Carbon-14 release from irradiated stainless steel

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1 Introduction

Carbon-14 (half-life 5,730 years) is a key radionuclide in the assessment of the safety of a geological disposal facility (GDF) for radioactive waste in the UK. In particular, the need to better understand the possible importance of gaseous carbon-14 bearing species has been recognised [1]. Carbon-14 is expected to be released from a GDF over a timescale of several thousand years. A number of radioactive gases will be generated from waste materials within a GDF, with carbon-14 bearing methane ($^{14}CH_4$) likely to be the dominant carbon-14 species transported in the gas phase, potentially reaching the biosphere at low activity concentrations.

The main sources of carbon-14 in UK radioactive wastes are: irradiated graphite, irradiated steels, irradiated reactive metals and spent fuel. There are 17,700 TBq of carbon-14 in the 2013 UK Derived Inventory of which 7,090 TBq is associated with irradiated steel wastes [2].

A generic post-closure assessment of the potential radiological impact of carbon-14 from a UK GDF has recently been carried out by Radioactive Waste Management's (RWM) Carbon-14 Project [3]. The assessment found that irradiated steel wastes are the major source of carbon-14 from a UK GDF at times greater than 500 years post-closure [4]. The potential radiological impact of any release of carbon-14 as gas from irradiated steels will be site-specific, depending on the gas migration characteristics of the host rock and the overlying geological formations. The calculated risks arising from steel wastes are highest where the gas-phase release migrates rapidly through the geosphere (e.g. through a fractured higher strength rock) and is focused to a small area (10^4 m^3) at the surface. However, even for a focused surface release, the risks arising from steel wastes will only be above the risk guidance level (10^{-6}) if a significant proportion (>30%) of the carbon-14 is released as methane.

In the calculations of gas generation performed by the Carbon-14 Project, carbon-14 was assumed to be released from the steels at a uniform rate as the wastes corrode. This leads to modest release rates of carbon-14 from these wastes during both the operational and post-closure periods. In the absence of suitable experimental data, no speciation was assigned to the carbon-14 released from steel wastes. Instead, different assumptions about the gas phase speciation were scoped in the biosphere to assess the potential consequences of the carbon-14 releases.

This paper describes work being carried out to measure the rates and speciation of carbon-14 release from irradiated stainless steel during corrosion under simulated disposal conditions to address this key gap in understanding. This work is being performed as part of the European **CA**rbon-14 **S**ource **T**erm, CAST, project, which started in October 2013 and will conclude in March 2018 [5]. It is one of a series of studies under CAST Work Package 2 concerned with carbon-14 release from steel wastes under conditions of a cement-based GDF. This paper describes the design of leaching experiments to measure the release of carbon-14 to both gas and solution phases from irradiated stainless steel under high-pH, anaerobic conditions, and the results obtained during the first three months of operation.

2 Experimental

2.1 Samples

Stainless steel samples from the irradiation experiment R268-7 (SIWAS[1] 07) in the High Flux Reactor (HFR) at Petten, were chosen for this study. The samples selected are 316L(N) EHRII-type austenitic stainless steel taken from a single steel plate. The composition of the stainless steel batch used is given in Table 1. Unirradiated material from the same batch of stainless steel is available and has been used in non-active trial and control experiments.

Table 1 Composition of the selected stainless steel samples (wt.%, Fe - balance)

Steel	C	N	Mn	Si	Cr	Ni	Mo	Cu	Co	Ti	S	P
316L(N)	0.02	0.08	1.8	0.4	17.2	12.2	2.4	0.1	0.08	--	--	0.02

The specimen holder R268-07 (SIWAS), was irradiated in the HFR up to a nominal target dose level of 2 dpa (displacements per atom) at a target temperature of 80°C. The specimens were in direct contact with the HFR core cooling water. The irradiation took 5 cycles (28 days per cycle) in the year 1996-1997.

The samples acquired for study are so-called CT (Compact Tension) specimens (see Fig. 1). Each CT specimen has outer dimensions of 30x28.8x12 mm^3, a geometric surface area of 38.14 cm^2 and mass 74g.

Fig. 1 CT specimen

The amount of carbon-14 (and other radionuclides) in the stainless steel specimens has been calculated using the ORIGEN computational code. The calculated activities for different samples vary by nearly a factor of two. This is caused by the variations in the thermal fluence which is dependent on the position of the samples during irradiation. The fluence, and thus the resulting extents of activation, are higher for those samples closer to the centre of the core. There is also a relatively strong gradient from 'North' to 'South' in the horizontal direction.

2.2 Experiment design

The specification for the experiments was to leach samples of irradiated stainless steel in a high-pH solution under anaerobic conditions for a period of one year and to periodically measure the releases of carbon-14 to both the gas and solution phases. Owing to the high gamma dose rates from the samples, it is necessary for the experiments to be performed in a shielded cell; the G1 chemical cell in NRG's Hot Cell Laboratories at Petten was selected.
Leaching is being performed in a 0.1 mol dm^{-3} sodium hydroxide solution (pH ~13) under a nitrogen atmosphere to simulate conditions in a cementitious near field. A sodium hydroxide rather than a calcium hydroxide solution was selected to avoid complications that may arise from the precipitation of any carbon-14 released from the steel in the form of CO_2 as calcium carbonate, and for consistency with the method used in studies of carbon-14 release from irradiated graphite [7]-[9].
For gas phase sampling and analysis, a gaseous carbon-14 capture and analysis methodology developed by Radio Carbon Dating (RCD) Limited for studies of carbon-14 releases from irradiated graphite [7]-[9] was known to provide a high sensitivity for the selective capture and quantification of carbon-14 species released to the gas phase. The RCD method involves the periodic purging of the head-space of the experimental container with nitrogen and the selective oxidation and capture of carbon species from the gas phase as CO_2 on a series of soda lime columns. After sampling, the soda lime columns are removed and returned to RCD for analysis. The oxidation catalysts and soda lime columns for carbon-14 capture are built into two sampling rigs, which were manufactured by RCD. To avoid potential cross-contamination, it has been necessary to place the sampling rigs in a dedicated glove box adjacent to the G1 chemical hot cell.

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[1] SIWAS – Simplified water-steel irradiation

Solution phase samples are taken from the leaching experiments after gas sampling and are analysed for total carbon-14 and cobalt-60. It is planned to sample each of the experiments six times: after 1 week, 3 weeks, 6 weeks, 3 months, 6 months and 1 year. The cobalt-60 analysis was intended to provide information on the rate of stainless steel corrosion. At the end of the experiments, the experimental containers will be emptied and the total amounts of cobalt-60, present as precipitate or sorbed to the container walls, will be determined by acid leaching.

2.2 Experimental container

The leaching container, has to meet different requirements to be suitable for the long term leaching tests on irradiated steel in the hot cell. Various materials were considered:

- steel – not suitable for leaching of steel, possible effect on the results;
- plastic – not resistant to long term exposure to radiation;
- glass – most suitable for the experiment because of its material properties, but fragile for manipulation with the manipulators.

The leaching container was required to have a volume of about 1-1.5 litres, with sufficient volumes of gas and liquid to allow sampling during the experiment execution while retaining enough leachant in the container. Systems for both gas and liquid phase sampling needed to be incorporated into the design. The container also needed to be sufficiently robust and simple to use remotely in the hot cell with manipulators. A suitable solution for fixing the CT specimens also had to be developed.

Many aspects of the design were considered during the development stage, and a number of different solutions were put forward for discussions. The final design (Fig. 2) consists of an outer vessel with cover, both made from borosilicate glass. The two parts of the vessel join at a flange. The flange seals on an acetylnitrile butadiene rubber (NBR) O-ring, which is known to have good radiation tolerance, and is secured using a clamp. An inert zirconia crucible serves as an inner container to hold the leachant during the leaching experiment. This is to avoid contact between leachant and glass that could potentially affect the experiment. It is known that the presence of silicate ions can reduce the corrosion rate of steels in water [6], and the borosilicate glass container would react with the high-pH solution to release silicate species into solution. The gas sampling system is formed by inlet and outlet valves located in the base of the container, with inlet connected to the nitrogen supply and outlet to the RCD rigs. Liquid sampling and leachant addition are performed via a dip leg made of quartz. The valves to be used for gas and liquid sampling are of the HighVac manual stopcock type, made from borosilicate glass. Each stopcock valve has a glass piston fitted with three elastomer (Viton) O-rings. Each stainless steel sample is hung from a triangle that is placed on the zirconia insert. The CT specimens are hung on stainless steel hooks. The containers are adapted to be handled by the manipulators.

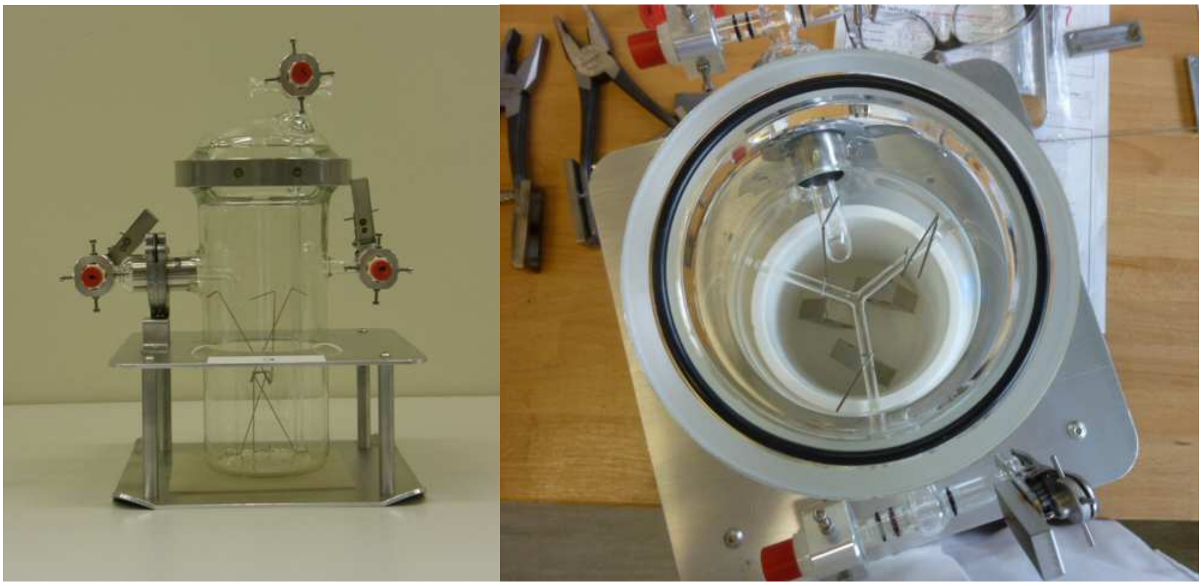

Fig. 2 Leaching container (left) and a detail of the fixed CT specimens in the container (right)

The procedures for liquid handling (leachant addition at the start of the experiment and liquid sampling during the experiment) were tested using experimental mock-ups.

2.3 Analytical methods

C-14 analysis in gas samples

The RCD method allows the separation and quantification of [7]:

- carbon-14 released as CO_2;
- carbon-14 released as CO (any volatile oxygen-containing organic species e.g. alcohols, aldehydes and ketones that escape from solution into the gas phase would also be collected in this fraction); and
- carbon-14 released as volatile hydrocarbons, principally CH_4, (any other volatile carbon-containing species that have passed through the “CO” collection column would also be collected in this fraction).

The three fractions are collected on separate soda lime columns. Each column is pre-loaded with fossil CO_2 to provide a bulk carrier during processing for the small amounts of gaseous carbon species released in the experiments. The CO_2 is recovered from each soda lime column by acidification, and is converted to benzene via reaction with lithium to produce lithium carbide, its hydrolysis to acetylene and catalytic trimerisation of the acetylene. The benzene produced is mixed with Opti-Fluor scintillant and the carbon-14 content measured by liquid scintillation counting (LSC) using a Wallac Quantalus counter. Counting times of up to 2000 minutes have allowed limits of detection down to about 0.04 Bq carbon-14 per sample.
Fuller details of the RCD method are provided in reference [9].

C-14 analysis in liquid samples

The liquid samples are first processed to release C-14 from the solution by acidification of the solution by nitric acid, purging by nitrogen and capture of released C-14 in Carbosorb E. The C-14 is determined by using a Liquid Scintillation Counting method (TriCarb 3180 TR/SL). Instagel is used as a scintillation cocktail. The samples are analysed by LSC in low-level count mode for a period of 60 minutes. The Minimum Detectable Activity (MDA) in this mode is 0.1 Bq in the sample. The effectiveness of the separation method has been validated using standard solutions of carbon-14 labelled sodium carbonate.

Co-60 analysis in liquid samples

The liquid samples are measured on a calibrated HPGe gamma spectrometer arrangement. Each sample contains approximately 400µL and is stored in a small polyethylene (PE) container. To avoid risks of potential sample leakage the containers are then placed into a second, one size larger PE container. The measurements are made for a period of 48 hours at distance of 10 cm from the detector. The data have been processed by the NIAGADA program which is part of the NEMO package. All the measurement parameters are known including the dead time, emission probability of the gamma-peaks and the efficiency of the HPGe detector, so that the counted pulses from the peaks could be transformed to activities. The results have been corrected for gamma-self-absorption, the dimensions of the sample, the shielding of the double PE containment and the background. The MDA of the detector for ^{60}Co is 1.0 Bq for a counting time of 48 hours.

2.4 Blank Experiment

A Blank Experiment was performed to test the equipment and all operational procedures for use in the experiments before they were transferred into the hot cell. It also provided a measure of the intrinsic carbon-14 background of the experimental methods. A schematic representation of the equipment is shown in Fig 3. The experiment was performed on the container filled with the required volume of 0.1 mol dm^{-3} sodium hydroxide solution, but without any steel specimens being present. The experiment took 10 days, with sampling after 24 hours and 9 x 24 hours.

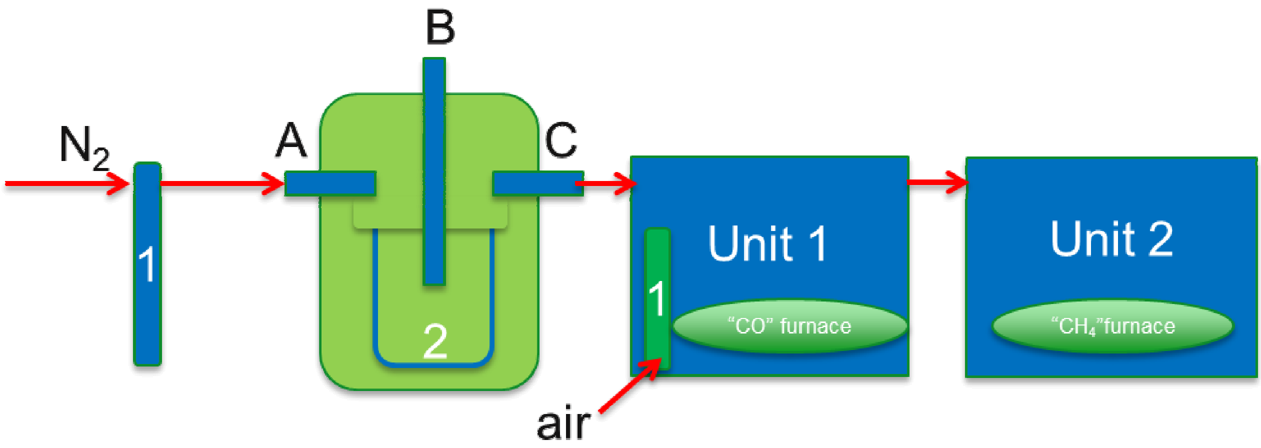

Fig. 3 Schematic representation of the equipment used for the Blank Experiment: *1* is a soda lime column for removing carbon-14 from the nitrogen feed and air, *2* is the leaching container where *A* is the N_2 inlet, *B* is the dip leg and *C* is the N_2 outlet, *Unit 1* and *Unit 2* are the two parts of RCD apparatus for gaseous C-14 capture, Unit 1 selectively captures the CO_2 and CO fractions , Unit 2 the CH_4 fraction

The samples have been taken for both gas and liquid and treated and analysed as described above. For gas samples, there is no significant difference between the carbon-14 specific activities measured in the samples and those measured in the aliquots of pre-loaded soda lime and it can be concluded that no carbon-14 was absorbed from the laboratory air during the sampling periods. The carbon-14 measurements showed that the amounts of carbon-14 in both solution samples are below the detection limit of LSC.

2.5 Experiment

After finishing all the preparation, design and development work, the experiments were assembled in the chemical hot cell. All procedures and the operation of the equipment by manipulators have been tested in the hot cell (see Fig. 4).

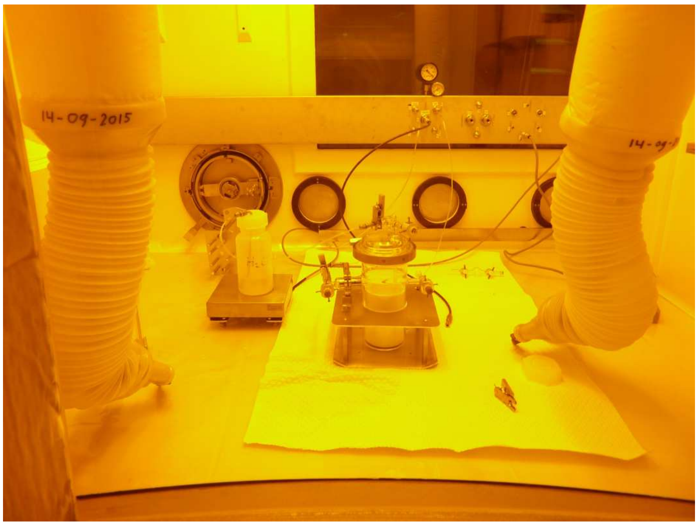

Fig. 4 Liquid addition test to the container in the hot cell

Finally, the containers have been assembled, the CT specimens have been fixed, the containers closed and leak tested. Three containers have been prepared each containing 3 CT specimens, container 1 with non-irradiated samples and containers 2 and 3 with irradiated samples. The carbon-14 and cobalt-60 contents of containers 2 and 3 are given in Table 2.

Table 2 Overview of samples in the containers and their activity content at 1 June 2016

	Container 2	Container 3
Total C-14 activity in container (Bq)	4.89×10^{7}	4.93×10^{7}
Total Co-60 activity in container (Bq)	1.60×10^{10}	1.62×10^{10}

The experiment has been started by the addition of 600 cm^3 of the leachant. The experiment is running; sampling has been performed according to the sampling schedule.

3 Results and Discussions

In this paper the results up to 3 months leaching are presented. During periodic sampling, first the gas phase carbon-14 has been collected by purging the container head-space with nitrogen for a period of 7 hours and passing the purge gas through the RCD sampling rigs, later a liquid sample (~7 cm^3 in volume) has been taken by filling an evacuated bulb through the dip leg.

The cumulative releases of carbon-14 to the gas phase collected in each of the gas fractions are presented for Containers 2 and 3 in Figure 5. The total activities of carbon-14 and cobalt-60 measured in the solution phase are presented in Figure 6.

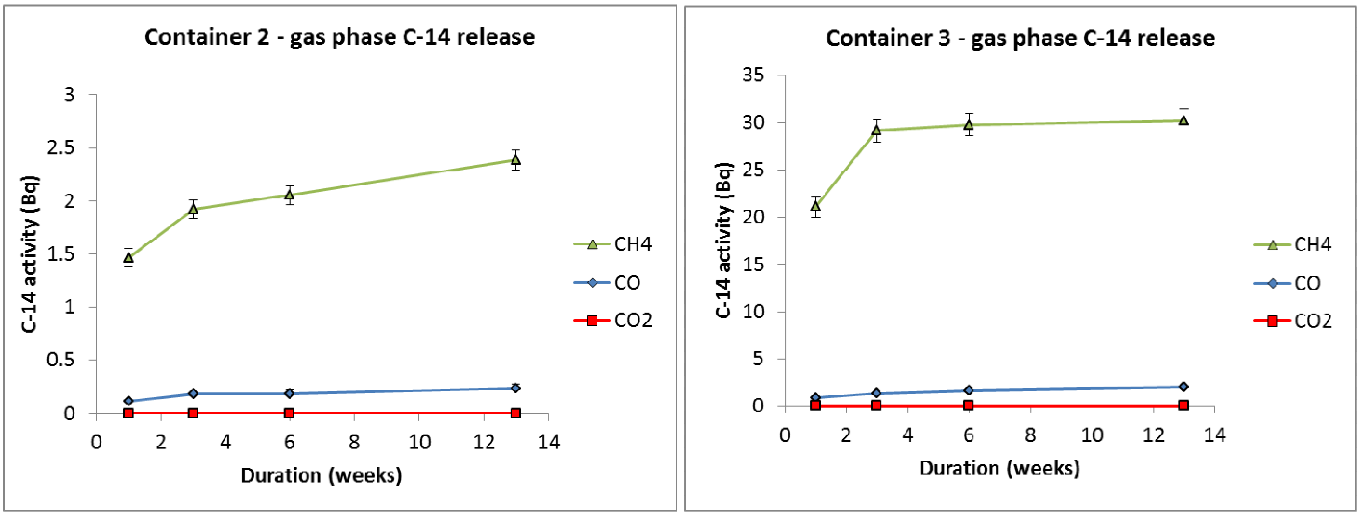

Fig. 5 Gas phase C-14 release in container 2 (left) and container 3 (right)

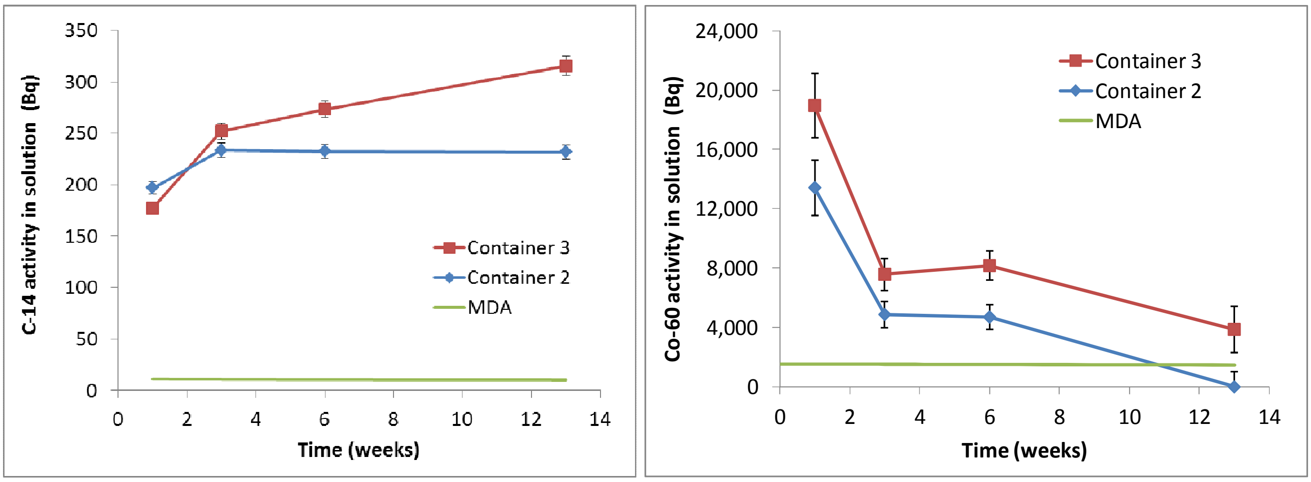

Fig. 6 C-14 activity in solution (left) and Co-60 activity in solution (right)

A fast initial release of carbon-14 is observed during the first three weeks of the experiments, followed by a rate decrease at longer times. The majority of the carbon-14 release occurs to the solution phase. In container 2 only about 1% of the C-14 release is to the gas phase, in container 3 a higher fraction, about 10% of the C-14 released is as gas. In both containers 2 and 3 the majority of the gaseous C-14 is released as hydrocarbons with a small amount captured in the CO fraction; no CO_2 has been found in the gas phase (in line with any being retained in the alkaline leachant).

In container 2, the C-14 activity in solution has not increased measurably between three weeks and three months (Figure 6, left); in contrast, in container 3 the C-14 activity in solution has continued to increase at a near constant rate. In the container with non-irradiated samples, no C-14 has been measured. It is noted that there is some uncertainty over whether the solution analysis gives a total dissolved carbon-14 measurement as the effectiveness of the acidification method for recovering carbon-14 in water-soluble organic forms (e.g. carboxylic acids) is uncertain.

The activity of Co-60 in the leachates is high after one week; however, the activity subsequently decreased (Figure 6, right). This decrease could be caused either by solubility limitations of cobalt and/or its sorption to the vessel walls or to the steel samples themselves. To study this behaviour, an additional test is running where a 0.1 M NaOH solution has been spiked by Co-60 of known activity, the solution is stored in the same container setup with zirconia insert; Co-60 in the solution is measured at the starting point and after 6 weeks.

The initial Co-60 and C-14 releases on immersion in solution were much larger than expected based on the corrosion rates of unirradiated stainless steel under anaerobic alkaline conditions. There are a number of possible explanations: higher C-14 and Co-60 concentrations at the surface of steel or higher initial corrosion rates than expected. The latter could be affected by a number of factors: (i) some residual oxygen contributing to faster initial (aerobic) corrosion, (ii) an effective surface area larger than expected (roughness of surface finish, effects of prior corrosion, radiation damage) (iii) sample history and/or (iv) the irradiated surface is more reactive than an unirradiated surface.

4 Summary and outlook

The experiment to study the C-14 release from irradiated stainless steel due to corrosion under aqueous high-pH, anaerobic conditions has been designed and commissioned, including the experimental equipment, leaching containers and the analytical methods. By December 2016, the leaching experiments have been running for a period of 6 months, with samples of gas and solution phases taken periodically and analysed according to the schedule.

Based on the results up to 3 months, preliminary conclusions can be made that there is a relatively fast initial release of accessible C-14 species from the surface of the steel on immersion in the high-pH solution. Most of the C-14 is released into solution, but a fraction is also released to the gas phase, primarily as hydrocarbons. The rate of carbon-14 release declines to near-zero over the first 6 weeks in container 2; the release continues at a measurable rate in container 3, which also has a higher gas phase release.

A high rate of Co-60 release was measured from the surface initially, followed by drop in solution activity. This could be the result of either solubility limitation and/or sorption to the vessel walls or the steel samples. It is therefore concluded that the release of Co-60 is not a suitable analogue to monitor the corrosion rate of the steel in these experiments.

Further sampling of the experiments will provide data on the rate and speciation of carbon-14 release from the irradiated steels due to corrosion in the longer term. The experiments are planned to run for a minimum period of one year; once terminated, the leaching vessels will be emptied and the walls acid washed to recover deposits for cobalt-60 analysis by γ-spectroscopy.

5 Literature

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