the gaseous carbon-14 was predominantly in the form of hydrocarbons and other volatile organic compounds and CO. The ratio of carbon-14 in organic compounds to CO was approximately 2:1. Less than 2% of the gas-phase release was in the form of $^{14}$CO$_2$.

- When the graphite was powdered, the rapidly releasable fraction of carbon-14 to the gas phase was found to be lower (by a factor of ~2) than from leaching intact segments, whereas the total solution phase release after 91 days was higher (by about 65%). This contrasting behaviour is most likely due to a loss of loosely-bound volatile carbon-14 species during the powdering process, but an overall increase in release rate (release is predominantly to solution), due to the increased surface area of the sample.

- At pH 7, the total carbon-14 release to the gas phase was at least an order of magnitude higher than at pH 13, predominantly as $^{14}$CO$_2$. This is due to the much lower solubility of CO$_2$ at pH 7 than at high pH, where it is predominantly retained in solution as carbonate. In contrast, levels of $^{14}$CO and carbon-14-bearing volatile organic compounds were similar to those measured at pH 13.

- There is some evidence for temperature effects on the release rate for carbon-14. At 50°C initial release was approximately twice that measure in the baseline experiments. The final rate appears to be closer to the baseline value, but this observation is based on a limited set of data.

- Under oxic conditions the total carbon-14 gaseous release rate was similar to the baseline condition values but the ratio of organic compounds to CO was closer to 1:1. The rates of carbon-14 release from Oldbury graphite were significantly lower than those measured previously from irradiated BEP0 graphite under oxic conditions, but the ratio of hydrocarbon / organic species to CO was higher.

- The differences between the fractional releases of carbon-14 from Oldbury and BEP0 graphites are likely to be due to differences between the original graphites, their irradiation histories, operating temperatures and coolant gases. The results of this study do not allow us to determine whether any one of these differences is a dominant effect although a wider comparison of irradiated graphites might.
Based on these experimental observations, an updated conceptual model for carbon-14 release from graphite has been proposed, and a revised mathematical model has been formulated. This model incorporates separate functions for an initial phase of rapid release and a longer-term phase of slower release, together with a recognition that a significant fraction of the inventory is fixed in the graphite matrix and is therefore unavailable for release. Based on data from experiments using a range of leaching techniques the fraction fixed in the graphite is between 5 and 27%. The data obtained in this study for leaching of Oldbury Magnox graphite under anoxic, high-pH conditions have been fitted to illustrate how the model may be parameterised. Results for Oldbury graphite show significant differences to those for other types of graphite, for example that from BEPO and WAGR reactors. These differences may be due to a variety of factors including differences in the composition and manufacture of the original graphites, their irradiation history, operating temperatures and the cooling gas chemistry. Parameterisation of a model for carbon-14 release from the different sources and types of graphite wastes in a GDF would require consideration of all available data to derive a range of parameter values.

Gaseous tritium releases were measured in one of the baseline experiments. A very rapid initial release of predominantly HT and organic-bound tritium was observed which represented ~0.1% of the tritium inventory in the graphite. After one week the rate decreased rapidly, and the subsequent release was primarily in the form of HTO (released from the solution phase by evaporation).

Gamma spectrometry of the leachate solutions showed cobalt-60 and caesium-137 to be the other significant isotopes leached from the Oldbury graphite. Cobalt-60, which appears to be relatively homogeneously distributed through the graphite, was found to be significantly more readily solubilised than carbon-14; about 5-6% of the cobalt-60 inventory was released in one year and its release was still continuing at this point. The leaching behaviour of caesium-137 is more typical of that of a surface contaminant; a high proportion of the caesium-137 was released into solution within the first two days of leaching. However, the solution concentration was observed to decrease steadily thereafter and had dropped by about 25% after one year. A possible explanation for this behaviour is that dissolved caesium-137 (originally concentrated on the external surfaces) had diffused into the porosity of the graphite where it may have been sorbed to pore surfaces.

8. Acknowledgements

The authors thank Steve Williams of NDA RWMD, for his valuable input and advice throughout this study. We also thank Joe Turner and David Baker of AMEC for radiochemical analysis of the leachate solutions and gamma spectrometry of graphite samples, and Jasper Hattink of Inutec for tritium and carbon-14 analysis carried out on the graphite. We thank Magnox for permission to use the irradiated graphite spacer samples and the National Nuclear Laboratory for cutting the samples for the experiments.
9. References


Appendices

Contents

Appendix 1. Analytical Method Tests - Gas Sampling Apparatus
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# Appendix 1
## Analytical Method Tests - Gas Sampling Apparatus

## Contents
- Uptake of $^{14}\text{CO}_2$ on soda lime columns
- Examination of conversion efficiency of the CuO and Pd catalysts
- Summary and conclusions
Analytical Method Tests - Gas Sampling Apparatus

Tests were conducted to measure the efficiency of three principal components of the gas sampling system.

1. Tests to measure the efficiency of the soda lime columns in extracting CO\(_2\) from gas passed through them. Soda lime columns were used in all of the gas sampling units to collect CO\(_2\) from the gas stream. Two methods were used:
   - volumetric tests, which measured the uptake of CO\(_2\) by passing CO\(_2\)-free air dosed with a calibrated quantity of CO\(_2\), through two soda lime columns in sequence. The second column was used to measure any ‘spill over’ from the first;
   - radiometric test, which measured uptake using a mix of labelled \(^{14}\)CO\(_2\) in air.

2. Tests to measure the efficiency of the CuO catalyst in oxidising CO to CO\(_2\), whilst minimising the oxidation of hydrocarbons and other volatile organic species.

3. Tests to measure the efficiency of the Pd catalyst in oxidising hydrocarbon / organic species to CO\(_2\). Methane was used to measure the conversion efficiency because the apparatus is not selective between hydrocarbons and volatile organic compounds.

Uptake of \(^{14}\)CO\(_2\) on soda lime columns

Volumetric tests

Method

The principle of the method was as follows. A measured volume of CO\(_2\), mixed with CO\(_2\)-free air, was passed through two columns in series containing the same quantity of soda lime (30g). This is the same type of column as used in the sampler units and used a constant flow rate similar to that used during routine operation of the sampler units. Each column was then acidified and the CO\(_2\) released was collected separately. Comparison of the volume of CO\(_2\) produced from each column was used to calculate the fraction that was not retained on the first column and thus derive the efficiency of CO\(_2\) uptake.

When used for carbon-14 measurements in the experiments the soda lime is pre-loaded with carbon-14-free CO\(_2\) to provide a sufficient volume of bulk gas for extraction and analysis. This was not done in the volumetric tests, because the pre-loaded CO\(_2\) cannot be distinguished from that collected during the tests, and the test gas contained sufficient CO\(_2\) for handling in analysis. However, pre-humidification of the soda lime was necessary to activate the absorbent (as moisture is required for the absorption reaction). This was achieved by the addition of distilled water in the ratio equivalent to 2.5 cm\(^3\) water per column and homogenisation of the wetted soda lime.

A schematic illustration of the apparatus used is given in Figure A-1. A custom 5 litre flask with side arm was designed to allow the accurate metering of the CO\(_2\) passed through the test columns. The side arm was used for the cryogenic collection of CO\(_2\) during transfer between a vacuum rig and the testing rig. This allowed transfer of a carefully measured quantity of gas from a calibrated vacuum rig facility to the test set up. During the test the flushing gas (CO\(_2\)-free air) purged the test gas into the soda lime columns and after a prescribed flushing time, the residual gas in the flush-flask was returned to the vacuum rig for a precise measurement of the residual CO\(_2\).

Results

The results are presented in Table A-1. The soda lime uptake efficiency given is corrected for the residual CO\(_2\) measured in the flushing vessel. These three tests gave a mean collection efficiency
of 95.9 ± 0.8 %, giving confidence that the sampling apparatus used in the graphite release experiments is effectively collecting carbon-14 in the gas phase for analysis. Spill over to the second soda lime column was less than 2% in all thee tests.

Table A-1. Uptake by soda lime column 1 using the flushing vessel technique.

<table>
<thead>
<tr>
<th>Test</th>
<th>Total volume through soda lime columns (litres)*</th>
<th>Residual CO$_2$ in flushing vessel (%)</th>
<th>Soda lime uptake efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>8.4</td>
<td>95.0</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>7</td>
<td>96.4</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>3.7</td>
<td>96.3</td>
</tr>
</tbody>
</table>

* Volume measured at digital meter and totaliser, see Figure A-1

**Radiometric tests**

An additional measurement was made using carbon-14 labelled CO$_2$ to measure the uptake of CO$_2$ in soda lime columns.

A carbon-14 reference standard was purchased from the National Physical Laboratory (NPL). The standard was supplied as a solution of carbon-14 as sodium carbonate in an aqueous solution of 0.1 mol dm$^{-3}$ sodium hydroxide solution also containing 5 mg g$^{-1}$ of inactive sodium carbonate. A nominal 10g of solution was supplied of activity 1.980 ± 0.032 kBq g$^{-1}$. The following solutions were prepared:

- **Solution A:** a 0.521g aliquot of the NPL standard solution was diluted to 500g in a 0.4M Na$_2$CO$_3$ solution to give a solution of 2.06 ± 0.033 Bq g$^{-1}$;
- **Solution B:** 20 g of the first dilution was made up to 6000 g with a 0.4M Na$_2$CO$_3$ solution to give a bulk standard solution of 0.00688 ± 0.00011 Bq g$^{-1}$.

Dilutions were carried out gravimetrically using an analytical balance for the initial weighing and a 3-figure top pan balance for the larger quantity dilutions.

**Comparison of standards**

Measurements of the carbon-14 activity in three aliquots of the solution B were carried out using RCD’s normal procedure: conversion to benzene followed by liquid scintillation counting. This provided a check on the RCD calibration against the NPL standard. The RCD carbon-14 calibration is directly related to the International Oxalic Acid standard used by radiocarbon laboratories worldwide (and used by ETH Zurich for the measurement of the intrinsic activity of normal soda lime as described in the next paragraph). A fresh sample of the oxalic acid standard was prepared and counted simultaneously with the bulk solution prepared from the NPL standard. The results of RCD’s analysis of the bulk standard are given in Table A-2 and show results using the RCD calibration to be slightly higher than the activity of the NPL standard. The NPL certificated activity of the standard was used in calculations of the $^{14}$C recovery given in Table A-5. If the RCD calibration is used a slightly lower column 1 yield of 93% is calculated.
Figure A-1. Flushing method for transfer of CO$_2$ to the soda lime columns.
Table A-2. RCD analysis of dilution of NPL reference standard (activity 6.88 ± 0.11 Bq/kg).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Measured Value against RCD calibration (Bq/kg ± 2σ)</th>
<th>Difference from calibration certificate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCD-7748</td>
<td>7.18</td>
<td>+ 4.4</td>
</tr>
<tr>
<td>RCD-7747</td>
<td>7.09</td>
<td>+ 3.1</td>
</tr>
<tr>
<td>RCD-7748</td>
<td>7.22</td>
<td>+ 5.0</td>
</tr>
<tr>
<td>Mean Value</td>
<td>7.16 ± 0.14</td>
<td>+ 4.1</td>
</tr>
</tbody>
</table>

Intrinsic carbon-14 activity in soda lime

In normal operation of the gas samplers during the experiments, the soda lime columns used for collection of $^{14}$CO$_2$ were pre-loaded with CO$_2$ to provide a sufficient quantity of carbon for the chemical processing prior to counting. Measurements were required of the background carbon-14 activity of CO$_2$ produced from soda lime. This was done for both untreated soda lime and for soda lime after pre-loading by RCD. This test involved the acidification of ~10g of soda lime and collection of the CO$_2$ produced. For the pre-loaded material, the benzene synthesis method was used for analysis. However, the quantity of CO$_2$ from the untreated soda lime was expected to be too small for the benzene synthesis process and an aliquot of the CO$_2$ obtained was prepared and sent to ETH Zürich Accelerator Mass Spectrometer Laboratory for analysis. (This is one of the laboratories normally used by RCD for samples too small for the benzene synthesis process).

These tests used the same set up as shown in Figure A-1. In common with the volumetric tests, soda lime column 1 was not preloaded with CO$_2$ because the test gas contained a sufficient volume of inactive CO$_2$ carrier to allow sample preparation for LSC analysis by the benzene synthesis route. However, soda lime column 2 was pre-loaded with $^{14}$C-free CO$_2$ because most of the inactive CO$_2$ carrier in the gas was expected to be retained at column 1, giving low bulk CO$_2$ on column 2.

The result of analysis of untreated soda lime and pre-loaded soda lime are given in Table A-3 and Table A-4 respectively. Carbon-14 concentrations are given in units of activity per typical mass of soda lime in a column. For untreated soda lime this is 30g, but for pre-loaded soda lime the equivalent mass is 36g.

Table A-3. Intrinsic carbon-14 activity in new soda lime.

<table>
<thead>
<tr>
<th>RCD Reference</th>
<th>Mass Soda Lime Acidified (g)</th>
<th>Mass carbon produced (g)</th>
<th>$^{14}$C Activity (Bq/30g soda lime *)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCD-7711</td>
<td>10.2</td>
<td>0.0154</td>
<td>0.01</td>
</tr>
</tbody>
</table>

* 30 g is an optimum packing quantity of dry soda lime in the glass columns used on the gas sampler units
Table A-4. Intrinsic carbon-14 activity of pre-loaded soda lime.

<table>
<thead>
<tr>
<th>RCD Reference</th>
<th>Mass Soda Lime Acidified (g)</th>
<th>Mass Carbon Produced (g)</th>
<th>$^{14}$C Activity (Bq/36g soda lime $^*$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCD-7786</td>
<td>36.13</td>
<td>2.20</td>
<td>0.017</td>
</tr>
<tr>
<td>RCD-7788</td>
<td>36.26</td>
<td>2.09</td>
<td>0.014</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td></td>
<td>0.015</td>
</tr>
</tbody>
</table>

* 36g is the normal packing of pre-loaded soda lime in the glass columns

Radiometric test

A $^{14}$CO$_2$ standard was prepared by acidification of an aliquot of the bulk reference standard (solution B, 6.88 Bq kg$^{-1}$), to give a known volume of carbon dioxide with a known carbon-14 activity (3.64 Bq). The $^{14}$CO$_2$ standard was flushed through two soda lime columns in series, using the same apparatus as the volumetric tests, shown in Figure A-1.

For this test the uptake efficiency was measured both by radiometric and volumetric analysis, because the test gas comprised of $^{14}$CO$_2$ with a volume of inactive CO$_2$ carrier. The results in Table A-5 show an efficiency for CO$_2$ uptake on the soda lime columns of $\geq 96\%$, confirming the value determined in the volumetric test (Table A-1).

Table A-5. Yields from radiometric test of soda lime uptake efficiency.

<table>
<thead>
<tr>
<th>Column</th>
<th>Radiometric analysis</th>
<th>Volumetric analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Activity out (Bq)</td>
<td>Yield (%)</td>
</tr>
<tr>
<td>Column 1 (humidified)</td>
<td>3.54 (RCD-7782)</td>
<td>97</td>
</tr>
<tr>
<td>Column 2 (pre-loaded)</td>
<td>0.01 (RCD-7783)</td>
<td>2</td>
</tr>
</tbody>
</table>

1. Not determinable above normal pre-load background variations.

Examination of conversion efficiency of the CuO and Pd catalysts

The aims of these tests were:

- to assess the efficiency in the CuO catalyst in the conversion of CO to CO$_2$;
- to confirm that organic species are not oxidised at the CuO catalyst (but pass through to the Pd catalyst); and
- to assess the efficiency of the Pd catalyst in the conversion of organic species to CO$_2$.

The tests were carried out by RCD using the CO/HT and Hydrocarbon/VOC sampling units prior to use in the graphite leaching experiments. For the first set of tests, an additional soda lime column was inserted in series, after both catalysts for the collection of CO$_2$. The second column was used to check for any carry-over from the first. Calibrated test gases were supplied from canisters: CO in air (100 or 250 ppm) was used to measure the CuO catalyst efficiency; and CH$_4$ in air (2.5%) was used to measure the oxidation of volatile organic compounds at the CuO and Pd catalysts. This system proved successful for the tests using a test gas of 2.5% methane in air, but gave an inconclusive result for the CO oxidation at the CuO catalyst, due to the low CO concentration of the available test gas (100 ppm CO) leading to high statistical uncertainty of the soda lime blank values relative to the small quantity of CO$_2$ produced from the oxidation of CO.
The soda lime columns were therefore replaced with cryogenic (liquid nitrogen) collection traps. The liquid nitrogen traps were connected externally to the sampler units (Figure A-2), but otherwise the sampling apparatus was the same as that to be used in the experiments measuring releases from irradiated graphite. A new supply of CO was obtained at a higher concentration of 250 ppm CO$^{[ii]}$ for the tests using the cryogenic traps.

**Results of CO tests**

In the first cryogenic test for CO the yield in the CO collector was only 65% and it was suspected that the CuO catalyst was not working effectively. It appeared that not all CO was oxidized over the CuO catalyst at 350°C, because some CO$_2$ was captured at the final soda lime column after the Pd catalyst (35% yield, indicating that a large proportion of the CO had passed through the Pd catalyst and was oxidised there). For a second test a fresh charge of CuO catalyst was put into the CO unit.

After refreshing the CuO catalysts, the result showed a distinct improvement in the yield giving 90% of the total collection in the trap following the CuO catalyst, with 3% yield in the trap after the Pd catalyst.

**Results of CH$_4$ tests**

The initial tests using the ‘CO/HT’ and ‘organics’ gas-sampling units with pairs of soda lime columns interposed, gave a collection efficiency for CH$_4$ of 101%. At this stage there appeared to be negligible conversion of CH$_4$ by the CuO catalyst.

In the final test, following the change to cryogenic collection for the CO tests and recharge of the CuO catalyst a repeat test was carried out to check if the results for CH$_4$ could be reproduced. This test gave a 97.9% collection efficiency for CH$_4$ at the Pd catalyst, from 56.3 litres of the 2.5% CH$_4$ gas and less than 2% conversion over the CuO catalyst.

$^{[ii]}$ The CO concentration that could be used was limited by safety considerations.
Figure A-2. Schematic diagram of the CO and CH₄ tests using the units and external cryogenic collectors.
Summary and conclusions

A series of tests were carried out by RCD to build confidence in the methods being applied for the determination of the gaseous carbon-14 release from graphite. The principal results obtained are summarised below.

- The measured efficiency of the standard humidified soda lime column for collection of CO$_2$ was 95.9 ± 0.8% (3 tests, volumetric analysis).
- The yield of the full RCD process for $^{14}$CO$_2$ collection, i.e. from uptake in soda lime to liquid scintillation counting was of ≥96% (1 test, radiometric and volumetric analysis).
- Intrinsic activities of soda lime relative to the quantities used in the collector columns:
  - Soda lime untreated 0.01 Bq/30g;
  - Soda lime pre-treated 0.016 ± 0.002 Bq/36g (2 tests);
- Conversion efficiency of CuO at 350°C to produce CO$_2$ from CO was 90% (1 test).
- Conversion efficiency of CuO at 350°C to produce CO$_2$ from CH$_4$ was <2% (2 tests).
- Conversion efficiency of Pd at 425°C to produce CO$_2$ from CH$_4$ was 97.9% by cryogenic collection and 101% by soda lime collection.

Overall, the results give confidence in the RCD techniques for the assessment of the trace quantities of carbon-14 emanating from irradiated graphite. The least confident result is that for the conversion of CO to CO$_2$ over the CuO catalyst (90% efficiency), this having been derived from only one test with a low concentration CO sample. Before recharging of the CuO, efficiencies of ~60% were measured suggesting there may be some drop of in efficiency with time. However, the results from the tests with methane show that there was no significant oxidation of methane over the CuO catalyst but essentially quantitative oxidation at the Pd catalyst. Thus, any CO not oxidised over CuO would be oxidised over the Pd catalyst and thereby included in the total inventory of gas-phase carbon-14.
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Appendix 2
Analytical Method Tests - Carbon-14 Measurement in Solution
Measurement of carbon-14 in solution

In a previous experimental study of carbon-14 release from BEP0 graphite [5], problems were encountered of poor reproducibility and inconsistent results from the solution phase analysis for carbon-14. The analysis technique involved the conversion of dissolved carbon species in the leachate to CO$_2$ by pyrolysis, the collection of the CO$_2$ in a bubbler containing CarbonTrap® (3-methoxypropylamine) and finally LSC analysis of the resulting bubbler solutions for carbon-14. The concentration of total dissolved carbon in the leachate solution would have been very low, in comparison to solutions usually analysed (e.g. groundwaters). It was suspected that the analysis problems arose because there was insufficient carbon present in the solutions to act as an effective carrier for the low levels of carbon-14 released.

A test was performed to test the reproducibility and quantitative analysis of relatively low-levels $^{14}$CO$_3^2-$ in solution. The aim was to determine if the standard pyrolysis method (used by AMEC Analytical Services) produced better results when additional inactive carbonate was added to act as a carrier.

The stock solution of carbon-14 (1.980±0.032 kBq g$^{-1}$) as sodium carbonate (see Appendix 1) was diluted with 0.1 mol dm$^{-3}$ sodium hydroxide solution also containing 5 mg g$^{-1}$ sodium carbonate to give the following:

- two solutions of ~10 Bq g$^{-1}$ carbon-14
- two solutions of ~20 Bq g$^{-1}$ carbon-14

These solutions were submitted to AMEC Analytical Services for carbon-14 analysis. In addition, the inactive sodium hydroxide/ sodium bicarbonate solution was analysed in duplicate to determine the background carbon-14 content.

Analysis was carried out by combustion of a known mass of sample in a two-stage catalytic pyrolyser (as described for the graphite analysis in Section 2.2.1).

The values for carbon-14 solution concentrations calculated for dilution of the NPL standard and results of analysis are shown in Table A-6.

**Table A-6. Results of carbon-14 analysis of dilutions of standard solution.**

<table>
<thead>
<tr>
<th>$^{14}$C activity added (NPL certified standard value) (Bq g$^{-1}$)</th>
<th>Measured activity (Bq g$^{-1}$)*</th>
<th>Variance from standard (Bq g$^{-1}$)</th>
<th>Variance from standard (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.05 ± 0.16</td>
<td>8.56 ± 0.76</td>
<td>-1.49</td>
<td>-15%</td>
</tr>
<tr>
<td>10.00 ± 0.16</td>
<td>9.04 ± 0.85</td>
<td>-0.96</td>
<td>-10%</td>
</tr>
<tr>
<td>20.11 ± 0.32</td>
<td>17.9 ± 1.7</td>
<td>-2.21</td>
<td>-11%</td>
</tr>
<tr>
<td>20.08 ± 0.32</td>
<td>15.5 ± 1.5</td>
<td>-4.58</td>
<td>-23%</td>
</tr>
<tr>
<td>0.00</td>
<td>&lt;0.024</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>&lt;0.026</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The quoted uncertainties are 2σ standard deviation.

The measured activities of the duplicates at both concentrations are consistent within the quoted uncertainties showing that the method gives reasonable reproducibility after the addition of a carbonate carrier to the solutions. However, the measured activities are consistently lower than the expected values (on average by 15%). Quality control standards of ~31 Bq g$^{-1}$, which are run routinely with samples for this analytical method are generally within ±10% for 90% of runs and
within 5% for 70% of runs. Although the activities measured for the standards were slightly outside the typical uncertainty for this method, the uncertainties were considered acceptable given the low levels being measured. The addition of sodium bicarbonate solution to the leachates before analysis was adopted as a standard protocol before analysis by the pyrolysis method.