



The requirement for proper storage of nuclear and related decommissioning samples to safeguard accuracy of tritium data

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ABSTRACT

Large volumes of potentially tritium-contaminated waste materials are generated during nuclear decommissioning that require accurate characterisation prior to final waste sentencing. The practice of initially determining a radionuclide waste fingerprint for materials from an operational area is often used to save time and money but tritium cannot be included because of its tendency to be chemically mobile. This mobility demands a specific measurement for tritium and also poses a challenge in terms of sampling, storage and reliable analysis. This study shows that the extent of any tritium redistribution during storage will depend on its form or speciation and the physical conditions of storage. Any weakly or moderately bound tritium (e.g. adsorbed water, waters of hydration or crystallisation) may be variably lost at temperatures over the range 100–300 °C whereas for more strongly bound tritium (e.g. chemically bound or held in mineral lattices) the liberation temperature can be delayed up to 800 °C. For tritium that is weakly held the emanation behaviour at different temperatures becomes particularly important. The degree of ³H loss and cross-contamination that can arise after sampling and before analysis can be reduced by appropriate storage. Storing samples in vapour tight containers at the point of sampling, the use of triple enclosures, segregating high activity samples and using a freezer all lead to good analytical practice.

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1. Introduction

A wide range of early generation nuclear facilities (military and civilian) are undergoing decommissioning throughout the world. These include civil nuclear power plants, research reactors, isotope production plants, experimental fusion facilities, particle accelerators and isotopic enrichment facilities. In the UK for example, most first- and second-generation nuclear research sites and nuclear power plants are either being decommissioned or are scheduled to begin decommissioning within the next decade. Decommissioning strategies vary from site to site but typically involve the extensive clean out and demolition of buildings and other facilities and remediation of the land. In many instances, novel radioanalytical approaches must be developed and validated to permit accurate quantification of radionuclides in diverse and complex matrixes. Concrete, cements, and other cementitious materials account for 22% of the total weight of low-level radioactive waste and 12% of the total weight of intermediate-level waste in the UK. Large volumes of potentially radioactive waste materials are generated during nuclear decommissioning that require

accurate characterisation prior to final waste sentencing. One of the radionuclides often widely disseminated is tritium. Estimates of ³H inventories require specific measurement as the nuclide is highly mobile and therefore cannot be reliably linked to a waste fingerprint. Such fingerprints are obtained by intrusively taking and analysing a range of samples in an operational area to identify all the radionuclides and to determine the ratios of their activities relative to easily measurable ¹³⁷Cs, ⁶⁰Co and ¹⁹²Ir. Fingerprints serve to mitigate decommissioning costs by reducing the need for wholesale, expensive radioanalytical work on every sample but are only effective for radionuclides that are chemically immobile. The potential mobility of tritium in different materials will depend on its speciation and will have an impact on sampling and storage [1].

Tritium exists as tritiated water (HTO) at many nuclear sites and can be produced in situ in construction materials through neutron induced reactions and ternary fission (fission yield <0.01%). At other sites (e.g. radiopharmaceutical laboratories) tritium may contaminate building and other materials via tritiation [2–6] or through accidental spillages of synthesised tritiated organic compounds onto floors or other surfaces (often called organically bound tritium OBT). The nuclide will interact with a range of construction and associated materials (e.g. structural concrete and metals) and become incorporated into the fabric of the materials via physical absorption, diffusion and isotope exchange [2–8]. The magnitude

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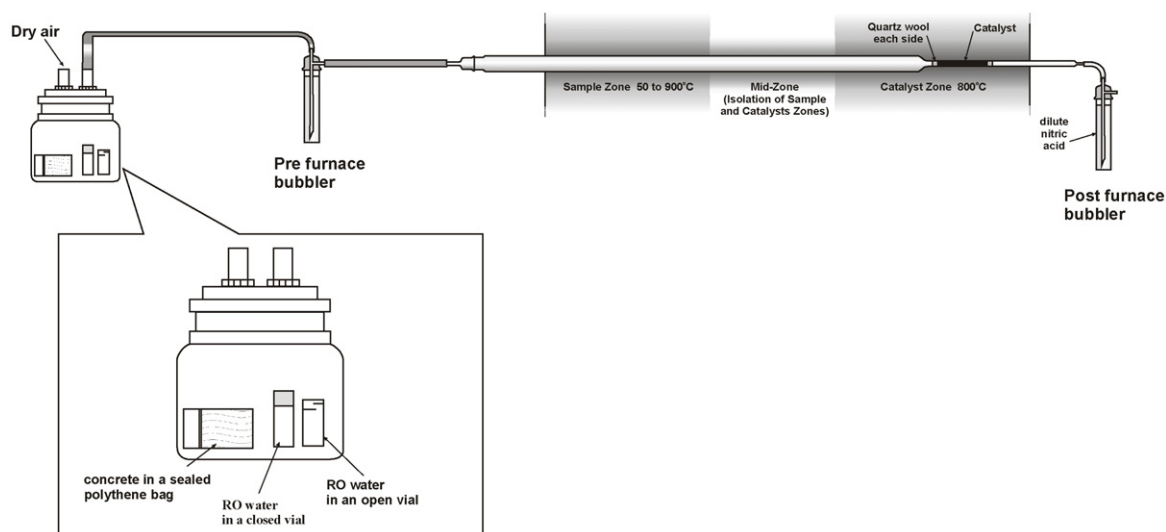


Fig. 1. Apparatus used to determine ^3H in water vapour following storage of ^3H -contaminated materials.

of ^3H incorporation will depend on a wide range of factors including the concentration and form of tritium, the exposure period, humidity, pressure and temperature, as well as the surface structure and composition of the exposed materials.

During decommissioning of a nuclear facility, large volumes of ^3H -contaminated wastes (e.g. concrete, asbestos, wood, desiccants, reactor metal work, graphite blocks and tiles, soft wastes, etc.) are generated which must be characterised prior to waste sentencing. The critical stages in waste characterisation for ^3H contamination include sample collection, packaging, transfer to the analytical laboratory, storage prior to analysis and quantification of the analyte. The accuracy of the final ^3H measurement is dependent on effective controls at every stage of the sampling and analysis process to prevent loss of ^3H and cross contamination between samples. In terms of ^3H loss, the rate of ^3H off-gassing is affected by ^3H form, mode of association with the sample matrix, temperature and degree of containment, whilst cross contamination is in addition controlled by the rate of ^3H uptake on the receptor material. An understanding of factors controlling the rate of ^3H off-gassing and ^3H adsorption on non-contaminated materials is therefore essential. Tritium adsorption [9], diffusion [2,3,5–9] and release rates [6,10–15] have been previously reported for a range of materials and Furuichi et al. [9] noted that loss of tritiated water may occur during sampling by drilling if excessive heat is generated. However, to date there has been no attempt to evaluate the importance of the form of ^3H , storage temperature, and materials composition on ^3H loss and cross-contamination rates and to assess the impact that this may have on protocols for sample preservation and analysis. This study aimed to determine the degree of ^3H loss and cross contamination under various storage conditions using operationally

exposed materials typically encountered during decommissioning operations and to consider the implication for sample storage and sampling strategy for decommissioning-derived material prior to waste sentencing and the waste management.

2. Experimental

The magnitude and rate of ^3H loss (emanation) from a range of materials derived from different nuclear decommissioning sites and contaminated with varying forms of ^3H , were investigated (Table 1). A cylindrical concrete core, traversing the reactor bioshield, was taken from the 100MW steam generating heavy water reactor (SGHWR) at Winfrith, Dorset and sectioned at 10 cm intervals (see Kim et al. [3] for the details of the sample collection and preparation). The bioshield concrete core section closest to the reactor had been exposed to the highest neutron flux and was found to predominantly contain strongly bound ^3H . A structural concrete (non-bioshield) was taken from a reactor building located away from any neutron source. The ^3H present in the structural concrete had originated from exposure to tritiated water vapour only. Concrete samples were carefully crushed using a fly press and pre-cooled Tema disc mill to produce a homogeneous concrete powder for subsequent trials. All procedures ensured that any heating was minimised. Active granular desiccant as used in a Magnox reactor gas dryer system (Hinkley A, UK) and mild steel operationally exposed to HTO vapour (Winfrith, UK) were also used as ^3H -emanating source materials. The steel sample was cooled and then filed to avoid heat generation. The nominal grain sizes of the materials used varied; concrete (0.1 mm), desiccant

Table 1
Summary of the tritium contaminated materials used to study emanation.

^3H source materials	Origin of sample	Origin of ^3H	Form of ^3H	^3H (Bq/g)
Structural concrete	Nuclear site building materials	Adsorbed tritiated water (HTO)	Weakly bound ^3H (HTO mainly)	9000
Bioshield concrete	Reactor bioshield	Neutron activation of ^6Li (n,α) ^3H	Strongly bound ^3H (mainly bonded with structural OH groups or in mineral lattices)	6000
Desiccant pellets	Reactor gas dryer system	Activated tritium gas and tritiated water (HTO)	Weakly and strongly bound ^3H	310,000
Metal	Nuclear site construction material	Adsorbed tritiated water (HTO)	Weakly bound ^3H (mainly) and structural OH groups	110

(0.4 mm), zeolite (1 mm pellets), CaSO₄ (2 mm granules), silica gel (1 mm grains), steel (0.3 mm filings).

Quantification of ³H in the source materials was performed using a Pyrolyser-Trio System (Raddec Ltd., Southampton, UK; Fig. 1), which permits simultaneous extraction/oxidation of up to six samples. This system was designed specifically for quantitative extraction of tritium and ¹⁴C from nuclear and environmental samples. Each sample was heated up to 900 °C in a stream of air using a preset heating cycle in individual silica glass work-tubes. Oxygen-enriched air was introduced when the sample zone reached 500 °C. The liberated gases passed through a zone containing 10 g of platinised alumina catalyst that oxidises any organic combustion products to CO₂ and H₂O (and HTO). Any water vapour, including HTO, was subsequently trapped in a bubbler containing 20 mL of 0.1 M HNO₃ (slightly acidified to prevent co-trapping of CO₂). Bubbblers were changed every 30 min and the ³H content of each bubbler measured separately to determine the ³H thermal desorption profile. The gas supply was isolated during the bubbler changeover. The quantities and proportion of ³H present in the sample as weakly bound and strongly bound were inferred from the thermal desorption profile.

To investigate the magnitude of ³H loss from concretes having different forms of ³H, a known amount of active structural (~1 kBq ³H) and bioshield concrete (~7 kBq ³H) powder (<125 μm, 1 g) contained in a sealable polythene bag (60 mm × 70 mm × 0.06 mm) were placed into a Kilner jar (635 mL volume) modified with inlet and outlet ports which permitted the measurement of ³H activity in the headspace of the container (Fig. 1). Ten millilitres of RO water in an open and a closed vial were placed in each of the Kilner jars and the jars sealed and stored in a freezer (−18 °C) and at room temperature (20 °C). After 2 weeks, dry air was introduced into the container for 10 min. The flush gas was then passed through a bubbler to trap HTO and then through a furnace containing Pt-alumina catalyst to convert other forms of ³H into HTO which was subsequently trapped in a second bubbler. The total ³H activity (Bq) measured in the flushed air was used to calculate ³H concentrations of the water vapour in the Kilner jar. Tritium activities were also determined in the RO water (de-mineralised water purified by reverse osmosis), card supports and all container surfaces by rinsing with water. Finally the quantity of ³H remaining in the concrete was determined by combustion/liquid scintillation analysis.

The rate of tritium transfer to water from concretes having different forms of ³H was further investigated and compared at various storage temperatures. Bioshield concrete powder (1 g with a total tritium activity of 6 kBq) sealed in a polythene bag was placed in one of eighteen Kilner jars fitted with airtight rubber seals. Ten millilitres of RO water in an open and closed vial were placed in each of the jars and the jars stored in a fridge (4 °C), a freezer (−18 °C) and at room temperature (20 °C) for 1 day, 5 days, 10 days, 15 days, 20 days and 30 days. At the end of each pre-defined storage time the ³H in the RO water was measured by liquid scintillation analysis. The experiment was repeated with active structural concrete powder (4 g with a total tritium activity of 36 kBq)

The relative magnitudes of contamination of different receptor materials exposed to various tritium emanating source materials was investigated. Initially structural concrete (37 kBq), desiccant pellet (170 kBq) or metal (300 Bq) in sealed polythene bag were stored adjacent to a non-contaminated silica gel (ca 5 g), cellulose paper (ca 0.15 g) or water (10 mL). The non-contaminated materials were either open to the tritiated atmosphere or stored in sealed bags or plastic vials. In a second experiment, concrete, plastic (polyethylene), metal wire (mild steel), and various desiccants (e.g. silica gel, Drierite™ (CaSO₄) and zeolite), were exposed to ³H-contaminated structural concrete contained in a polythene bag. The non-contaminated materials were open to the tritiated atmosphere. Samples were stored at 20 °C (room temperature), 4 °C

(fridge) or −18 °C (freezer). After 2 weeks, the ³H activity in the previously non-contaminated materials was measured and the proportion of ³H activity that had transferred to the non-contaminated materials was determined.

The impact of sample storage conditions on measured ³H activities was assessed using samples supplied as part of a radioanalytical campaign linked to a UK decommissioning programme (UKAEA Winfrith site). Operationally exposed materials were sampled and the sub-samples immediately transferred to vials containing water to leach ³H. The activity of ³H leached was then determined by liquid scintillation counting. Separate sub-samples were then either stored at room temperature or refrigerated (at 4 °C) for a period of storage/transport prior to analysis by total combustion. Tritium activities measured by total combustion from each sample stored at different temperature conditions were compared with its ³H activity measured by leaching at sampling point.

All tritium measurements were performed using a 1220 liquid scintillation counter (Wallac Quantulus™). Eight millilitres of aqueous sample were mixed with 12 mL of Gold Star™ (Meridian) scintillation cocktail in a 22 mL polythene vial. The counter was calibrated for ³H using a traceable tritiated water standard (TRY-44, Nycomed Amersham PLC, Bucks, UK). For all samples, the measured quench levels (SQPE) ranged from 700 to 850 which correspond to ³H counting efficiencies of 17–31%. All uncertainties are quoted at the 95% confidence level and refer to propagated method uncertainties.

3. Result and discussion

A significant difference in the magnitude of ³H loss was observed between structural concrete and bioshield concrete (Table 2). For structural concrete stored at room temperature, 55% of the original ³H inventory was lost from the sample after 14 days. However, for bioshield concrete, only 6% of the original inventory had been lost. Of the ³H liberated, approximately 65% was detected in the RO water exposed to the tritiated atmosphere. For structural concrete, 7.5% of the liberated ³H was detectable in the vessel airspace whilst for bioshield concrete, only 4.3% of the liberated ³H was present in the air. All ³H in the air flushed from the storage vessel after 14 days was trapped in the pre-furnace bubbler indicating that the ³H is predominantly present as HTO vapour. The remaining liberated ³H was distributed between cardboard supports used to hold the vials containing water, vessel walls and polythene bags used to hold the source material. Freezing the system significantly reduced the loss of ³H from the structural concrete with only 6% of the original ³H inventory being lost. Similar low losses were observed for bioshield concrete stored in the freezer. Monitoring of ³H activities in RO water exposed to tritiated structural and bioshield concretes for periods of 1–30 days also confirmed that the rate of ³H loss from bioshield concrete was significantly lower than from structural concrete (Fig. 2). The rate of loss appeared to be relatively constant over the 30-day measurement period. By correcting the activity measured in the RO water for the proportion of total liberated ³H which is transferred to the water (determined from the first experiment as 65%), it is possible to calculate a rate of loss of ³H from the source material as a percentage of the original ³H inventory. A loss rate from the structural concrete of 2.3%/day was lower than observed from the first experiment. For bioshield concrete, the loss rate of 0.4%/day was considerably lower than observed for structural concrete but comparable to that observed for bioshield concrete in the first experiment. Refrigeration of the structural concrete reduced the loss rate to 0.9%/day whilst freezing the concrete further reduced the loss rate to <0.01%/day.

The magnitude of ³H loss was also determined relative to structural concrete for ³H contaminated desiccant and metal samples

Table 2
Tritium redistribution after storage.

³ H contaminated into	Activity of ³ H (Bq) (% of total ³ H)			
	Structural concrete		Bioshield concrete	
	Room temp.	–18 °C freezer	Room temp.	–18 °C freezer
Air in the Kilner jar	45.9(4.1)	4.4(0.4)	18.5(0.3)	2.7(<0.1)
Jar walls	0.7(0.1)	0.1(<0.1)	0.2(<0.1)	0.1(<0.1)
Polythene bag ^a	5.2(0.5)	9.8(0.9)	8.0(0.1)	5.8(0.1)
Polythene bag ^b	0.1(<0.1)	0.1(<0.1)	0.1(<0.1)	0.1(<0.1)
Water (open vial)	377(33.9)	0.4(<0.1)	282(4.3)	0.1(<0.1)
Water (closed vial)	0.2(<0.1)	0.1(<0.1)	0.2(<0.1)	0.1(<0.1)
External wash of scintillation vial	0.1(<0.1)	0.1(<0.1)	0.1(<0.1)	0.1(<0.1)
Cardboard support ^c	146(13.2)	17.7(1.6)	33.8(0.5)	5.2(0.1)
³ H remaining in the concrete	499(45)	1046(94)	6148(94)	6383(97)
Total Bq (%)	1075(97)	1078(97)	6491(99)	6397(97)
Original ³ H (Bq) in concrete	1112(100)	1112(100)	6577(100)	6577(100)

^a ³H activity washed from inside of polyethylene bag which contained concrete.

^b ³H activity washed from outside of polyethylene bag which contained concrete.

^c Cardboard support used with the open vial containing water.

using a range of uncontaminated receptor materials (Table 3). For structural concrete at room temperature, the loss of ³H of 52% and the proportion of that ³H transferred to water of 65% was comparable to that observed in the first experiment. Significantly higher loss rates were observed for ³H-contaminated metal samples where 98% of the original inventory was liberated in 14 days (equivalent to a loss rate of 7%/day). The lowest loss at room temperature was observed for desiccant with only 0.6% of the original inventory being lost in 14 days (equivalent to a loss rate of 0.04%/day). In general the proportion of ³H lost from the source material was reduced by refrigeration and more significantly by freezing. However, for desiccant, a greater ³H loss (4.4%) was observed for the refrigerated sample compared with that stored at room temperature. In all instances, the proportion of liberated ³H transferred to exposed water was comparable with that observed for the first experiment with 65%, 50% and 60% being transferred to water from structural concrete, desiccant and metal, respectively.

The magnitude of ³H loss from a contaminated material is highly dependent on the form of ³H, with a greater proportion of ³H being lost from structural concrete compared to bioshield concrete (Table 2). A previous study [3] identified two distinct forms of tritium in concrete which are referred to as weakly bound ³H and strongly bound ³H. The structural concrete and bioshield concrete

used in the present study have significantly different proportions of the two forms of ³H (Fig. 3). The structural concrete mainly contains the weakly bound form of tritium (mostly HTO) which exists as free water or crystallisation water [5]. This form rapidly equilibrates with water vapour in air and is therefore quickly lost [6,16]. Conversely, bioshield concrete dominantly contains a strongly bound form of ³H arising from neutron activation of trace lithium-6 [3]. This ³H form is less-available since it may be locked/trapped inside mineral lattices and only interacts slowly with water vapour [3]. This demonstrates that ³H loss is significantly dependent on the form of ³H contaminated on material and would be mostly derived from weakly bound form of ³H (HTO) by absorption/diffusion and isotopic exchange.

Numerous studies have demonstrated persistent tritium release from various materials (e.g. stainless steel, cement and ceramic breeder materials) previously exposed to tritiated water vapour [6,10–13]. The degree of ³H loss is dependent on the physical and compositional characteristics of ³H-contaminated source materials [6]. The significant ³H loss from structural concrete (Table 3) is due to the high porosity of the concrete whereby HTO can rapidly diffuse through the matrix and subsequently desorb to ambient air. However, the desiccant has high water absorption capacity compared to other materials and absorbed water including HTO is strongly

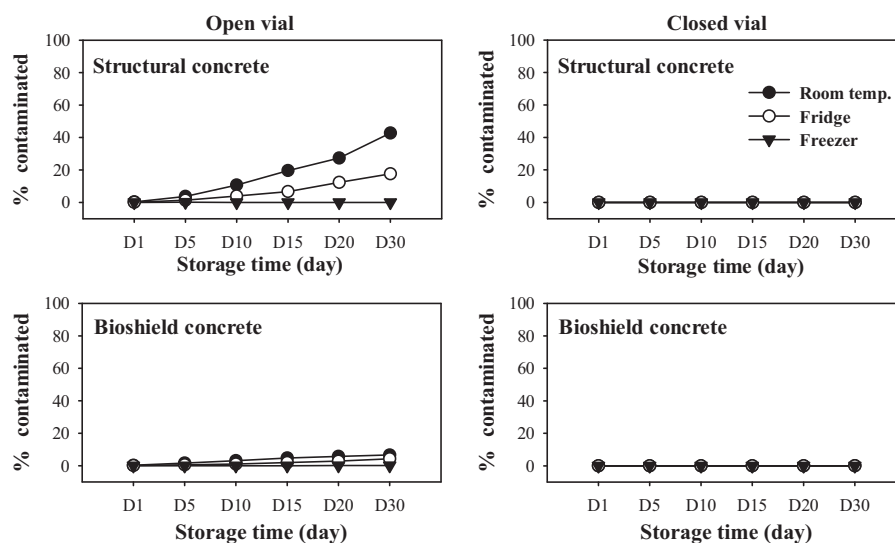


Fig. 2. Variations of ³H contamination in water from different types of tritium emitting materials (structural concrete and bioshield concrete).

Table 3
 ^3H cross-contamination arising from various source materials.

Source materials	Storage condition	$^3\text{H}_{\text{total}}$ % of source activity transferred						Total (%)
		Silica gel (open)	Silica gel (single bag)	Silica gel (double bag)	Cellulose paper (open)	Water (open)	Water (closed)	
Concrete (structural)	Room temp	8.8	4.7	3.0	<0.1	34	<0.1	52
	4 °C Fridge	9.2	0.4	0.3	0.1	7.1	<0.1	17
	-18 °C Freezer	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Desiccant	Room temp	0.2	0.1	<0.1	<0.1	0.3	<0.1	0.6
	4 °C Fridge	2.3	0.2	0.1	<0.1	1.9	<0.1	4.4
	-18 °C Freezer	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Metal	Room temp	22	13	4.1	0.2	59	0.1	98
	4 °C Fridge	6.1	0.7	0.3	0.6	4.1	<0.1	12
	-18 °C Freezer	0.5	0.2	0.3	<0.1	0.1	<0.1	1

retained with only slow exchange with water vapour in ambient air [17]. Conversely most ^3H contamination in the metal exposed to tritiated atmosphere is confined to the surface, oxyhydroxide layer [11,18,19], as HTO which is relatively easily liberated by exposure to heat or moisture.

The magnitude of ^3H loss during storage can be effectively minimised by controlling sample storage temperature and choice of appropriate packaging. The greatest ^3H loss from concrete (55% of $^3\text{H}_{\text{total}}$ for 2 weeks) occurred at room temperature (Table 2) due to high exchange rates between ^3H in free water of concrete and water vapour in ambient air which is significantly decreased at lower temperature [5,9,10,20]. Ono et al. [6] reported similar ^3H loss at 30 °C from tritiated cement showing ^3H loss from three different states of water (capillary water, gel water and crystal water). The tritium loss apparently occurred in two stages; the initial rapid ^3H loss arising mainly from free water and the later slower ^3H loss from gel water. The initial rapid loss of ^3H followed by a prolonged slower rate of loss reported by Ono et al. [6] for cement was not apparent in the current study although it is unlikely that such detail would be observable using the experimental approach adopted in this study.

3.1. Transfer to atmosphere

The ^3H emanated to atmosphere can be transferred to any proximal materials via physical contact with the surface of a material where absorption, diffusion and isotope exchange process occur. Theoretically 1 m³ of air has a mass of 1.17 kg and contains 22 g H₂O/kg air at normal temperature (25 °C), therefore the mass of air in the Kilner jar with a volume of 6.35 × 10⁻⁴ m³ is 0.74 g and the mass of water vapour in the Kilner jar is 16 mg. The tritium inventory of the air in the Kilner jar was 8.2 Bq, therefore the ^3H concentration of the water vapour in the container was 502 Bq/g. This is significantly higher than ^3H concentration in the water exposed to

the atmosphere (38 Bq/g). This implies that ^3H equilibrium within the container was not reached during the storage time used and ^3H contamination to proximal materials will continue until equilibrium within the container is achieved.

3.2. Transfer to non-contaminated materials

Transfer to other materials was generally lower than for open RO water. For silica gel open to the atmosphere at room temperature, between 17% and 28% of the liberated ^3H was transferred to the gel, whilst for cellulose paper <1% was transferred. Comparison of transfer rates for zeolite, anhydrous CaSO₄, silica gel, concrete, plastic and metal (Fig. 4) exposed to ^3H -contaminated structural concrete demonstrated that ^3H uptake on the zeolite, CaSO₄ and silica gel were comparable at between 22% and 27% of the estimated ^3H liberated. Lower uptake was observed for the powdered concrete (8%) whilst uptakes on plastic and metal were insignificant at 0.04% and 0.003%, respectively.

The extent of tritium contamination is mainly controlled by diffusion [6] which is highly dependent on physical and compositional characteristics of materials being contaminated [21,22]. Greater contamination of materials exposed to a tritiated atmosphere occurred with drying agent materials [e.g. silica gel, Drierite™ (CaSO₄) and zeolite] due to their active uptake of water vapour (Fig. 4). Typically porous hydrophilic material (e.g. concrete) and items with large moisture content will be easily contaminated compared with non-porous surfaces [6]. Furuichi et al. [9] also reported that a material with high water content, porosity and hydration will be more highly contaminated. In the current study, higher contamination levels were observed for porous concrete and cardboard which was used to support the open vial containing RO water (Table 2) compared with non-porous plastic and metals where negligible contamination was observed (Fig. 4) [23]. Other studies

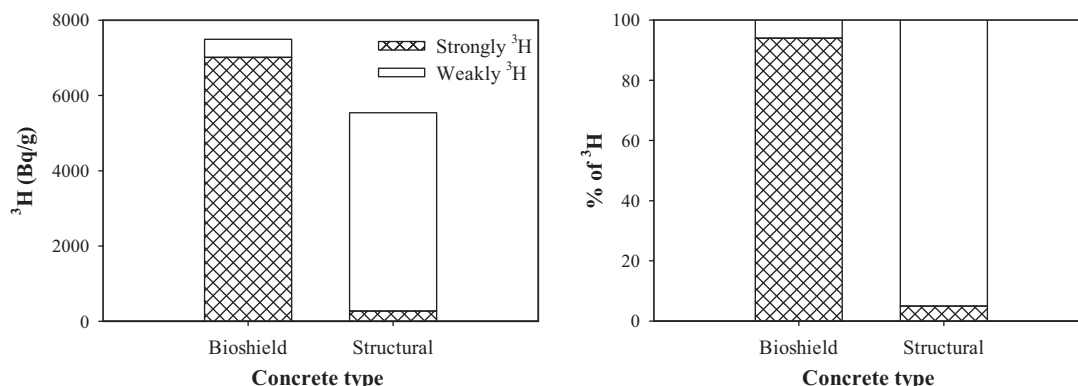


Fig. 3. Total ^3H activity (left) and the percentage of ^3H species (strongly bound and weakly bound) in the concrete (right).

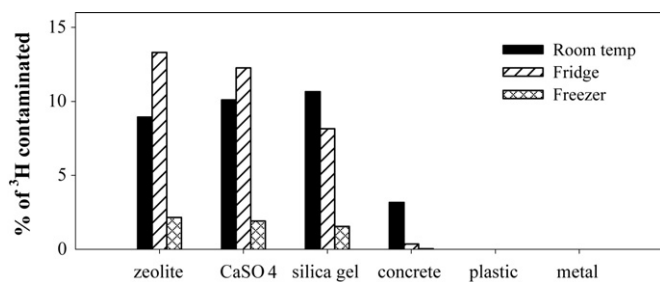


Fig. 4. ³H contamination of various materials from high active structural concrete (the total activity of the sample was 28 kBq) following 2 weeks of storage (room temperature, 4 °C fridge and –18 °C freezer).

demonstrated high ³H absorption capability of high water content materials (e.g. concrete) compared with rubber, linoleum, metal and plastics, glass [6,23,24].

Ono et al. [6] reported that the extent of ³H cross contamination caused by ³H loss or leakage from a source material increased at higher temperature. This implies that tritium transfer/cross-contamination to proximal materials is dependent on sample storage temperature with the magnitude of cross contamination being significantly reduced (<3% of source) by freezing the sample limiting ³H emanation from source materials [5,6,9,10,20]. However, the highest contamination arising from desiccants was observed at 2.4 °C (Table 3 and Fig. 4). At low temperatures (ca 3–4 °C) the rate of ³H emanation from the source material is reduced but this is offset by an increase in surface condensation of atmospheric water vapour, resulting in a net increase in surface HTO concentrations on non-contaminated materials. However, at significantly lower temperatures (–20 °C) the magnitude of ³H emanating from a source material is negligible, reducing the possibility of cross contamination.

3.3. Effect of packaging

Bagging the silica gel receptor reduced the proportion of liberated ³H transferred to 9–17% whilst double bagging further reduced the proportion transferred to 4–6%. Tritium contamination of water held in capped polythene scintillation vials was not measurable (<0.04% of the ³H_{total}) even at room temperature and when stored over the 30-day duration of the experiment (Table 3 and Fig. 4).

Sample storage experiments during a real sampling campaign to assess the impact on measured ³H activities highlighted the importance of storing samples at low temperature immediately following sample collection to preserve ³H and prevent cross-contamination of samples. A comparison of leached ³H determined immediately following sampling versus total ³H indicated significant differences in ³H activity concentrations for samples stored at room temperature. Total combustion results were low compared with the initial leach data (Fig. 5 open symbols). However, a good agreement was observed between leaching and combustion for samples refrigerated immediately after sampling (Fig. 5 solid symbols). These results clearly demonstrated that immediately following sample collection, samples must be stored in low temperature to preserve ³H of samples and prevent cross contamination. This further supports the significance of sample storage immediately after sample collection. The results also confirmed that leaching (ideally immediately following sampling) was a suitable technique for determining ³H in some solid materials exposed to tritiated water vapour. However, previously reported data have demonstrated that such an approach is not suitable for bioshield concrete [3] as a proportion of the ³H is tightly locked into the mineral structure.

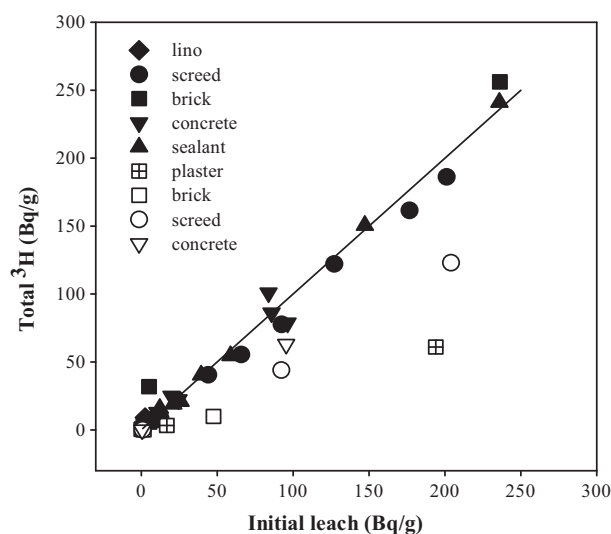


Fig. 5. Relationship between ³H extracted from various construction materials by aqueous leaching immediately following sampling and combustion for samples stored under different conditions. The solid symbol represents samples refrigerated (4 °C) immediately after sampling. Open symbols represent samples stored at room temperature. Lino is a generic term for flooring that is composed of mineral and wood powders mixed with linseed oil but is also loosely used for vinyl materials. Screed is a sand and cement mix used as a base for floors and walls.

4. Conclusions

The large nuclear decommissioning programmes occurring in the UK have required large volumes of potentially radioactive waste materials to be accurately characterised prior to final waste sentencing. Tritium, because of its potential mobility and volatility has required specific sampling, storage and measurement to avoid the possibility of loss of analyte and or cross contamination between samples. This study has shown that the proportion of tritium lost from a material depends on the form of ³H in the material, its mode of sampling, sample storage temperature and storage environment. Any tritium trapped in mineral lattice sites (e.g. irradiated bioshield concrete) or chemically bound into desiccants, hydroxides or metal oxyhydroxides is held more strongly than adsorbed 'free' water. The low loss of tritium from bioshield concrete and graphite is attributed to the small proportion of free HTO and the locking-in of tritium into crystal lattice sites in clays and other minerals. Similarly for desiccants the relatively low loss at normal temperatures is explained by its being converted to forms such as Ca(TO)₂ in calcium desiccants and as SiO₂.HTO in silica gel. The extent to which tritium can migrate depends on its chemical and physical associations (e.g. being incorporated relatively weakly in hydrated compounds or more strongly in mineral lattices). For general analytical security all samples should be triply contained and sealed in vapour tight containers (glass or high density plastic) and frozen to minimise ³H loss. Additionally low activity samples and porous hydrophilic samples (e.g. concrete, brick, cellulose paper, etc.) should be well segregated (e.g. triple bagged) from high activity samples to further reduce the possibility of cross contamination.

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