



# Release of $^3\text{H}$ and $^{14}\text{C}$ during sampling and speciation in activated concrete

Anumaija Leskinen<sup>1</sup> · Jouni Hokkinen<sup>1</sup> · Teemu Kärkelä<sup>1</sup> · Tommi Kekki<sup>1</sup>

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## Abstract

Characterisation of contaminated and activated decommissioning waste require sampling of the studied material for the analysis of different radionuclides. The volatility of  $^3\text{H}$  and  $^{14}\text{C}$  can lead to the loss of the analytes in sampling of solid materials since most often at least some heat is involved in the sampling technique. Especially  $^3\text{H}$  can be lost in cases when it is present as tritiated water (HTO) due to the evaporation of water even at low temperatures. Therefore, in this study, the  $^3\text{H}$  and  $^{14}\text{C}$  speciations are discussed. Consequently, a drilling sampling technique was developed in order to capture the released  $^3\text{H}$  and  $^{14}\text{C}$  in absorption solutions and measured using liquid scintillation counting. The sampling technique was tested on an activated concrete core. The collected samples were analysed for  $^3\text{H}$  and  $^{14}\text{C}$  (activity concentration and speciation) using a thermal oxidation technique. The results showed that a significant amount of  $^3\text{H}$  was released during sampling even though the majority of  $^3\text{H}$  was strongly bound in the activated concrete. The studied activated concrete did not contain measurable amount of  $^{14}\text{C}$  and therefore speciation studies were not possible.

**Keywords** Volatile radionuclides · Characterisation of decommissioning waste · Sampling · Speciation · Thermal oxidation

## Introduction

The reliability of difficult to measure (DTM) radionuclide analyses of solid decommissioning waste is affected by the volatility of the radionuclide, sampling technique and radiochemical analysis method. In theory, volatile DTMs, such as  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{36}\text{Cl}$  and  $^{125}\text{I}$ , can be at least partly lost due to thermal decomposition when heat is involved in the sampling process. Thermal decomposition is chemical decomposition caused by heat, which is required to break chemical bonds. Phase transformations from solid to liquid (melting) or from solid to gas (sublimation) may be possible. Some heat is involved in the majority of sampling processes e.g. sawing, coring and drilling, and depending on the speciation, unknown amounts of the volatile elements can be released. Materials contaminated with tritiated water (HTO) are especially problematic due to evaporation even at room temperature. Additionally, the release of DTMs can occur also during sampling when it exposes pores with volatile

DTM trapped in them or increases the surface area of the material enabling higher number of interactions with the surroundings causing a negative bias in the radiochemically analysed activity concentration results.

One of the major factors in the reliability of the experimental results (both radiochemical and gamma spectrometric) is the representativeness of the sample. Heterogeneity of the material needs to be considered and if possible, homogenisation should be carried out. However, sometimes homogenisation is not possible or feasible, for example in cases when large volumes of inhomogeneous legacy waste is characterised. In these cases, statistical tools can be used to develop a sampling plan. Recommended approaches for data and sampling design strategies in all characterisation studies are presented in Ref. [1] and references therein. Depending on the sampling technique and the sample matrix, also further treatment of the sample may be needed in order to obtain a fine powder, which can be carried out using a mortar and pestle or a sample mill. Fine powder is especially beneficial for low solubility matrices such as concrete and graphite [2–4]. Additionally, every additional step in sample preparation is not only a potential source of cross contamination, but also requires more work, lengthening the analytical procedure.

✉ Anumaija Leskinen  
anumaija.leskinen@vtt.fi

<sup>1</sup> VTT Technical Research Centre of Finland, Kivimiehentie  
3, 02044 Espoo, Finland

Radiochemical analysis methods require destructive techniques, such as acid digestion, combustion or fusion, in order to extract the radionuclide of interest from the solid matrix [5]. In some cases, the solubility of the solid material is not problematic. For example, the complete destruction of steel can be carried out using different mixtures of acids and heating [6]. On the other hand, the complete destruction of concrete (especially heavy concrete) and graphite are more difficult to achieve [3, 7, 8]. The silicates and oxides in heavy concrete require alkali fusion to completely break them down [7]. Even though fusion can break even the most strongly bound bonds, the heat applied in the process can volatilise radionuclides making the technique un-useful for a volatile DTM analysis unless the released DTM is trapped in-situ [9]. The solubility of graphite can also be overcome by small grain size and digestion with strong oxidative acids, thermal oxidation, or fusion.

In this paper, the release of  $^3\text{H}$  and  $^{14}\text{C}$  during the sampling of an activated concrete core originating from the FiR 1 research reactor biological shield is presented. The sampling configuration was developed after having considered the volatilities of the  $^3\text{H}$  and  $^{14}\text{C}$  (i.e., speciation), representativeness of the collected sample (i.e., heterogeneity) and the need for finely powdered sample (i.e., solubility). A plan to slice the core and crush the slices was rejected, since an additional step would have been needed to homogenise and pulverise the sample using milling or other similar techniques. The procedure would have been laborious and there would not have been any way to determine how much of the volatile DTMs would be released during the sampling and homogenisation. Therefore, a drilling configuration with in-situ trapping of volatilised  $^3\text{H}$  and  $^{14}\text{C}$  were developed and utilised. Additionally, speciation studies of the non-volatilised  $^3\text{H}$  and  $^{14}\text{C}$  in activated concrete were studied using a combustion method. This paper presents the sampling development procedure, discusses the effect of speciation and applied sampling technique on the release of  $^3\text{H}$  and  $^{14}\text{C}$ , and discusses the results from sampling carried out on an activated concrete core. The results showed release of  $^3\text{H}$  during sampling and therefore, the volatile DTM characterisation requires special attention already in sampling phase.

## Studied activated FiR1 concrete

The studied activated concrete originated from the biological shield of the FiR1 TRIGA Mark II type research reactor, which is undergoing decommissioning in Finland. A chemical analysis for the purposes of activation calculations was carried out in the 2010s by drilling an inactivated part of the FiR1 biological shield concrete and carrying out a chemical composition analysis. The results presented in Table 1 show that the most interesting elements for this study (i.e., activating elements  $^3\text{H}$  and  $^{14}\text{C}$ ) were approximately 34 ppm of Li, approximately 1910 ppm C and less than 200 ppm N. Additionally, thermo-analytical results showed that the samples contained 0.6–0.8%  $\text{CO}_2$  as carbonates, an  $\text{H}_2\text{O}$  content of 4.4–4.6%, 1.3–1.7%  $\text{Ca}(\text{OH})_2$  and 1.4–1.9%  $\text{CaCO}_3$ .

A second drilling campaign was carried out in 2018 from the activated parts of the FiR1 biological shield. Figure 1 shows the most activated core from which the most activated end was drilled in this study. It can be seen that the concrete was heterogeneous with different sizes of stones up to 80 mm in diameter.



**Fig. 1** Picture of the FiR1 biological shield concrete core (diameter 7 cm)

**Table 1** Concentrations of elements of interest in three inactive concrete subsamples (internal data), activation reactions and thermal activation cross sections [8]

Element	Concentrations of three inactive concrete subsamples ( $\text{mg kg}^{-1}$ )	Activation reaction	Reaction thermal neutron cross section (barns)
Li	36/27/39	$^6\text{Li}(\text{n}, \alpha)^3\text{H}$	$936 \pm 6$
C	1730/1835/2165	$^{13}\text{C}(\text{n}, \gamma)^{14}\text{C}$	$(0.9 \pm 0.30) \times 10^{-3}$
N	<200	$^{14}\text{N}(\text{n}, \text{p})^{14}\text{C}$	$1.75 \pm 0.05$

## Theory of speciation and release of $^3\text{H}$ and $^{14}\text{C}$ from activated concrete

In activated concrete, the  $^3\text{H}$  originates mainly from the activation of  $^6\text{Li}$ , but also from the activation of  $^2\text{H}$  and  $^3\text{He}$  [10]. In general, the  $^3\text{H}$  in activated concrete is found as HT or HTO in the pores and gaps of the concrete [10]. Further studies by Kim et al. [11] have shown that  $^3\text{H}$  can be present in activated concrete in free water, water of crystallisation, structural OH-groups or is lattice bound. Additionally, Kim et al. [11] divided the  $^3\text{H}$  speciation in activated concrete into strongly bound and weakly bound  $^3\text{H}$ . Strongly bound  $^3\text{H}$  originates from trace Li within mineral phases and requires in excess of 350 °C to achieve quantitative recovery in a radiochemical analysis. Weakly bound  $^3\text{H}$  can be released at 100 °C as HTO [11]. In this case,  $^3\text{H}$  is associated with the dehydration of hydrous mineral components [11]. The studies have also shown that relatively more strongly bound  $^3\text{H}$  is found nearer the irradiation source, whereas relatively more weakly bound  $^3\text{H}$  is found further from the irradiation source [11]. Cement is the most significant component of concrete due to its abundant structural water capable of trapping tritium by isotopic exchange [11]. In contrast,  $^3\text{H}$  is rapidly released from HTO-contaminated concrete above 95 °C and the total  $^3\text{H}$  is extracted at below 350 °C [12]. Therefore, some  $^3\text{H}$  release would be expected from the FiR1 activated concrete, since water has a significant vapor pressure in air already at room temperature, which could lead to the release of tritiated water into the gas phase, for example during storing and especially during the drilling of concrete.

The  $^{14}\text{C}$  in activated concrete originates from the activation of  $^{14}\text{N}$ ,  $^{13}\text{C}$  and  $^{17}\text{O}$  [10]. The main contributor of  $^{14}\text{C}$ , however, is the  $^{14}\text{N}$  activation due to the high neutron reaction cross section and isotopic abundance [10]. The  $^{14}\text{C}$  speciation in activated concrete has not been studied as well as the  $^3\text{H}$  speciation.  $^{14}\text{C}$  speciation as carbon, organic matter or as carbonates, i.e.,  $\text{Na}_2\text{CO}_3$ ,  $\text{CaCO}_3$ ,  $\text{BaCO}_3$  have been suggested [10]. The  $^{14}\text{C}$  in  $\text{Na}_2\text{CO}_3$  is the most difficult to decompose due to its high melting point of 850 °C [10]. On the other hand, the release of  $^{14}\text{C}$  in low temperatures (e.g. this study's drilling temperature) can be estimated to be insignificant due to the carbonation phenomenon in which  $\text{CO}_2$  from the air penetrates into concrete through pores and reacts with calcium hydroxide to form calcium carbonates. This is essentially a reversal of the chemical process that occurs when making the cement used in the concrete, i.e., the calcination of lime ( $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ ) that takes place in cement kilns at high temperatures. The calcination results in a favourable environment for carbonation and not in release of

$\text{CO}_2$ . The resulting precipitates of  $\text{CaCO}_3$  may be a source of airborne particles containing  $^{14}\text{C}$  generated during the drilling of concrete. The free water existing in the pores of concrete is an essential factor affecting the reactivity and diffusivity of carbon dioxide. With insufficient water, the  $\text{CO}_2$  and calcium hydroxide will not be fully ionised in order to form  $\text{CaCO}_3$  [13]. On the other hand, too much water limits the reaction due to the blockage of the pores in the concrete. The diffusivity of  $\text{CO}_2$  is  $10^4$  times smaller in water than in air [14]. Therefore, one hypothetical  $^{14}\text{C}$  release mechanism as a gaseous compound could be the dissolution of the formed  $^{14}\text{C}$  into the pore water of concrete and the subsequent release of  $^{14}\text{C}$  (e.g. as  $\text{CO}_2$ ) from the water during the drilling of the concrete, especially in the case when the formation of  $\text{CaCO}_3$  is incomplete, as described above.  $^{14}\text{C}$  release could even be enhanced if the  $^{14}\text{C}$  formation takes place in the pore water instead of the diffusion of the formed  $^{14}\text{C}$  through the concrete matrix into to the pore water. Drilling concrete increases its temperature, thus enhancing the vaporisation of water and the formation and release of airborne species (gas and particle species) from the compounds in the pore water. Therefore,  $^{14}\text{C}$  release was considered to be possible from the FiR1 activated concrete. However, due to much lower thermal cross sections, the  $^{14}\text{C}$  content in the activated concrete was expected to be much lower than the  $^3\text{H}$  content.

## Experimental

### Reagents and equipment

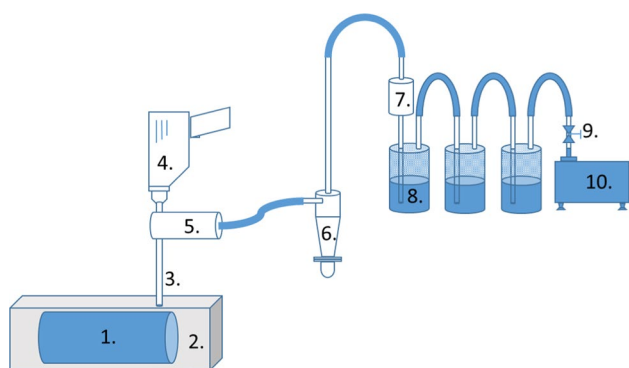
A 0.1 M  $\text{HNO}_3$  absorption solution for trapping  $^3\text{H}$  was prepared by mixing analytical grade concentrated  $\text{HNO}_3$  with deionised water. A 0.4 M  $\text{NaOH}$  absorption solution for trapping  $^{14}\text{C}$  was prepared by mixing analytical grade  $\text{NaOH}$  pellets with deionised water. The liquid scintillation cocktail HiSafe was purchased from Perkin Elmer. A Hidex 300 SL liquid scintillation counter (LSC) was used in the measurement of  $^3\text{H}$  and  $^{14}\text{C}$ . The measurement protocols used were provided by Hidex using a CoreF function to convert TDCR (triple to double count rate) results to measurement efficiencies.

$^3\text{H}$  and  $^{14}\text{C}$  analysis and speciation studies of the activated concrete were carried out using a Pyrolyser TRIO2 by RADDEC International with three furnaces for two samples. The sample was placed in the first furnace, and the temperature was increased using a material-specific heating profile. The second furnace was automatically heated to 500 °C when the first furnace reached 500 °C. The second furnace ensured evaporation of the analytes. The third furnace contained a Pt-alumina catalyst and it was preheated to 800 °C and remained at the same temperature throughout

the analysis. The catalyst ensured the oxidation of the  $^3\text{H}$  and  $^{14}\text{C}$  species to HTO and  $\text{CO}_2$ , respectively. Pressurised air with a 200–250  $\text{ml min}^{-1}$  flow rate was passed through the pyrolyser until the temperature in the first furnace rose to 500 °C after which oxygen flow was added with a combined flow rate of 200 to 250  $\text{ml min}^{-1}$ .  $\text{O}_2$  introduction at 500 °C ensured oxidation of more thermally stable organic species as readily combustible materials had been already oxidised. The 20 ml 0.1 M  $\text{HNO}_3$  absorption solution for trapping  $^3\text{H}$  was prepared as above and the 20 ml Carbo-Sorp® E (Carbosorp) absorption solution for trapping  $^{14}\text{C}$  was purchased from Perkin Elmer. The absorption bottles were placed in a styrox box with an ice cooler in order to reduce the trapping solution temperature and consequently possibly increase the absorption efficiency [2] and lower volatilisation rate of the absorption solutions. 5 ml of the 0.1 M  $\text{HNO}_3$  and Carbo-sorp were put into LSC bottles and mixed with 10 ml of a HiSafe liquid scintillation cocktail. The LSC measurement times were 1800s unless mentioned otherwise.

### Drilling set-up

The sample drilling set-up was first tested using an inactive concrete core. The drilling set-up is presented in Fig. 2. A concrete core was placed inside a safety crate and secured using a screw vice. The safety crate had a 2 cm diameter hole in the lid, through which a 12 mm diameter hollow bore bit (DeWalt Hollow Bit) was introduced. The safety crate acted as a barrier preventing the spreading of contamination to the surrounding area. Air was sucked from the safety crate through the drill and rest of the drilling set-up using a vacuum pump. A small negative pressure in the safety crate also acted as a barrier to the spreading of contamination into the surroundings. The sample powder was collected in a gravitational settling chamber (the bore bit handle) and in a VTT custom-made cyclone. The finest powder was



**Fig. 2** Drilling set up (1) concrete core, (2) safety crate, (3) hollow bore bit, (4) drill, (5) gravitational settling chamber, (6) cyclone, (7) filter, (8) absorption bottle battery, (9) adjusting valve and (10) vacuum pump

collected in a filter (Sartofluor Midicap, 0.2  $\mu\text{m}$  pore size). The cyclone had a 10 ml reservoir for sample collection in the bottom secured with a vacuum clamp. The gravitational settling chamber and cyclone were emptied into a separate container at regular intervals. Some of the finest particles from the filter were collected by tapping. The air was sucked through three absorption bottles with absorption solutions, which acted as volatile  $^3\text{H}$  and  $^{14}\text{C}$  collectors. The flow rate was adjusted using an adjusting valve (Swagelog Integral Bonnet needle valve). Ideally, the flow rate would have been as high as possible for effective powder collection, but it had to be low enough that the air bubbles in the absorption bottles had enough contact time with the absorption solutions. The adjusted flow rate was 14  $\text{l min}^{-1}$  measured from the vacuum pump outlet using a rotameter (Brooks Instruments B.V.). At this flow rate, approximately half of the particles were collected in the gravitational settling chamber and half in the cyclone.

Different techniques to measure the drilling temperature were considered. First, an infra-red sensor, a pyrometer, was considered to measure the temperature of the drill when lifted outside of the concrete. This idea was rejected because the pyrometer reading area diameter is typically larger than the bore bit diameter and the emissivity of the metal surface of bore bit varies because of concrete dust and neither can the bore bit be painted or taped black. The second idea was to place a sensor inside the drill to measure the temperature online. This idea was rejected due to contamination of the sensor and also possible mechanical breaking of the sensor due to the concrete powder. In the end, the test with an inactive concrete showed that the temperature in the drill increased during drilling to be warm to the touch but not burning. Therefore, the temperature was estimated to be from 50 to 100 °C. In retrospect, the drilling hole in the concrete block might have been a possible target for temperature measurement.

Three absorption bottles were connected in a row between the filter and the pump (Fig. 2). First absorption bottle for trapping  $^3\text{H}$  and second and third absorption bottles for trapping  $^{14}\text{C}$ . The detection limits for the  $^3\text{H}$  and  $^{14}\text{C}$  depended on the amount of sorption solution in the bottles and their effectiveness to absorb the analytes of interest. Similar absorption bottles have been utilised in the collection of volatile DTMs during acid digestion [3, 15] and such bottles without a filter disc were also tested in the drilling set-up. Initial tests showed that the airflow required for the collection of the powdered sample was so high that the solutions in the absorption bottles moved too vigorously which risked sucking the solutions out of the bottles. Therefore, larger bottles with an angular decrease of diameter in the mouth of the bottle were tested and found to be successful. The larger bottles also meant larger absorption solution volumes lowering the detection limit. In the end, the tests were carried

out with first absorption bottle containing 400 ml of 0.1 M HNO<sub>3</sub> and second and third absorption bottles containing 400 ml of 0.4 M NaOH.

The initial tests showed that the set-up was suitable for the collection of powdered samples without spreading the powdered concrete outside of the crate. The effectiveness of the absorption bottles to absorb <sup>3</sup>H and <sup>14</sup>C was first tested by drilling small wells on the inactive concrete, adding <sup>3</sup>H and <sup>14</sup>C standard solutions to the wells, allowing them to dry and then drilling and measuring the released <sup>3</sup>H and <sup>14</sup>C in the absorption bottles. However, most likely due to the loss of the analytes during drying, the tests were not successful. On the other hand, further tests could have been carried out by mixing the standard solutions in the concrete paste [2]. However, this was not considered necessary, since the speciation of the <sup>3</sup>H and <sup>14</sup>C dictate their volatility and spiked samples would not be completely comparable with activated concrete. Additionally, possible inefficient absorption of <sup>3</sup>H in the first absorption bottle would mean possible sorption in second and third absorption bottles. Additionally, the distribution of <sup>14</sup>C in the second and third absorption bottles can give an indication of efficiency. E.g. similar concentrations in both the second and the third absorption bottles would indicate inefficient absorption or higher concentration of <sup>14</sup>C in the second absorption bottle would mean efficient absorption. The grain size distribution was determined using sieves of 0.5, 0.25, 0.149, 0.074 and 0.044 mm.

### Drilling of activated FiR1 concrete

The FiR1 activated concrete core had been taken from the biological shield approximately 1.5 years earlier and the most active section of the core was pulverised. Since the dose rate of the core was low (<5 μSv h<sup>-1</sup>), additional shielding was not needed. However, personal protection equipment (PPE) was used to minimise the risk of internal contamination. The drilling was carried out during several approximately one hour long sampling sessions, since wearing the PPE and the hardness of the concrete due to the stones made the drilling very tiring. In total, 183 g of activated concrete was drilled during 2 working days totalling 6.5 h of drilling. A relatively large amount of concrete was pulverised to obtain a representative and homogenous sample for the characterisation studies and for an intercomparison exercise [8].

The released <sup>3</sup>H and <sup>14</sup>C were collected in the absorption bottles and measured using LSC. Due to the long lasting luminescence in the 0.4 M NaOH solutions, all the samples were allowed to stabilise in the dark for at least 24 h. The detection limit was calculated using Eq. 1 [10].

$$CLd = (2.71 + 4.65(N_b)^{1/2})/t/\eta/m \quad (1)$$

where N<sub>b</sub> = blank counts

t = counting time (s)

η = counting efficiency

m = sample weight (g)

So called method blanks were collected by pumping air through a fresh set of absorption bottles for the same amount of time as the sample collection and with the same flow rate. The solutions were measured by LSC in the same way as the samples.

### <sup>3</sup>H and <sup>14</sup>C analysis in activated FiR1 concrete

The activity concentrations of <sup>3</sup>H and <sup>14</sup>C in the activated FiR1 concrete powder were analysed using the RADDEC pyrolyser. The samples (100 mg to 5 g) were placed in the first furnace and the temperature was increased by 10 °C min<sup>-1</sup> until it reached 900 °C and was then held at 900 °C for 90 min. The LSC measurements were carried out in the same way as explained previously.

The speciation studies were carried out based on references by [11, 12, 16]. Water loss in the set-up occurs in three key stages at approximately 105 °C, 170 °C, and 300 °C, whereas mineral-bound <sup>3</sup>H was expected to be released at higher temperatures [11]. The heating profile had three steps and the absorption bottles with 20 ml 0.1 M HNO<sub>3</sub> were changed in the end of each step. In step one, the temperature was increased by 2 °C min<sup>-1</sup> until it reached 200 °C and was then held at 200 °C for 20 min. <sup>3</sup>H as HTO was expected to be released during step 1. In step two, the temperature was increased by 3 °C min<sup>-1</sup> until reaching 300 °C and was held at 300 °C for 20 min. The water of crystallisation was expected to be released between 200 and 400 °C. In step three, the temperature was increased by 5 °C min<sup>-1</sup> until it reached 500 °C, after which an O<sub>2</sub> flow was added. Then temperature was increased by 10 °C min<sup>-1</sup> until reaching 900 °C and was then held at 900 °C for 90 min. Mineral-bound <sup>3</sup>H correlating to Li activation was expected to be released during step three. The LSC measurements were carried out in the same way as explained previously. Further information on the RADDEC tube furnace and <sup>3</sup>H thermal desorption profiles of various materials can be found in reference [12]. As seen in the results section, the activated concrete powder did not contain <sup>14</sup>C and thus, speciation studies were carried out only for <sup>3</sup>H.

## Results and discussion

The drilled FiR1 activated concrete was very fine grain sized which was advantageous in the complete dissolution of the matrix in the radiochemical analysis. Even though sampling was laborious, no further pre-treatment was needed. The grain size analysis results showed that 85% of the sample

had a lower grain size than 0.044 mm in diameter, while rest of the sample was evenly distributed between 0.25, 0.149, 0.074, and 0.044 mm with 3–4% of the sample in each sieve. The particle size generated during drilling probably depends mostly on the matrix of the object, but it can also depend on the drill rotation speed and the suction flow rate. It would be also possible to connect an online aerosol measurement device to the set-up, for example before the cyclone or the filter, to analyse the powder particle size properties in situ.

### **Release of $^3\text{H}$ and $^{14}\text{C}$ during the drilling of FiR1 activated concrete**

The LSC results in the first absorption bottle showed that 3.3 kBq of  $^3\text{H}$  was released during the two days of drilling. The  $^3\text{H}$  detection limit was 1.0 mBq/g calculated from the method blank. The  $^{14}\text{C}$  LSC results showed that a 200 CPM signal was measured in the second absorption bottle whereas the signal was below the detection limit in the third absorption bottle. A closer study of the spectrum showed that the detected counts in the second absorption bottle seemed to originate from  $^3\text{H}$ . In cases when  $^3\text{H}$  and  $^{14}\text{C}$  are measured separately, the measurement windows in Hidex are channels 5–200 and 5–600, respectively. However, when double labelled samples with  $^3\text{H}$  and  $^{14}\text{C}$  are measured simultaneously, the measurement channels are 5–200 and 201–650, respectively. Therefore, the sample from the second absorption bottle was re-measured using a narrower 201–650 channel window and a longer measurement time (14 400 s) in low background mode using a guard. The results showed that the signal was below the detection limit. The sample was then re-measured using the  $^3\text{H}$  protocol. The results showed that 1.0 kBq of  $^3\text{H}$  had leaked from the first absorption bottle into the second. Therefore, in total 4.4 kBq of  $^3\text{H}$  in a gaseous form was released during drilling and 76% was absorbed in the first absorption bottle and 24% in the second. The  $^3\text{H}$  release was therefore  $24 \pm 5 \text{ Bq g}^{-1}$  whereas there was no measurable amount of  $^{14}\text{C}$  released. The  $^{14}\text{C}$  detection limit was 0.7 mBq/g calculated from the method blank. The efficiency of the 0.1 M  $\text{HNO}_3$  absorption solution and absorption bottle can be estimated to be efficient even though 24% of released  $^3\text{H}$  was trapped in the second absorption bottle. This phenomenon is not too problematic since  $^3\text{H}$  and  $^{14}\text{C}$  can be measured in the same sample using the double labelling measurement protocol of LSC.

Evaporation of the absorption solutions during the drilling were not monitored because relatively small volumes were estimated to evaporate. However, if evaporation would be a problem, cooling of the solutions with ice blocks, for example, could be easily carried out. Additionally, the measurement of the weight at the beginning and end of drilling would have enabled correction calculations for evaporation. Furthermore, in the studied set-up, the absorption bottles

were at a lower than ambient pressure. If the absorption bottles would be placed at the outlet of the vacuum pump, the bottles would be at ambient pressure plus the hydrostatic pressure caused by the bottles themselves lowering the evaporation.

### **Analysis of $^3\text{H}$ and $^{14}\text{C}$ in FiR1 activated concrete**

The pyrolyser results for a 100 mg drilled sample showed that the activated concrete contained  $43 \pm 7 \text{ Bq g}^{-1}$  of  $^3\text{H}$ . Therefore, the total  $^3\text{H}$  concentration (released during sampling and analysed using the pyrolyser) in the activated concrete was  $67 \pm 18 \text{ Bq g}^{-1}$ . This means that approximately 36% of the total  $^3\text{H}$  was released during sampling. On the other hand, there was no detectable amount of  $^{14}\text{C}$  even when a 5 g sample was analysed. A much lower level of  $^{14}\text{C}$  compared to  $^3\text{H}$  was expected to be present in the activated concrete according to the amount of activating elements and cross sections. The same activated concrete sample was also studied in the intercomparison exercise mentioned earlier [8]. The sample was divided into 20 g subsamples and measured homogenous using gamma spectrometry prior to the sending of the samples to the partners [8]. The volatility of especially  $^3\text{H}$  was already considered in the beginning of the intercomparison exercise and the possibility of varying results due to evaporation was acknowledged. However, the submitted results did not indicate that evaporation had occurred during storage. Five  $^3\text{H}$  and five  $^{14}\text{C}$  results were submitted for statistical analysis according to the ISO 13528 standard [17]. The assigned value calculated from participants' results for  $^3\text{H}$  was  $55 \pm 4 \text{ Bq g}^{-1}$  (not corrected with release during sampling) which was comparable to the results of this study. All four thermal oxidation analyses of  $^{14}\text{C}$  were below the detection limit whereas only one  $^{14}\text{C}$  result (i.e.  $70 \text{ mBq g}^{-1}$ ) was produced using oxidative acid digestion.

The speciation studies in the drilled concrete sample showed that on average  $3 \text{ Bq g}^{-1}$  of  $^3\text{H}$  was released below  $200 \text{ }^\circ\text{C}$ ,  $2 \text{ Bq g}^{-1}$  was released between  $200$  and  $300 \text{ }^\circ\text{C}$ , and  $39 \text{ Bq g}^{-1}$  was released between  $300$  and  $900 \text{ }^\circ\text{C}$ . The combination of these results with the released  $^3\text{H}$  during the sampling shows that approximately 35% of  $^3\text{H}$  was loosely bound in the activated concrete sample and was released already during sampling. Heating the sample up to  $200 \text{ }^\circ\text{C}$  released the remaining approximately 4% of  $^3\text{H}$  as HTO. Approximately 3% of  $^3\text{H}$  in the water of crystallisation was released between  $200$  and  $300 \text{ }^\circ\text{C}$ . The majority (58%) of the  $^3\text{H}$  was mineral-bound originating from the activation of Li and required a temperature up to  $900 \text{ }^\circ\text{C}$ . Not all the Li originated  $^3\text{H}$  is strongly bound since conversion from a strongly bound form to a loosely bound form can occur via migration out of the mineral lattice [11]. Loosely bound  $^3\text{H}$  can then diffuse through the biological shield [11]. On the

other hand, concrete contains hydrous minerals that might exchange with tritiated water vapour, resulting in more strongly bound  $^3\text{H}$  [12].

## Conclusions

The developed sampling set-up was suitable for sampling activated concrete and the collection of released  $^3\text{H}$  and also possibly  $^{14}\text{C}$ . Additionally, the set-up will be utilised in sampling of activated graphite, and it should be suitable also for any drillable material. In the case of graphite, the drilling is expected to be easier as the material is softer. However, the softness of the material can also mean a higher contamination risk.

In this study, additional information on the release and speciation of  $^{14}\text{C}$  in activated concrete was not collected due to the unmeasurable amount of  $^{14}\text{C}$  in the gaseous and solid samples extracted from the studied activated concrete sample. Therefore, future studies on activated graphite which contains both  $^3\text{H}$  and  $^{14}\text{C}$  will be interesting especially for  $^{14}\text{C}$  behaviour. Additionally, as 35% of the  $^3\text{H}$  was released in a gaseous form during drilling, the release of  $^3\text{H}$  needs to be considered not only during sampling but also during dismantling when large amounts of concrete are cut especially when dismantling the biological shield of power reactors. Additionally, the release of  $^3\text{H}$  during the storing of the drilled sample needs to be considered and analysis should be carried out promptly after sampling.

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