

Rate and speciation of volatile carbon-14 and tritium releases from irradiated graphite

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ABSTRACT

The release and migration of gaseous carbon-14 has been identified as a key issue for geological disposal of intermediate-level radioactive wastes in the UK. A significant fraction of carbon-14 in the UK inventory is in irradiated graphite. This paper describes measurements of gaseous carbon-14 releases from irradiated graphite on immersion in alkaline solution. Apparatus has been developed to discriminate organic and inorganic ($^{14}\text{CO}/^{14}\text{CO}_2$) species in the gas phase by means of selective oxidation and capture. In the initial experiment, small amounts of gaseous carbon-14 (~4 Bq) were released from 9 g of crushed graphite within a two-week period. In a long-term experiment, cumulative releases were measured periodically from an intact specimen of graphite over a 14 month period. A small fraction of the graphite carbon-14 inventory was released to the gas phase (~0.004% as CO/CO₂ and ~0.001% associated with organic compounds). A larger quantity of carbon-14, about 0.1%, was released to the solution phase and was thought to be mainly $^{14}\text{CO}_2$, with some possible organic component. In general, the rate of gaseous carbon-14 release decreased with time. The results suggest a small initial release of relatively labile, accessible carbon-14, with longer term release occurring at a much slower rate. Tritium (T) releases were also measured.

KEYWORDS: graphite, carbon-14, tritium.

Introduction

AT present, a number of generic geological disposal concepts for UK radioactive waste are under consideration by the Nuclear Decommissioning Authority (NDA). One concept envisages the placement of packages of conditioned intermediate-level wastes (ILW) and some low-level wastes (LLW) in underground vaults and subsequent backfilling with a cementitious material. The cement backfill forms part of a multi-barrier disposal system that provides

chemical conditioning of the near field to ensure that alkaline, anaerobic conditions are maintained for a long period after the closure of a geological disposal facility (GDF) (Nuclear Decommissioning Authority, 2010a).

The generation of gases from the wastes and the engineered barriers is unavoidable, the principal mechanisms being corrosion, microbial activity and radiolysis (Nuclear Decommissioning Authority, 2010b). The gases may dissolve in groundwaters, but there is also potential for a free gas phase to exist, which could migrate away from the GDF. As well as those gases formed in relative bulk, radioactive gases would include carbon-14 labelled species such as methane and carbon dioxide and tritiated hydrogen and

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methane (Nuclear Decommissioning Authority, 2010b).

Carbon-14 has a sufficiently long half-life (5730 years) for its release to be of relevance after closure of a GDF. Carbon dioxide is expected to be retained within the repository by dissolution and precipitation as calcium carbonate under the alkaline conditions of a cementitious near field and so the $^{14}\text{CO}_2$ that forms is not expected to enter the gas phase. However, some gaseous species containing carbon-14, such as $^{14}\text{CH}_4$ and ^{14}CO , could migrate with bulk gas and may reach the biosphere as gaseous or dissolved species. Tritium (T) has a relatively short half-life (12.3 years), and therefore, information on the release of tritium-containing gases is of interest from the viewpoint of the operational safety of a GDF, but is only significant for a relatively short period post-closure (Nuclear Decommissioning Authority, 2010b).

One possible source of gaseous compounds of carbon-14 and tritium is irradiated graphite. There are significant uncertainties associated with the accessibility of the carbon-14, its chemical form(s), its reactions and the resulting products. These uncertainties make estimation of the rate of release of carbon-14 from irradiated graphite difficult and consequently some cautious assumptions are made. In current performance assessments graphite is predicted to account for a significant fraction of carbon-14 gaseous release over the lifetime of the GDF (Hoch *et al.*, 2008).

Work has been carried out measuring the leaching of carbon-14 from irradiated graphite into solution (Gray *et al.*, 1988, 1989; Takahashi *et al.*, 2001). However, studies of the release of gaseous carbon-14 in a cementitious environment are few. Handy (2006) measured releases from irradiated graphite immersed in a pH 13 solution. Gaseous concentrations were determined by use of a catalyst to oxidize CO, CH₄ and H₂, with the resulting CO₂ and H₂O collected in bubblers containing alkaline solutions, followed by direct liquid scintillation counting. In these experiments some gaseous release was measured in the early stages, but the majority of bubbler solutions had activities below the limit of detection. For the work described here, a method of gas sampling has been developed based on 'dry-bed' soda-lime and silica gel absorbers, which offers lower limits of detection and so has allowed changes in release rates with time to be examined in greater detail. In addition, gas sampling apparatus employing two different catalysts in series has allowed organic

species to be distinguished from inorganic species. The aim of this ongoing study is to gain a more thorough understanding of the release of volatile carbon-14 and tritium species from irradiated graphite under alkaline conditions, to provide the basis for a more realistic treatment in the models used for performance assessment. Two experiments have been undertaken to date: (1) an initial experiment, in which a single measurement was made of total carbon-14 and tritium release from a sample of irradiated graphite powder, on immersion in alkaline solution under air, over a 14 day period; and (2) a second, long-term experiment in which measurements of carbon-14 and tritium releases from a block of irradiated graphite immersed in alkaline solution under air, were made periodically over 14 months, to allow changes in release rates with time to be measured. For this experiment, the sampling apparatus was modified to allow discrimination between $^{14}\text{CO}_2$ / ^{14}CO and organically bound carbon-14 and also between HT and tritium derived from organic compounds. Both experiments were carried out at the ambient laboratory temperature.

Experimental methodology

Outline procedure

The experimental apparatus consisted of a scrubber unit to remove CO₂ and H₂O from the incoming air stream, a reaction vessel containing the graphite and gas sampling units. A schematic diagram of the apparatus is shown in Fig. 1. Air was drawn through the reaction vessel, which contained the graphite immersed in an alkaline solution. The air then passed to the gas-sampling units. The design of the gas samplers was based on dry-bed absorber systems, which allow the selective oxidation and capture of carbon-14 and tritium species released to the gas phase, and is described in more detail below.

Materials

For the initial experiment a 9 g sample of core graphite from the Windscale advanced gas-cooled reactor (WAGR) was used. The graphite was crushed to a fine powder immediately prior to being placed in the reaction vessel. No analysis was carried out on this sample, but a typical radionuclide inventory for WAGR core graphite is provided in Table 1.

For the long-term experiment a block of BEPO (British experimental pile '0') graphite, mass

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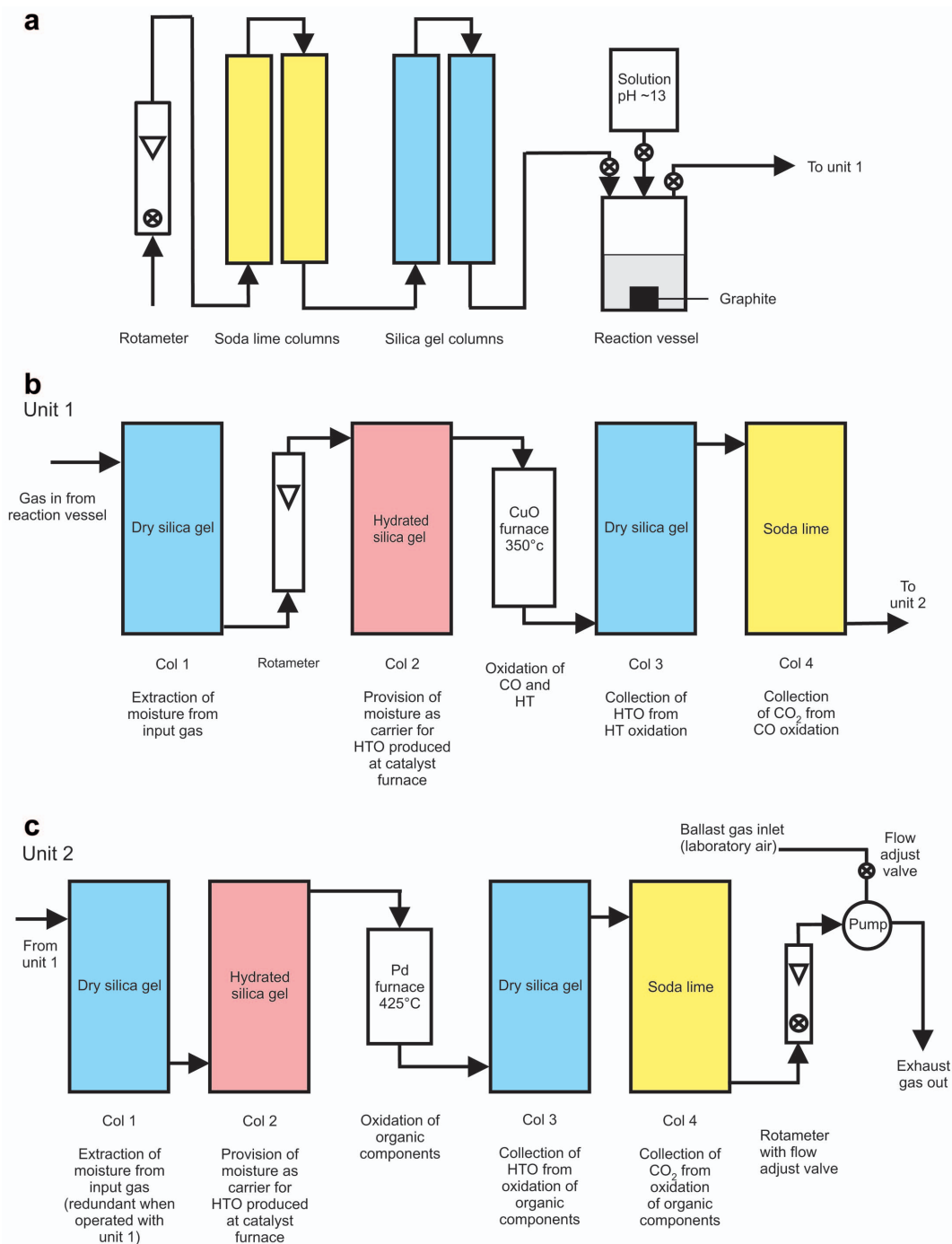


FIG. 1. Schematic diagram of the experimental design. (a) Pre-conditioning columns and reaction vessel. (b) First gas-sampling unit. (c) Second gas-sampling unit.

TABLE 1. Typical radionuclide inventory for WAGR core graphite.

Radionuclide inventory	(Bq per 10 g sample)
^3H	4×10^6
^{14}C	1×10^6
^{36}Cl	2×10^4
^{54}Mn	trace
^{60}Co	1×10^5
^{63}Ni	2×10^5
^{94}Nb	trace
^{152}Eu	9×10^1
^{154}Eu	1×10^5

148 g, was made available. It was taken from an original four-inch cylindrical section cored from the air-cooled reactor at Harwell in 1975. An intact sample of mass 58.6 g, and approximate geometric surface area 250 cm², was taken for use in the experiment and two further non-adjacent samples of 10 g each were taken from the block for determination of carbon-14 and tritium content.

Gas sampling system and analysis

The gas sampling system design was based on apparatus developed for ^3H , ^{14}C and ^{35}S speciation studies of discharges from nuclear establishments (Otle *et al.*, 1992) and for tritium discharge monitoring in use at the JET4 Joint Undertaking facilities (Walker *et al.*, 1998). In the initial experiment, gas passed directly from the reaction vessel to the second of the two sampling units shown in Fig. 1. With this method of sampling, the total gas phase release of carbon-14 was measured, without discrimination of the different volatile species. In the case of tritium, only HTO was discriminated from other volatile species. An additional unit was added in series before the existing unit for the second, long-term experiment to allow ^{14}C to be separated from ^{14}C -organic compounds and for HTO, HT and tritiated organic compounds to be collected and analysed separately.

The sequence of columns, in the first sampling unit is shown in Fig. 1b. Tritiated water was collected on the first silica gel column. The gas was then re-humidified by passing it over silica gel, charged with tritium-free water, in column 2.

Conversion of CO to CO₂ and HT to HTO was achieved by passage over a copper oxide catalyst at 350°C. This temperature was chosen to minimize oxidation of organic components at this stage. The HTO generated by oxidation of HT was collected on silica gel column 3 (re-humidification at column 2 was necessary to provide sufficient volume of H₂O carrier, for efficient collection on column 3). Column 4 contained soda lime for the collection of the carbon dioxide as $^{14}\text{CO}_2$ (from oxidation of ^{14}CO over the catalyst and possibly $^{14}\text{CO}_2$ not retained in the alkaline solution).

The gas then passed to the second sampling unit shown in Fig. 1c. 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 first sampler this column was redundant and so was not analysed. The gas was re-humidified at column 2. Conversion of the organic components was achieved by passing the gas over a palladium catalyst at 425°C. The HTO generated from the oxidation of tritiated organics was collected on column 3. Column 4 contained soda lime for the collection of $^{14}\text{CO}_2$ from the oxidation of carbon-14-containing organic components.

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 second 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 dm³ min⁻¹ with only a proportion (~200 cm³ min⁻¹) drawn through the reaction vessel and columns.

The 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. Absorbed water was extracted from the silica gel by distillation in a vacuum vessel for two hours at 105°C. The extracted water was then collected in a double trap system cooled to -78°C with a solid carbon dioxide/acetone mixture. Absorbed CO₂ was

extracted from the soda lime by acidification. The CO₂ gas collected was then converted to benzene via lithium carbide and acetylene. The benzene produced was mixed with a proprietary scintillant. Tritium and carbon-14 activities were determined by liquid scintillation counting (LSC) using a Wallac Quantalus instrument calibrated against standard samples.

Procedure

For the initial experiment, the graphite was immersed in 250 cm³ of an alkaline solution, of sodium/potassium/calcium hydroxide (0.024, 0.048, 0.019 mol dm⁻³, respectively). The composition of the solution was designed to simulate that of a typical waste encapsulation grout porewater. The reaction vessel was continuously flushed with air for the duration of the experiment. Background levels of carbon-14 and tritium were measured immediately prior to the initial experiment using the same procedure, but with no graphite present in the reaction vessel.

In the long-term experiment a solid graphite block was submerged in 300 cm³ of 0.1 mol dm⁻³ sodium hydroxide, rather than the sodium/potassium/calcium hydroxide solution used in the initial experiment, to avoid the possibility of calcium carbonate precipitation. Sampling columns were changed and analysed after 1, 3, 7, 28, 66 and 431 days. The sampling pump was operated continuously for the first 7 days. After this the reaction vessel containing the graphite was flushed with gas for periods of 6 to 8 hours each week. At other times the reaction vessel was sealed.

In all experiments, including the background determination, the air passed through soda lime and silica gel columns before entering the reaction vessel, to remove carbon dioxide and water (thus extracting any ¹⁴CO₂ and HTO that may have been present in the laboratory atmosphere). All solutions were made up in low tritium-content demineralized water and prepared in a nitrogen atmosphere glove box, to minimize the dissolution of atmospheric carbon dioxide.

Graphite analysis

Two non-adjacent samples were cut from each of the fresh and leached portions of the BEPO graphite segment. Each sample was ~10 g in mass. Sub samples of ~2 g were taken from each

for carbon-14 or tritium analysis, to determine activities in the graphite pre- and post-leaching. Carbon-14 analysis was carried out by heating to 850°C in the presence of a catalyst to convert carbon to CO₂, which was collected in a bubbler trap containing Carbo-sorb and counted by LSC. Tritium was analysed by heating to 850°C in the presence of a catalyst to convert tritium species to HTO. The HTO was collected in a series of water traps, the contents of which were distilled to remove interfering radionuclides and analysed for tritium by LSC.

Solution analysis

After the leaching experiments, the reaction vessel solution was filtered to 0.45 µm and then to 10,000 nominal molecular weight cut-off (nMWCO). The filtrates were analysed for tritium (by distillation and LSC) and carbon-14 (by pyrolysis and LSC).

To estimate the fraction of carbon-14 present in solution as inorganic species an aliquot of the 10,000 nMWCO filtrate was acidified and the ¹⁴CO₂ collected into a bulk volume of low-¹⁴C-content CO₂. This dilution was necessary to provide sufficient quantity for subsequent conversion to benzene via lithium carbide and acetylene. The benzene was then mixed with scintillant and carbon-14 determined by LSC on a Wallac Quantalus instrument.

Results and discussion

Graphite radionuclide content

Results from analysis of the BEPO graphite samples are given in Table 2. The range of values is greater than would be expected from the analysis uncertainties alone, suggesting that within the sample segment (mass 148 g) the distribution may not be homogenous. For the purposes of calculating the inventory in the experiment, the mean of the four sample values (two pre-leaching and two post-leaching) was used to derive a specific activity. This ignores the activity removed from the leached samples, but the error introduced is negligible compared to the overall uncertainty. As inclusion of the leached samples increases the mean values, this is considered to be more representative than mean values based on unleached material only. This gives a total carbon-14 inventory in the 58.6 g of graphite used in the experiment of 2.1±0.2 MBq and a tritium inventory of 8.2±0.4 MBq.

TABLE 2. Specific activities for tritium and ^{14}C in BEPO graphite.

Sample	^{14}C (Bq g $^{-1}$)*	Tritium (Bq g $^{-1}$)*
Unleached 1	$3.21 \times 10^4 \pm 0.16 \times 10^4$	$2.03 \times 10^4 \pm 0.36 \times 10^4$
Unleached 2	$3.41 \times 10^4 \pm 0.18 \times 10^4$	$5.97 \times 10^3 \pm 0.95 \times 10^3$
Leached 1	$4.05 \times 10^4 \pm 0.20 \times 10^4$	$1.66 \times 10^4 \pm 0.27 \times 10^4$
Leached 2	$3.86 \times 10^4 \pm 0.20 \times 10^4$	$1.29 \times 10^4 \pm 0.21 \times 10^4$

* Errors represent 2σ counting uncertainties.

Background measurements

The background levels of carbon-14 and tritium in the laboratory air (after removal of any $^{14}\text{CO}_2$ and HTO prior to passing into the reaction vessel) were below detection limits of 0.03 Bq and 0.2 Bq, respectively. These background levels equate to $<9 \times 10^{-5}$ Bq h $^{-1}$ for tritium and $<6 \times 10^{-4}$ Bq h $^{-1}$ for carbon-14. To calculate the background for each sampling period, the running time (i.e. the time gas was being drawn through the reaction vessel) was multiplied by the Bq h $^{-1}$ value. As, the background levels were calculated from limits of detection, they may be overestimated, but because they are only a small fraction of the activity measured, this has no impact on the results presented.

Releases to the gas phase

In the initial experiment with WAGR graphite, over the two-week (336 hour) duration, 3.6 ± 0.2 Bq of carbon-14 were measured in the gas phase. Only the second gas sampling unit was used in this experiment, so the carbon-14 detected would be from both CO and organic species. In addition,

11 ± 0.6 Bq of tritium derived from HT and tritiated hydrocarbon gases, was released from the graphite and captured on column 3; 60 ± 4 Bq of tritium as HTO vapour was also collected in the experiment. This represents a lower-bound value for the quantity of HTO released from the graphite, as some would remain in the aqueous phase. The tritium content of the water in the reaction vessel at the end of this experiment was not determined. The quantity of $^{14}\text{CO}_2$ released from the irradiated graphite and retained in the reaction vessel was also not determined. Although the elapsed time between crushing the graphite sample and adding to the reaction vessel was kept to a minimum, it is possible that gaseous carbon-14 or tritium-containing species trapped in closed porosity in the graphite may be lost immediately on crushing before the crushed sample was added to the reaction vessel, as has been suggested by results from similar experiments (Handy, 2006).

The carbon-14 measurements in the gas phase for the long-term experiment with BEPO graphite are shown in Table 3 and tritium measurements in Table 4. The long-term experiment ran for a total of 431 days, over which 87.5 Bq of ^{14}CO and

TABLE 3. Carbon 14 average release rates into gas phase from BEPO graphite.

Sampling period (h)	Average release rate (Bq h $^{-1}$)		
	CO*	Organic*	CO + organic
0–23	0.0404 \pm 0.0004	0.0161 \pm 0.0001	0.0565 \pm 0.0005
23–71	0.0494 \pm 0.0004	0.0177 \pm 0.0002	0.0671 \pm 0.0005
71–169	0.0434 \pm 0.0005	0.0138 \pm 0.0001	0.0572 \pm 0.0005
169–672	0.0310 \pm 0.0003	0.00674 \pm 0.00006	0.0377 \pm 0.0003
672–1584	0.0167 \pm 0.0001	0.00643 \pm 0.00004	0.0231 \pm 0.0001
1584–10344	0.00562 \pm 0.00004	0.00148 \pm 0.00001	0.00710 \pm 0.00005

* Errors represent 2σ counting uncertainties.

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TABLE 4. Tritium average release rates into gas phase from BEPO graphite.

Sampling period (h)	Average release rate (Bq h ⁻¹)		
	HTO*	HT*	Organic*
0–23	0.109±0.004	0.066±0.003	0.0313±0.0041
23–71	0.646±0.020	0.068±0.002	0.0376±0.0029
71–169	0.905±0.028	0.045±0.0010	0.0225±0.0024
169–672	0.077±0.002	0.011±0.0004	0.0070±0.0005
672–1584	0.088±0.003	0.0025±0.0001	0.0044±0.0002
1584–10344	0.337±0.010	0.0018±0.0001	0.0009±0.0001

* Errors represent 2σ counting uncertainties.

24.8 Bq of organic carbon-14 were released into the gas phase. The ratio of ¹⁴CO to organic ¹⁴C remained similar for each sampling period at values between 2.5 and 3.9. Tritium released in the gas phase over the same period totalled 3244 Bq, of which 98.4% was as HTO, with 1.0% HT and 0.6% associated with organically bound tritium.

Average (linear) release rates for carbon-14 and tritium were calculated, by dividing the activity measured by the sampling period. These are shown in Tables 3 and 4. It can be seen that generally these rates were high in the initial stages, with the maximum over the 23 to 71 hour period, then steadily decreasing. For example, the total carbon-14 release rate was 0.67 Bq h⁻¹ in the initial period and 0.007 Bq h⁻¹ in the final period. The exception to these trends is the release of tritium as HTO, where the rate is high over the final period. This is to be expected. Whereas most of the gas phase species collected (CO, H₂, low molecular weight hydrocarbons) are volatile and so would rapidly partition predominantly into the gaseous phase during flushing of the reaction vessel headspace, the majority of the tritiated water would remain in the aqueous phase with only a small fraction released as vapour. Therefore, the quantity of HTO collected on the sampling column would be a function of the time gas was flushed through the reaction vessel as well as the HTO/H₂O ratio.

The rate of carbon-14 release generally decreased with time and the plot of activity released *versus* time was found to correspond fairly well to an exponential function:

$$a(t) = Af(1 - e^{-kt}) \quad (1)$$

where a is the total activity released up to time t ; A is the initial activity in the graphite; and f and k are fitted parameters.

Differentiation of equation 1 gives the rate of release:

$$\frac{da}{dt} = Afke^{kt} \quad (2)$$

Fitting of the experimental data for carbon-14 release to equation 1, using the solver function in *Microsoft Excel* with the least squares method, gave a reasonable fit as shown in Fig. 2. The model represents a first-order reaction for the release, with rate constant, k . Conceptually, f can be thought of as the fraction of total activity that may potentially be released to the gas phase; f may be simply a proportion of the total carbon-14 content of the graphite. However, it may depend on other factors. For example, if the carbon-14 release measured in the experiment was predominantly from that on the graphite surface, then the surface area may be a factor. It may also be dependent on the ease with which the graphite porosity can be accessed by the solution.

The results for release of HT and tritiated organic compounds to the gas phase were fitted to the model described by equation 1 and plots are shown in Fig. 3. The model appears to underestimate the initial gaseous release rates, but provides an approximate fit overall. As discussed above, the measured gaseous HTO releases depend upon the headspace flushing time so would not be expected to fit this function and are not included in the plot.

At this stage the model is based on limited data and further work is required to confirm the trends observed and reduce the uncertainty in the derived parameters. It should also be remembered that although this model represents release over 14 months it may not be appropriate for estimating behaviour over significantly longer periods.

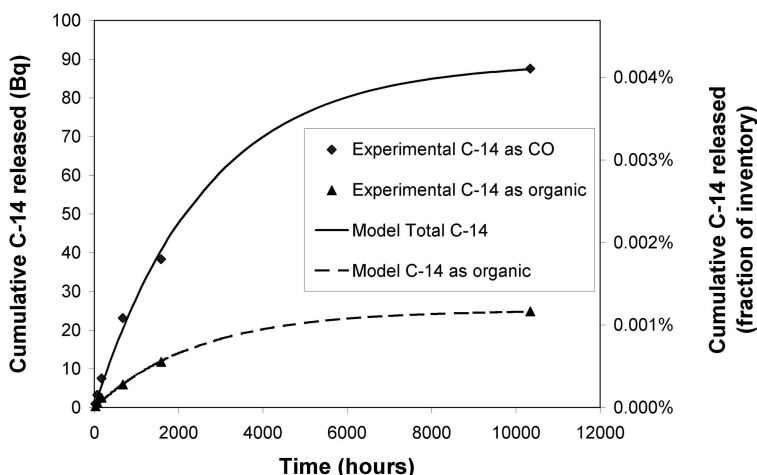


FIG. 2. The ^{14}CO and ^{14}C -organic release from graphite. Model CO parameters: $f = 4.2 \times 10^{-5}$, $k = 3.8 \times 10^{-4} \text{ h}^{-1}$. Model organic parameters: $f = 1.2 \times 10^{-5}$, $k = 4.1 \times 10^{-4} \text{ h}^{-1}$.

Equation 1 predicts that the cumulative carbon-14 released would never exceed Af and equation 2 requires that values for da/dt be close to zero, when t is high. However, it is possible that the trend observed represents the behaviour of a small labile fraction of the carbon-14 inventory (e.g. that associated with sorbed species on the graphite surface). Carbon-14 bound more strongly or held in the graphite lattice may be released at much slower rates, but in the early stages would be a small fraction of the total release and would therefore have no significant influence on the shape of the plot of release *versus* time. At longer

timescales, when this labile fraction is no longer a significant proportion, a different function may dominate the overall carbon-14 release. This could only be confirmed by making more measurements at longer timescales.

Releases to the aqueous phase

Radionuclide concentrations in the alkaline solution were not measured in the initial experiment. From sampling at the end of the long-term experiment the carbon-14 inventory in solution was determined as $2.1 \pm 0.1 \text{ kBq}$ for both

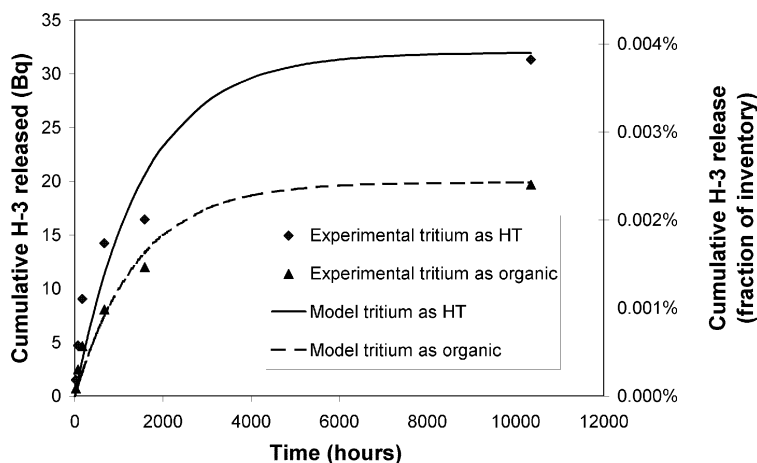


FIG. 3. Comparison of HT and organic tritium results with model. Model HT parameters: $f = 3.9 \times 10^{-5}$, $k = 6.5 \times 10^{-4} \text{ h}^{-1}$. Model organic parameters: $f = 2.4 \times 10^{-5}$, $k = 7.0 \times 10^{-4} \text{ h}^{-1}$.

0.45 μm and 10,000 nMWCO filtered samples; 720 ± 21 Bq of carbon-14 remained in solution after acidification and 1050 ± 51 Bq were measured in the gas released. These results indicate that some ^{14}C may be associated with organic material that is retained in solution, although a quantitative recovery of $^{14}\text{CO}_2$ released was not achieved.

The majority of the tritium released from the graphite remained in the aqueous phase, with 19 kBq in the solution at the end of the long-term experiment and is assumed to be predominantly in the form of HTO.

Comparison with previous studies

In the initial experiment, 4 Bq of carbon-14 was generated as gas, over a period of 14 days, from crushed WAGR graphite containing ~ 1 MBq of carbon-14. To enable comparison, this may be expressed as a linear function over the sampling period, giving an average release rate as a fraction of the graphite inventory of $1 \times 10^{-4} \text{ yr}^{-1}$. In the long-term experiment the highest release rate measured was $2 \times 10^{-4} \text{ yr}^{-1}$, which decreased to $3 \times 10^{-5} \text{ yr}^{-1}$, in the final sampling period. Handy (2006) also measured gaseous releases from WAGR graphite under similar conditions. A release rate for carbon-14 of $6 \times 10^{-4} \text{ yr}^{-1}$ over the first 7 days is reported. Subsequent measurements were below or close to the limit of detection of $\sim 4 \times 10^{-4} \text{ yr}^{-1}$.

The initial experiment also measured $7.9 \times 10^{-5} \text{ yr}^{-1}$ of tritium release attributed to

HT and tritiated hydrocarbons. In the long-term experiment, the maximum HT/hydrocarbon release rate was $2.3 \times 10^{-2} \text{ yr}^{-1}$ and the release rate decreased with time to $2.9 \times 10^{-4} \text{ yr}^{-1}$ during the final sampling period. Handy (2006) measured a release rate of 0.2 yr^{-1} for HT and tritiated hydrocarbons for an intact sample of graphite which was not seen for the crushed graphite. Subsequent measurements were close to or below the detection limits of $\sim 2 \times 10^{-4} \text{ yr}^{-1}$.

Summary

The final distributions of tritium and carbon-14 measured in the experiments are summarized in Table 5. As noted in the preceding text, there is some uncertainty associated with the measurements of the total carbon-14 and tritium in the BEPO graphite, as the analysis results suggest the distribution may be inhomogeneous.

The release of tritium is dominated by HTO, with less than 2% of the gaseous tritium measured attributable to HT and organic compounds. The results show that a significant fraction ($>2\%$) of the tritium initially present in the graphite was leached into solution, and is probably present as HTO. The gaseous tritium release in the experiments would then primarily be by HTO evaporation.

Conclusions

In experiments contacting irradiated graphite samples with alkaline solutions, the rate of

TABLE 5. Summary of the final distribution of tritium and ^{14}C in the long-term experiment with BEPO graphite.

Fraction	Attributed species	Activity (Bq)	Fraction of inventory
Estimate in graphite $^{14}\text{C}^*$		$2.1 \times 10^6 \pm 0.2 \times 10^6$	
Estimate in graphite $^3\text{H}^*$		$8.2 \times 10^5 \pm 3.6 \times 10^5$	
Aqueous [†]	$^{14}\text{CO}_2$	2145 ± 73	0.10%
Column 4, unit 1 [†]	^{14}CO	87.5 ± 1.8	0.004%
Column 4, unit 2 [†]	organic ^{14}C	24.8 ± 0.4	0.001%
Aqueous [†]	HTO	$1.9 \times 10^4 \pm 0.1 \times 10^4$	2.30%
Column 1, unit 1 [†]	HTO as vapour	3192 ± 184	0.39%
Column 3, unit 1 [†]	HT	32.8 ± 1.2	0.004%
Column 3, unit 2 [†]	organic tritium	20.5 ± 0.6	0.002%

* Errors represent standard deviation on 4 samples.

† Errors represent 2σ counting uncertainties.

release of carbon-14 into the gas phase generally decreased with time. The highest release rate measured was 24 Bq day⁻¹ per kg graphite, which decreased to 3 Bq day⁻¹ per kg over the final sampling period (based on the assumption of a linear release rate over the sampling period). The lower value is thought to represent an upper bound for the release rate over the longer term and is probably a considerable overestimate. The total carbon-14 released in the gaseous phase as ¹⁴CO/¹⁴CO₂ represented approximately 0.004% of the estimated total inventory, with a further 0.001% associated with organic species. The carbon-14 released from the graphite and retained in solution was 0.10% of the estimated total inventory and this appears to consist of both dissolved ¹⁴CO₂ and organic species.

Although the experiments were primarily designed to measure carbon-14 gaseous releases, the apparatus also allowed the measurement of tritium. The tritium released was dominated by HTO, with 2.3% of the total inventory in the aqueous phase and a further 0.4% as gaseous HTO, via evaporation from the aqueous phase; HT and organic tritium were also measured in the gas phase but together represented only 0.006% of the total inventory. Thus the release of tritium into the gaseous phase was predominantly as HTO through purging of the headspace. Evaporation may occur quite differently from packaged waste, where the graphite would be encapsulated in cement, in vented containers. Therefore, HTO release rates measured in this experiment are probably of limited relevance to HTO release during package storage or pre-closure operations in a GDF.

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References

- Gray, W.J. and Morgan, W.C. (1988) *Leaching of ¹⁴C and ³⁶Cl from Hanford Reactor Graphite*. Pacific Northwest Laboratory Report PNL-6769.
- Gray, W.J. and Morgan, W.C. (1989) *Leaching of ¹⁴C and ³⁶Cl from Irradiated French Graphite*. Pacific Northwest Laboratory Report PNL-6989.
- Handy, B.J. (2006) *Experimental study of C-14 and H-3 Release from irradiated graphite spigot samples in alkaline solution*. NNC Report 11996/TR/001.*
- Hoch, A.R., Thorne, M.C., Swift, B.T. and Bate, F. (2008) *Update of the GPA (03) assessment of the consequences of gas*. Serco Report SA/ENV-0948 Issue 2, August 2008.*
- Nuclear Decommissioning Authority (2010a) *Geological disposal – Near-field Evolution Status Report*. RWMD Report NDA/RWMD/033.*
- Nuclear Decommissioning Authority (2010b) *Geological disposal – Gas Status Report*. NDA Report NDA/RWMD/037.*
- Otlet, R.L., Walker, A.J. and Caldwell-Nichols, C.J. (1992) Practical environmental, working area and stack discharge samplers, passive and dynamic, for the measurement of tritium as HTO and HT. *Fusion Technology*, **21**, 550–555.
- Takahashi, R., Toyahara, M., Maruki, S. and Ueda, H. (2001) Investigation of morphology and impurity of nuclear grade graphite, and leaching mechanism of carbon-14. In: *Nuclear Graphite Waste Management*. Proceedings of a Technical Committee meeting held in Manchester, United Kingdom, 18-20 October 1999. International Atomic Energy Agency, Vienna.
- Walker, A.J. and Otlet, R.L. (1998) Studies on gaseous species of tritium and carbon-14 in environmental air around nuclear establishments. Pp. 159–169 in: *Environmental Radiochemical Analysis* (G.W.A. Newton, editor). Royal Society of Chemistry, London.
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