CArbon-14 Source Term

CAST

C-14 release and speciation from irradiated stainless steel under alkaline reducing conditions (D2.8)

Updated up to 13 months sampling

Author(s):

Eva de Visser-Týnová, Marcel Stijkel (NRG)

Steve Swanton (Amec Foster Wheeler)

Bob Otlet, Jill Walker (RCD)

Date of issue of this report: 01/03/2018

The project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no. 604779, the CAST project'

Dissemination Level		
PU	Public	**x**
RE	Restricted to the partners of the CAST project	
CO	Confidential, only for specific distribution list defined on this document	

CAST – Project Overview

The CAST project (CArbon-14 Source Term) aims to develop understanding of the potential release mechanisms of carbon-14 from radioactive waste materials under conditions relevant to waste packaging and disposal to underground geological disposal facilities. The project focuses on the release of carbon-14 as dissolved and gaseous species from irradiated metals (steels, Zircaloys), irradiated graphite and from ion-exchange materials as dissolved and gaseous species.

The CAST consortium brings together 33 partners with a range of skills and competencies in the management of radioactive wastes containing carbon-14, geological disposal research, safety case development and experimental work on gas generation. The consortium consists of national waste management organisations, research institutes, universities and commercial organisations.

The objectives of the CAST project are to gain new scientific understanding of the rate of re-lease of carbon-14 from the corrosion of irradiated steels and Zircaloys and from the leaching of ion-exchange resins and irradiated graphites under geological disposal conditions, its speciation and how these relate to carbon-14 inventory and aqueous conditions. These results will be evaluated in the context of national safety assessments and disseminated to interested stakeholders. The new understanding should be of relevance to national safety assessment stakeholders and will also provide an opportunity for training for early career researchers.

For more information, please visit the CAST website at:
http://www.projectcast.eu

CAST

C-14 release and speciation from irradiated stainless steel under alkaline reducing conditions (D2.8)

CAST		
Work Package: 2	CAST Document no. D2.8	Document type: R
Task: 2.3	CAST-2017-D2.8	R = report, O = other
Issued by: NRG		Document status: Final
Internal no. : NRG-23476/18.147473		Draft/Review/Final

Document title
C-14 release and speciation from irradiated stainless steel under alkaline reducing conditions

Executive Summary

This report is a deliverable D 2.8 of the CAST project. It has been compiled from different reports and notes prepared within the CAST and preparatory projects; these have been prepared both by NRG and Amec Foster Wheeler to report progress to RWM within these projects.

In this deliverable, the details about the experiments focusing on the study of C-14 release from irradiated steel are presented. It includes the samples, experiment design, description of analytical methods, experiment and its results, and discussions of the results. This version of the deliverable is updated with results up to 13 months of running of the experiment.

In the two experiments containing irradiated steel specimens, a relatively fast initial release of accessible carbon-14 species from the surface of the steel is observed within the first week of leaching, followed by a drop in the rate of release at longer times. Most of the carbon-14 is released into the solution, but about 1% and 12% of the carbon-14 releases are to the gas phase in Containers 2 and 3, respectively. Not only are the proportions of gas phase releases different between Containers 2 and 3 but also the rates and speciation of gas phase release after the first week.

The experiment is planned to run for a period of one year, with a possibility of prolongation. The additional results will be presented in a new report to be prepared by Amec Foster Wheeler and NRG and will be published on the website of RWM.

Acknowledgement

The project has received funding from the European Union’s Seventh Framework Programme for research, technological development and demonstration under grant agreement no. 604779, the CAST project. (www.projectcast.eu)

Co-funding from Radioactive Waste Management is gratefully acknowledged.

Oene Zwaagstra and Jan Kok (NRG) are acknowledged for performing the C-14 measurements. Adri Paardekooper and Ben Straathof (NRG) are acknowledged for performing the Co-60 measurements.

List of Contents

1 Introduction

Work to develop understanding of the release of carbon-14 release from radioactive waste materials under conditions relevant to waste packaging and disposal to underground Geological Disposal Facilities (GDFs) is being performed under the International CAST (CArbon-14 Source Term) project, part-funded through the Euratom Seventh Framework Programme. The project is focusing on carbon - 14 releases from irradiated metals (steels and Zircaloy), irradiated graphite and spent ion exchange materials as dissolved and gaseous species. The scientific understanding obtained from these studies will then be considered in terms of national disposal programmes and the impact on safety assessments.

Work Package 2 (WP2) of the CAST project is concerned with carbon - 14 releases from irradiated steels. The main objectives of WP2 Steels are:

- to develop analytical techniques for the identification and quantification of carbon 14 species formed during corrosion of irradiated steels under conditions relevant to cement-based GDFs;
- to validate activation models by measuring carbon 14 inventories in irradiated steel;
- to carry out experiments and modelling to develop further understanding of the speciation and rate of carbon-12/carbon-13 and carbon - 14 release from corrosion of irradiated and unirradiated steels under conditions relevant to GDFs;
- to incorporate information from existing and ongoing projects elsewhere on steel corrosion into the work package to make the current understanding available.

The objective of this work is to measure the rate and speciation of carbon-14 release from irradiated stainless steel on leaching under high-pH anaerobic conditions, representative of a cement-based near field for intermediate- and some low-level wastes (ILW/LLW). In particular, this includes measurements of releases to the gas phase as well as to solution.

2 Experimental

2.1 Samples

The irradiated samples comprise Compact Tension (CT) specimens of 316L(N) EHRII-type austenitic stainless steel that were irradiated in the High Flux Reactor at Petten to a nominal dose of 2 dpa (two displacements per atom) in experiment R268-07 during 1996-97. The composition of the stainless steel batch used is given in Table 1. Unirradiated material from the same batch of stainless steel has been used to manufacture additional CT specimens for use in the control experiment.

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

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 samples acquired for study in this project are so-called CT (Compact Tension) specimens designed for use in material property tests. The dimensions of the samples are marked on the drawings in Figure 1; an example is shown in Figure 2. Eight irradiated CT specimens have been acquired for use in these experiments.

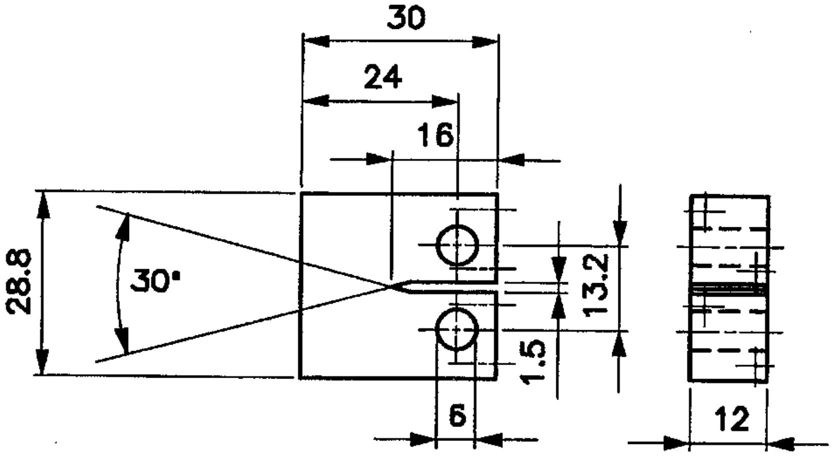


Figure 1 Drawings of a CT specimen (dimensions in mm)

Figure 2 Photograph of a CT specimen

The samples have been stored for a period of almost 20 year in a Waste Disposal Facility (WSF) of NRG. Before using the samples, they were cleaned by a tissue, no other cleaning has been performed.

The amount of carbon-14 (and other radionuclides) in the irradiated stainless steel specimens has been calculated by NRG from their irradiation history, using the ORIGEN computational code (for details see App. A).

2.2 *Experimental design*

Due to the high dose rates from the irradiated samples, the experiments need to be undertaken in a shielded cell. Therefore, the experiment has been designed specifically to meet the requirements for isolation and handling (with manipulators) in NRG's Hot Cell Laboratory at Petten. The leaching experiments are taking place in the G1 chemical cell which has an inert, nitrogen atmosphere. The temperature of the hot cell is slightly above ambient temperature (~30°C).

Three leaching containers were manufactured at the University of Amsterdam. Each container (Figure 3) consists of an outer vessel with lid, 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 solution during the leaching experiment. 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 gas sampling rigs, which are located in a glovebox adjacent to the hot cell. 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 experiment contains three CT specimens which are suspended on stainless steel hooks from a glass triangle that is placed on the top of the zirconia insert (see Figure 3, right).

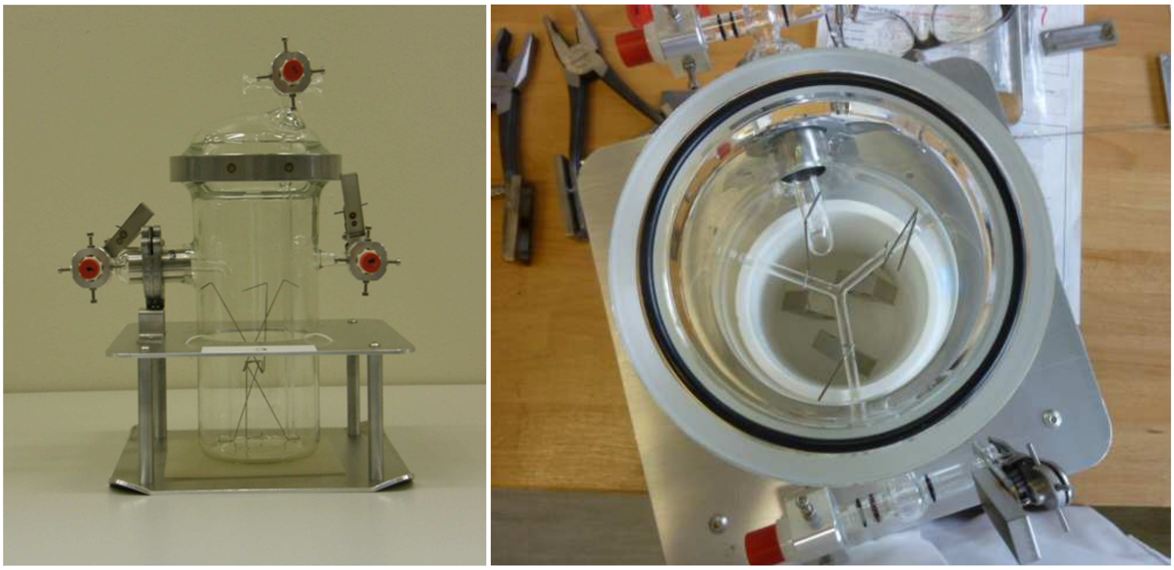


Figure 3 Two views of the experimental container being used for the CAST experiments

2.3 Inventory of the experiments

There are three containers within the experiment:

- Container 1 – non-irradiated samples
- Container 2&3 – irradiated samples.

The non-irradiated samples (each weighing 76 g, total surface area 106 cm^2) have been placed in the first container (Container 1). An estimate of the carbon-14 activity content of Container 1, based on the total mass of steel, the mass fraction of carbon in the steel (0.0238%) and assuming natural abundance for carbon-14, is about 0.1 Bq.

Six irradiated CT specimens have been divided between other two of the three containers according to the scheme in

Table 1, so that the carbon-14 and cobalt-60 contents of each container are similar.

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

	Container 2			**Container 3**		
Sample	**b102**	**b116**	**b121**	**b103**	**b112**	**b117**
Mass (g)	73	74	74	74	74	74
Total surface area (cm^2)	117			117		
C-14 activity ($Bq\ g^{-1}$)	1.55E+05	2.87E+05	2.21E+05	1.81E+05	2.85E+05	2.01E+05
Total **C-14** activity in container (Bq)	**4.89E+7**			**4.93E+7**		
Co-60 activity ($Bq\ g^{-1}$)	5.13E+07	9.36E+07	7.25E+07	5.96E+07	9.32E+07	6.60E+07
Total **Co-60** activity in container (Bq)	**1.60E+10**			**1.62E+10**		

2.4 CAST experiments

The experiments were assembled in the G1 chemical cell, the specimens inserted, the lids closed and then each container was leak tested. Each experiment was started with the addition of 600 cm^3 of 0.1 mol dm^{-3} sodium hydroxide solution via the dip leg. The NaOH solution has been prepared from very pure NaOH pellets in a glovebox, the solution was purged by inert gas to remove CO_2. The experiments were started on consecutive days to allow a full day for gas and liquid sampling of each container when sampling periodically.

Periodic sampling involves first sampling the gas phase and then the removal of a small volume of leachate solution. The gas phase is sampled by purging the head space of the container with nitrogen and passing the purge gas through the RCD sampling rigs. The head space of the container was purged for seven hours to collect the carbon-14 species released into the gas phase. Sampling of the liquid phase, removing about 7 cm^3 of solution, was then performed via the dip leg into an evacuated bulb. The volume of solution removed is not replaced.

2.5 Carbon -14 analysis

The gas sampling rigs were supplied by RadioCarbon Dating (RCD) Limited and are based on a design that has been used previously by Amec Foster Wheeler to measure gas phase carbon-14 releases from irradiated graphite on leaching [[1][2]]. A schematic design of the rigs is shown in Figure 4. The method involves the selective oxidation and capture of carbon-14 species in the gas stream as $^{14}CO_2$ on a series of three soda lime columns. The RCD method allows the separation and quantification of:

- 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 were not collected by the CO column would also be collected in this fraction).

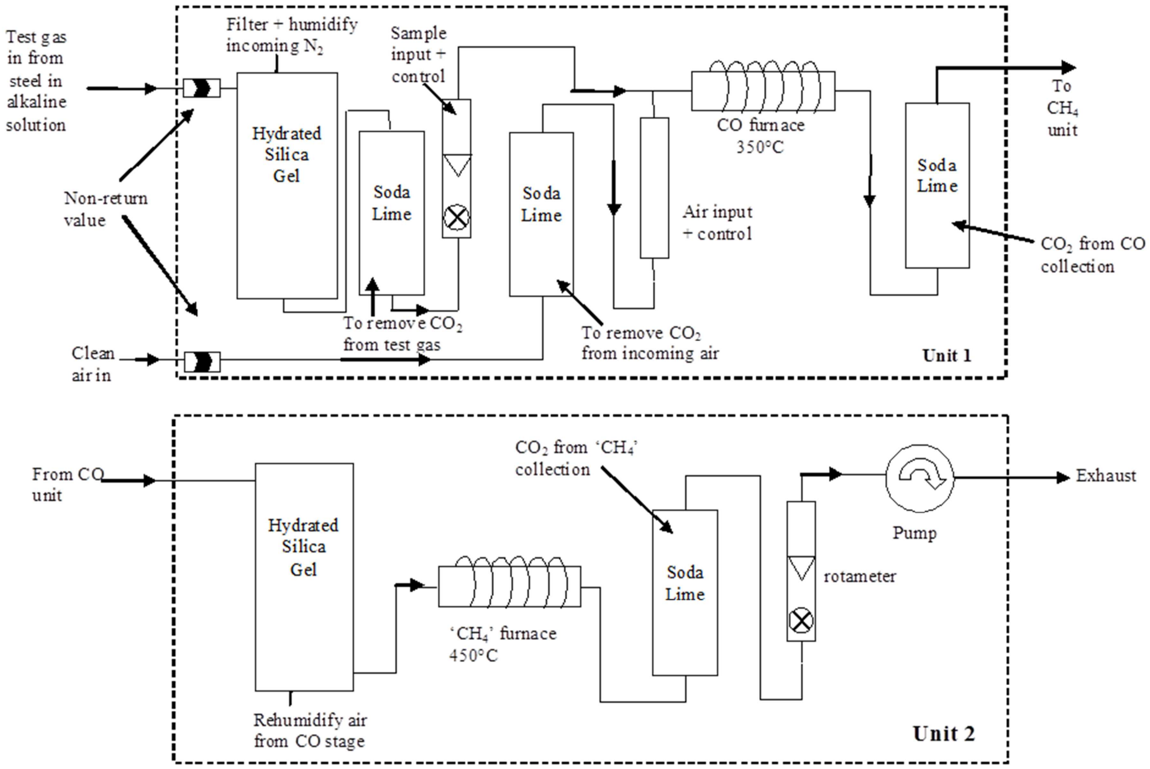


Figure 4 Schematic design of RCD sampling rigs for collection of gas phase carbon-14

The three soda lime columns from each sampling of each container have been returned to RCD for carbon-14 analysis.

The solution phase samples have been divided, with about 0.4 cm^3 being used for Co-60 analysis by gamma spectroscopy and ~5.5 cm^3 for carbon-14 separation and analysis.

The method for carbon-14 separation is setup as follows (see Figure 5). 5 cm^3 of the leachate solution, 0.1 mol dm^{-3} sodium hydroxide (NaOH), is acidified through drop-wise addition to 5 cm^3 nitric acid contained within a reaction tube; this addition takes about 10 minutes. The pH drop triggers the release of carbon-14, dissolved in the solution as carbonate, in the form of CO_2 gas. The method is based on the assumption that the leached carbon-14 is present only in the form of carbonate. A nitrogen carrier gas is bubbled through the mixture to pick up the CO_2.

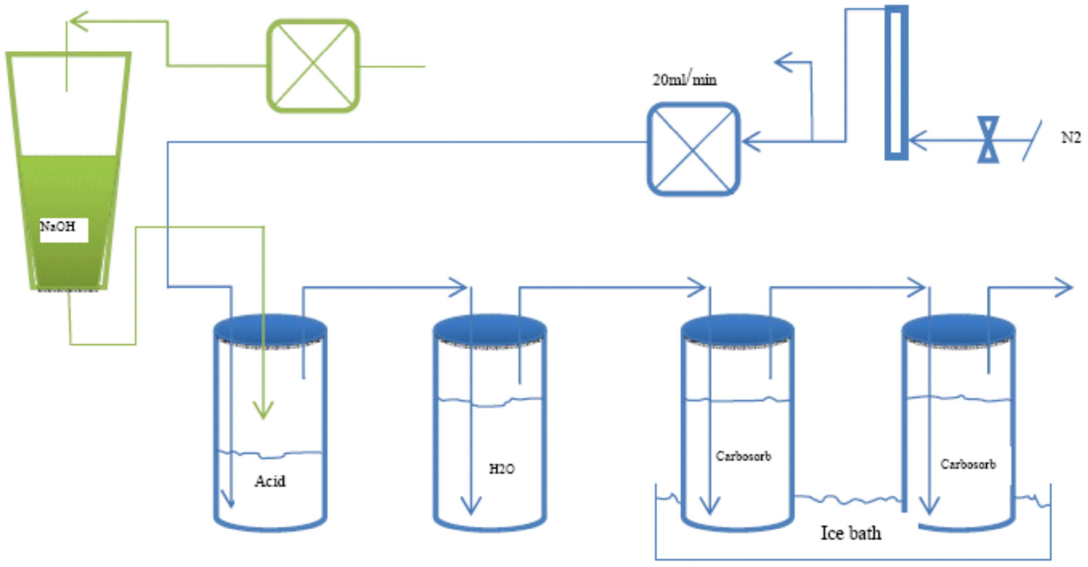


Figure 5 A schematic overview of the method used for C-14 release

2.6 Cobalt-60 analysis

400µL aliquots of the leachate samples are placed into small polyethylene (PE) containers for gamma spectrometry. To avoid risks of potential sample leakage, the containers are then placed in a second, one-size larger PE container. The liquid samples where measured on a calibrated HPGe gamma spectrometer. The following measurement parameters and constraints were used:

- Measurement time:48 hours
- Distance to detector surface:10 cm
- Sample volume:0.400 cm^3
- Density 0.1 mol dm^{-3} NaOH:1.002 g cm^{-3}

The gamma spectra files are used as an input for the NIAGADA program, which is part of the NEMO software 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 can be transformed to activities. The data are corrected for gamma-self-absorption, for the dimensions of the sample, the shielding of the double PE containment and for the background. Quoted activities have been corrected to a reference date of 1 June 2016 at 00:00 am.

Measurement uncertainties (1σ) have been evaluated and account for the uncertainties in the counting statistics, the gamma-self-absorption, the geometry and the mass of the samples (only included in the specific activity) and the nuclear data for cobalt-60. The Minimal Detectable Activity (MDA) of the detector for cobalt is 1.0 Bq for a counting time of 48 hours.

3 Results

3.1 Carbon-14 release to the gas phase

The measured specific activities of carbon-14 in each soda lime column analysed to date are presented in Table 2. Based on the amount of soda lime in each column and taking account of the background specific activity of each soda lime batch used, the results have been converted into total carbon-14 activities per column (Table 3). The cumulative activities of carbon-14 captured in each chemical form from each experiment with time are given in Table 4 and shown in Figure 6.

The uncertainties in the measured activities are based on the counting errors for carbon-14 analysis by LSC. In deriving uncertainties in the cumulative activities of carbon-14, where a result has been recorded as below the limit of detection (LoD), the LoD itself has been used as an upper limit for the positive uncertainty on a zero measurement (the negative uncertainty is zero).

It will be noted from Table 3 that carbon-14 has not been detectable in any of the soda lime columns for collection of $^{14}CO_2$ in the CO/CO_2 unit above the LoD, with the exception of the 3-month sample for Container 3 (RCD-8735). In this case, no carbon-14 was measured in the equivalent ^{14}CO column (RCD-8734), where some would be expected. It appears that the two columns (or their contents) have been inadvertently swapped at same stage between their delivery to NRG at Petten and their processing at RCD. A full QA audit of the records for the two samples during their processing at RCD has been undertaken, but no inconsistencies have been found that would point to an accidental swap of the samples in RCD's laboratory . Likewise no accidental switch was noted at NRG. However, based on the results for Container 2, the previous results for Container 3 and preliminary count rates for the month 5 Container 3 samples, the decision has been taken to reassign the data in Table 3: RCD-8735 as ^{14}CO and RCD-8734 as $^{14}CO_2$.

Table 2 Carbon-14 specific activities of soda lime columns from sampling after 1, 3, 6 weeks and 3 months

Sampling date	RCD reference No.	Carbon-14 specific activity (Bq kg^{-1} carbon)			Experiment
		CO	CO$_2$	CH$_4$	
1 week					
7/ 6/16	RCD-8701 – CO RCD-8702 – CO$_2$ RCD-8703 – CH$_4$	17 ± 0.9	7 ± 0.7	60 ± 1.1	Container 1
8/ 6/16	RCD-8704 – CO RCD-8705 – CO$_2$ RCD-8706 – CH$_4$	46 ± 1.1	9 ± 0.8	496 ± 4.0	Container 2
9/ 6/16	RCD-8707 – CO RCD-8708 – CO$_2$ RCD-8709 – CH$_4$	293 ± 2.2	13 ± 0.9	6980 ± 49	Container 3
3 weeks					
20/ 6/16	RCD-8710 – CO RCD-8711 – CO$_2$ RCD-8712 – CH$_4$	34 ± 1.0	10 ± 0.8	23 ± 0.9	Container 1
22/ 6/16	RCD-8713 – CO RCD-8714 – CO$_2$ RCD-8715 – CH$_4$	32 ± 1.0	11 ± 0.8	161 ± 1.8	Container 2
23/ 6/16	RCD-8716 – CO RCD-8717 – CO$_2$ RCD-8718 – CH$_4$	167 ± 2.4	19 ± 0.9	2546 ± 29	Container 3
6 weeks					
11/ 7/16	RCD-8719 – CO RCD-8720 – CO$_2$ RCD-8721 – CH$_4$	12 ± 0.7	8 ± 0.8	12 ± 0.9	Container 1
13/ 7/16	RCD-8722 – CO RCD-8723 – CO$_2$ RCD-8724 – CH$_4$	21 ± 1.0	9 ± 0.8	51 ± 1.2	Container 2
14/ 7/16	RCD-8725 – CO RCD-8726 – CO$_2$ RCD-8727 – CH$_4$	120 ± 1.6	15 ± 0.9	214 ± 2.4	Container 3
3 months					
29/ 8/16	RCD-8728 – CO RCD-8729 – CO$_2$ RCD-8730 – CH$_4$	6 ± 0.8	7 ± 0.8	15 ± 0.9	Container 1
31/ 8/16	RCD-8731 – CO RCD-8732 – CO$_2$ RCD-8733 – CH$_4$	25 ± 1.2	6 ± 0.8	123 ± 1.8	Container 2
1/ 9/16	RCD-8734 – CO RCD-8735 – CO$_2$ RCD-8736 – CH$_4$	5 ± 0.8	121 ± 2.1	170 ± 2.2	Container 3

Sampling date	**RCD reference No.**	**Carbon-14 specific activity (Bq kg^{-1} carbon)**			**Experiment**
		CO	**CO_2**	**CH_4**	
5 months					
31/10/16	RCD-8737 – CO RCD-8738 – CO_2 RCD-8739 – CH_4	7 ± 1.0	7 ± 0.8	11 ± 0.8	Container 1
02/11/16	RCD-8740 – CO RCD-8741 – CO_2 RCD-8742 – CH_4	43 ± 1.0	6 ± 0.8	215 ± 2.3	Container 2
03/11/16	RCD-8743 – CO RCD-8744 – CO_2 RCD-8745 – CH_4	60 ± 1.2	6 ± 0.8	49 ± 1.0	Container 3

Table 3 Measured carbon-14 content of soda lime columns from sampling after 1, 3, 6 weeks and 3 months

Sampling date	**RCD reference No.**	**Total carbon-14 activity in sample (Bq)**			**Experiment**
		CO	**CO_2**	**CH_4**	
1 week					
7/ 6/16	RCD-8701 – CO RCD-8702 – CO_2 RCD-8703 – CH_4	< 0.04	< 0.04	0.158 ± 0.009	Container 1
8/ 6/16	RCD-8704 – CO RCD-8705 – CO_2 RCD-8706 – CH_4	0.111 ± 0.007	< 0.04	1.47 ± 0.08	Container 2
9/ 6/16	RCD-8707 – CO RCD-8708 – CO_2 RCD-8709 – CH_4	0.865 ± 0.05	< 0.04	21.1 ± 1.10	Container 3
3 weeks					
20/ 6/16	RCD-8710 – CO RCD-8711 – CO_2 RCD-8712 – CH_4	0.070 ± 0.004	< 0.04	< 0.04	Container 1
22/ 6/16	RCD-8713 – CO RCD-8714 – CO_2 RCD-8715 – CH_4	0.069 ± 0.004	< 0.04	0.453 ± 0.03	Container 2
23/ 6/16	RCD-8716 – CO RCD-8717 – CO_2 RCD-8718 – CH_4	0.478 ± 0.03	< 0.04	8.03 ± 0.4	Container 3

Sampling date	RCD reference No.	Total carbon-14 activity in sample (Bq)			Experiment
		CO	CO_2	CH_4	
6 weeks					
11/ 7/16	RCD-8719 – CO RCD-8720 – CO_2 RCD-8721 – CH_4	< 0.04	< 0.04	< 0.04	Container 1
13/ 7/16	RCD-8722 – CO RCD-8723 – CO_2 RCD-8724 – CH_4	< 0.04	< 0.04	0.131 ± 0.008	Container 2
14/ 7/16	RCD-8725 – CO RCD-8726 – CO_2 RCD-8727 – CH_4	0.349 ± 0.02	< 0.04	0.622 ± 0.03	Container 3
3 months					
29/ 8/16	RCD-8728 – CO RCD-8729 – CO_2 RCD-8730 – CH_4	< 0.04	< 0.04	< 0.04	Container 1
31/ 8/16	RCD-8731 – CO RCD-8732 – CO_2 RCD-8733 – CH_4	0.05 ± 0.007	< 0.04	0.33 ± 0.04	Container 2
1/ 9/16	RCD-8734 – CO RCD-8735 – CO_2 RCD-8736 – CH_4	0.33 ± 0.04 [†]	< 0.04 [†]	0.48 ± 0.06	Container 3
5 months					
31/10/16	RCD-8737 – CO RCD-8738 – CO_2 RCD-8739 – CH_4	< 0.04	< 0.04	< 0.04	Container 1
02/11/16	RCD-8740 – CO RCD-8741 – CO_2 RCD-8742 – CH_4	0.10 ± 0.007	< 0.04	0.62 ± 0.08	Container 2
03/11/16	RCD-8743 – CO RCD-8744 – CO_2 RCD-8745 – CH_4	0.15 ± 0.02	< 0.04 [†]	0.12 ± 0.02	Container 3

[†] The assignment of results 8374 and 8375 has been switched based on comparison with the previous results, the results from Container 2 and the results for Container 3 samples after 5 months.

Table 4 Cumulative releases of carbon-14 by chemical form from each experiment with leaching time; the evaluation of uncertainties has taken account of the limit of detection (LoD) as an upper limit for the carbon-14 activity in those samples where the activity is below LoD

Leaching time (weeks)	**Cumulative carbon-14 release to the gas phase in each experiment (Bq)**		
	CO_2	**CO**	**CH_4**
Container 1			
1	<0.040	<0.040	0.158 ± 0.009
3	<0.057	0.070 + 0.040 - 0.004	0.158 + 0.041 - 0.009
6	<0.069	0.070 + 0.057 - 0.004	0.158 + 0.057 - 0.009
13	<0.080	0.070 + 0.069 - 0.004	0.158 + 0.070 - 0.009
22	<0.089	0.070 + 0.080 - 0.004	0.158 + 0.081 - 0.009
Container 2			
1	<0.040	0.111 ± 0.007	1.470 ± 0.080
3	<0.057	0.180 ± 0.008	1.923 ± 0.085
6	<0.069	0.180 + 0.041 - 0.008	2.054 ± 0.086
13	<0.080	0.230 + 0.041 - 0.011	2.384 ± 0.095
22	<0.080	0.330 + 0.043 - 0.015	3.004 ± 0.124
Container 3			
1	<0.040	0.865 ± 0.050	21.10 ± 1.10
3	<0.057	1.343 ± 0.058	29.13 ± 1.17
6	<0.069	1.692 ± 0.062	29.75 ± 1.17
13	<0.080	2.022 ± 0.073	30.23 ± 1.17
22	<0.089	2.172 ± 0.076	30.35 ± 1.17

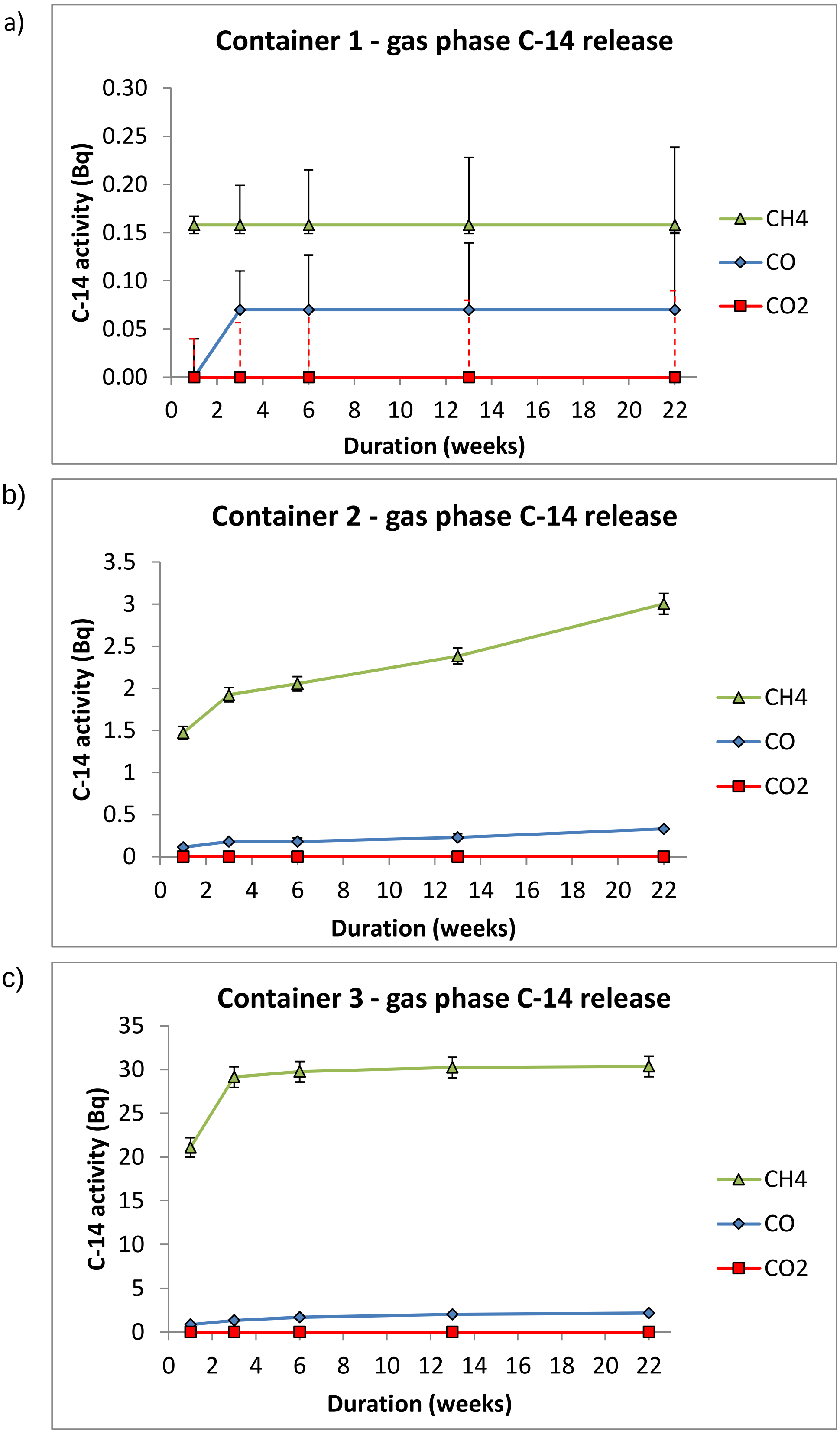


Figure 6 Cumulative releases of carbon-14 to the gas phase from the three CAST experiments

3.2 Carbon-14 release to solution

The results of carbon-14 measurements on sub-samples of the leachate solutions to date are provided in Table5 . These results provide the specific activities of carbon-14 in the solution phase at the time of each measurement. The total carbon-14 activities in the solution phase at the time of each sampling, based on the estimated residual volumes of the leaching solution, are presented in Table 6. At this stage, it is assumed that a constant volume of 7.0 cm^3 of solution is removed during each sampling.

The estimated total activity of carbon-14 released to the solution phase with time is given in Table 7. This takes account of the amount of carbon-14 removed in each solution sample (assumed to be 7.0 cm^3 in volume).

It should be noted that separation procedure (acidification with nitric acid and capture of the released CO_2 in Carbosorb) has been verified for the quantification of carbon-14 as carbonate, but not in organic forms (e.g. as small carboxylic acids). Additional tests have been performed to establish its effectiveness in separating and capturing water-soluble organic carbon-14 species in addition to carbonate; these tests have shown that this method measures inorganic carbon-14 only. Measurements of total carbon -14 (including any organic carbon – 14 species) will be made using a pyrolysis method on solution samples collected after 1 year.

Table5 6 Results of carbon-14 activity measurements for leachate samples after applying the separation procedure

Leaching time (weeks)	**Sample code †**	**Sample weight (g)**	**Carbon-14 activity (Bq)**				**Carbon-14 specific activity (Bq g^{-1})**
			Carbosorb trap 1	**Carbosorb trap 2**	**Total**	**Uncertainties 2σ, trap 1, 2 (%)**	
1	C1W1	5.4911	<0.1	<0.1	<0.1	-	<0.02
	C2W1	5.6232	1.83	<0.1	1.83	-	0.325 ± 0.010
	C3W1	5.8294	1.72	<0.1	1.72	-	0.295 ± 0.009
3	C1W3	5.5801	<0.1	<0.1	<0.1	-	<0.02
	C2W3	5.4280	2.12	<0.1	2.12	3	0.391 ± 0.012
	C3W3	4.7205	2.00	<0.1	2.00	3	0.424 ± 0.013
6	C1W6	5.6710	<0.1	<0.1	<0.1	-	<0.02
	C2W6	5.6978	2.24	<0.1	2.24	3	0.393 ± 0.012
	C3W6	5.5935	2.44	0.16	2.60	3, 8	0.465 ± 0.014
13	C1M3	5.7568	<0.1	<0.1	<0.1	-	<0.02
	C2M3	5.6604	2.15	0.1	2.25	3	0.397 ± 0.012
	C3M3	5.7123	3.10	<0.1	3.10	3	0.543 ± 0.016
22	C1M5	5.5758	<0.1	<0.1	<0.1	-	<0.02
	C2M5	5.9064	2.54	<0.1	2.54	3	0.430 ± 0.013
	C3M5	5.6862	2.73	<0.1	2.73	3	0.498 ± 0.014

† The sample codes are based on the container (C) and the week or month (W or M) at which the sample was taken, so, C1W1 is the week 1 sample from Container 1, for example.

Table 6 Total carbon-14 activity in the solution phase in each experiment with time

Leaching time (weeks)	**Total carbon-14 activity in the solution phase in each experiment (Bq)**		
	Container 1	**Container 2**	**Container 3**
1	<11.2	197 ± 6	178 ± 5
3	<10.9	234 ± 7	252 ± 8
6	<10.6	232 ± 7	273 ± 8
13	<10.3	232 ± 7	315 ± 9
22	<10.5	248 ± 7	276 ± 8

Table 7 Estimated total carbon-14 activity released to the solution phase in each experiment with time

Leaching time (weeks)	**Estimated total carbon-14 activity released to the solution phase in each experiment (Bq)**		
	Container 1	**Container 2**	**Container 3**
1	<11.2	197 ± 6	178 ± 5
3	<10.9	236 ± 7	254 ± 8
6	<10.6	237 ± 7	278 ± 8
13	<10.3	240 ± 7	324 ± 9
22	<10.5	259 ± 7	288 ± 8

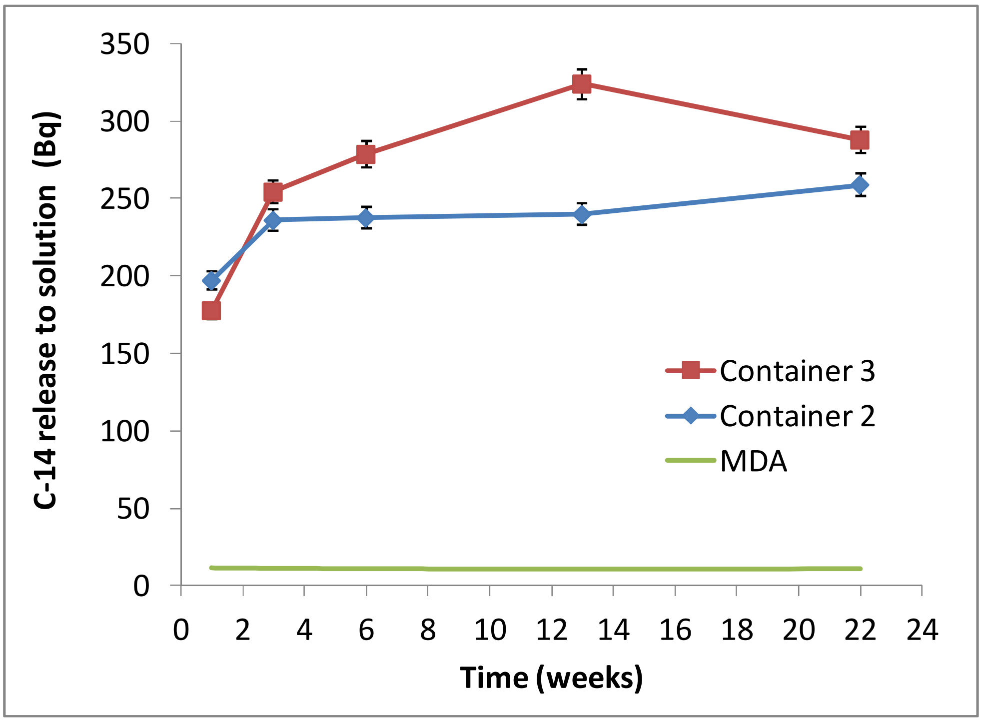


Figure 7 Cumulative carbon-14 activity released to solution over time during leaching of irradiated stainless steel samples in 0.1 mol dm^{-3} NaOH solution; no carbon-14 has been detectable in the leachate samples from Container 1, i.e. it is below the minimum detectable activity (MDA)

3.3 Cobalt-60 release to solution

The results of cobalt-60 measurements on sub-samples of the leachate solutions to date are provided in Table 8 . These results provide the specific activities of cobalt-60 in the solution phase at the time of each measurement. The total cobalt-60 activities in solution at the time of each sampling, based on the estimated volume of the leaching solution, are presented in

Table9 and are shown in Figure8. At this stage, it is assumed that a constant volume of 7.0 cm^3 of solution is removed on sampling.

Table 8 Cobalt-60 activity in the solution phase samples from periodic sampling of each experiment

Sample	**Leaching time (weeks)**	**Mass (g)**	**Co-60 corrected activity (Bq)**	**Uncertainty in activity, 1σ, (%)**	**Specific Activity ^{60}Co (Bq g^{-1})**	**Uncertainty in specific activity, 1σ, (%)**
C1W1	1 week	0.400	< 1.0	–	–	–
C2W1		0.399	8.86	6.9	22.19	7.0
C3W1		0.400	12.60	5.6	31.49	5.7
C1W3	3 weeks	0.397	< 1.0	–	–	–
C2W3		0.396	3.23	9.0	8.16	9.0
C3W3		0.400	5.10	7.1	12.75	7.2
C1W6	6 weeks	0.394	< 0.6	–	–	–
C2W6		0.399	3.17	9.0	7.96	9.1
C3W6		0.398	5.53	5.9	13.89	6.0
C1M3	3 months	0.400	< 1.0	–	–	–
C2M3		0.395	< 0.7	–	–	–
C3M3		0.400	2.66	20.2	6.65	20.3
C1M5	5 months	0.396	< 1.0	–	–	–
C2M5		0.400	< 1.0	–	–	–
C3M5		0.399	2.331	18.45	5.842	18.5

Table9 Total cobalt-60 activity in the solution phase in each experiment with time

Leaching time (weeks)	**Cobalt-60 activity in the solution phase in each experiment (kBq)**		
	Container 1	**Container 2**	**Container 3**
1	<1.5	13.4 ± 1.9	19.0 ± 2.2
3	<1.5	4.9 ± 0.1	7.6 ± 1.1
6	<9.1	4.7± 0.1	8.2 ± 1.0
13	<1.5	<1.0	3.9 ± 1.6
22	<1.5	<1.4	3.4 ± 1.2

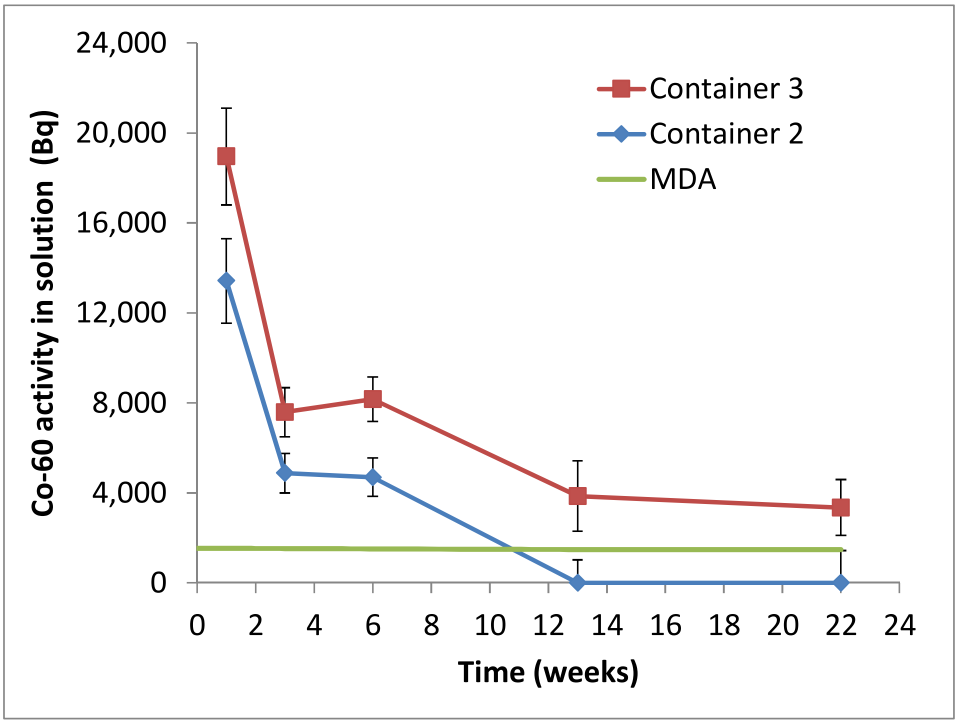


Figure8 Cobalt-60 activity measured in solution with time during leaching of irradiated stainless steel samples in 0.1 mol dm^{-3} NaOH solution; no cobalt-60 has been detectable in the leachate samples from Container 1, i.e. it is below the Minimum Detectable Activity (MDA)

4 Discussion

4.1 Carbon-14 releases

4.1.1 Container 1 – unirradiated steel blank

A small amount of gas phase carbon-14 was detected on the $^{14}CH_4$ column for Container 1 at the end of week one. In addition, a small amount of carbon-14 was detected on the ^{14}CO column at the end of week three. Otherwise, gas phase carbon-14 measurements after six weeks, three months and five months have all been below LoD, as expected.

Given that Container 1 contains no significant carbon-14, nitrogen is being used as the purge gas, and the air inlet to the RCD rigs is passed through a soda lime column before the first catalyst, the source of the carbon-14 collected in these two gas sampling columns is uncertain. It is noted that no carbon-14 was detectable in the blank experiment when the RCD samplers were run continuously for 9 days, far longer than the seven hours used in this study. Whether there may be some slight carry-over of carbon-14 between experiments, e.g. due to hold-up in the pipework, is a possible explanation for the week three CO results but not for week one CH_4.

No carbon-14 has been detectable in the solution phase in Container 1, as expected (noting that a total carbon-14 release in excess of ~11 Bq to the 600 cm^3 of solution would be required for carbon-14 to be detectable in solution samples by LSC).

4.1.2 Containers 2 and 3 – irradiated stainless steel

In both Containers 2 and 3, there is an initial fast release of carbon-14 from the surface of the steel during the first week of leaching, followed by a drop in the rate of release at longer times. Carbon-14 is released primarily to the solution phase, but about 1% of the release occurs to the gas phase in Container 2 and 12% in Container 3. The predominant gas-phase species are hydrocarbons collected on the $^{14}CH_4$ column with about 4-10% of the cumulative gas phase release collected on the ^{14}CO column. No $^{14}CO_2$ is detected in the gas phase from either Containers 2 or 3.

As noted in the experimental section, there is some uncertainty about the quantification of the carbon-14 in the solution phase and whether water-soluble organic species are being measured quantitatively by the analysis procedure. Thus it is possible that the total carbon-14 release from the irradiated steel may be underestimated. Nevertheless, some preliminary discussion and interpretation of the data can be made.

About 200 Bq of carbon-14 is released from the steel during the first week of leaching in both Containers 2 and 3, corresponding to a release fraction of about 4 x 10^{-6} of the estimated carbon-14 inventory of each experiment. This was significantly higher than had been expected. If the carbon-14 is distributed uniformly through the irradiated steel and is assumed to be released congruently with the corrosion of the steel, then the equivalent mass of corroded steel in each experiment would be about 0.9 mg. Given an estimated surface area for each irradiated CT specimen of 38.14 cm^2, this would correspond to a thickness loss of about 10 nm in 1 week or about 520 nm yr^{-1}.

Beyond 3 weeks, the rate of carbon-14 release from the steels in Container 2 drops significantly, but remains measurable to both the gas and solution phases. The ratio of gas phase hydrocarbon species to CO collected from Container 2 is about 13:1 in the first week then remains constant at about 6:1 from 1 week through to five months. A least squares fit to the total carbon-14 release over the period from three weeks to five months indicates a total carbon-14 release rate of about 0.17 ± 0.07 Bq day^{-1}. In contrast to the first week, this would correspond to a significantly lower congruent corrosion rate for the steel of ~3 nm yr^{1}.

For container 3, beyond the first week, the release of carbon-14 continues at a higher rate than in Container 2, with a higher proportion of the release being to the gas phase (10-12%). The average total carbon-14 release rate over the period from three weeks to three months was about 1.0 Bq day^{-1}. However, there is an unexpected drop in the measured carbon-14 activity in solution in the five month sample. The reason for this is unclear at this stage.

It is also notable that the ratio of gas phase hydrocarbon species to CO collected from Container 3 decreases with time, dropping from about 25:1 in week 1 to about 3:2 between 6 weeks and 3 months leaching and dropping further to 4:5 between 3 and 5 months. The total rate of gas phase release in Container 3 has continued to decrease in each sampling interval and between 3 and 5 months is lower than in Container 2.

The equivalent corrosion rates estimated above can be compared with long-term corrosion rates measured recently for unirradiated 18/8 (304-type) stainless steel under alkaline, anaerobic conditions in the Japanese programme. The Japanese data indicate a mean anaerobic corrosion rate of 0.8 nm yr^{-1} for the stainless steel at 30°C after two years exposure to a pH 12.5 solution. However, the data also show a decrease of the anaerobic corrosion rate over the two years of the experiments; the corrosion rate measured after about 90 days was ~1.5 nm yr^{-1}. Thus the equivalent corrosion rate measured in the Container 2 experiment beyond 3 weeks leaching seems broadly consistent with the Japanese results.

As noted at the start of this sub-section, there is an initial fast release of accessible carbon-14 from the surface of the irradiated steel samples on immersion in water. One can speculate about the possible reasons for this initial fast release. Contributory factors might include higher concentrations of carbon-14 at the surface of the steel than in the bulk, or that the presence of some residual oxygen in the experiment contributes to faster initial (aerobic) corrosion. It is also possible that the effective surface area of the samples is larger than expected due to the roughness of their surface finish, the effects of prior corrosion and/or radiation damage. It is also possible that the surface of the irradiated samples may be more reactive than an unirradiated surface.

The reasons for the differences in carbon-14 release rates and speciation between Containers 2 and 3 are also not understood. This must be related in some way to differences between the CT samples in each experiment and may be related to differences in their surface condition and/or prior losses of more accessible and volatile carbon-14 species, for example.

4.2 Cobalt-60

The measurement of the release of cobalt-60 to the solution phase has been included as a potential marker for the overall corrosion rate of the steel. This approach assumes that the release of cobalt-60 into solution is congruent with the rate of steel corrosion.

In both Containers 2 and 3, a significant release of Co-60 is observed from the surface of the steel in the first week of leaching. However, the cobalt-60 activity in solution was found to have dropped after three weeks and by three months was below the LoD in Container 2 and was continuing to drop slowly in Container 3.

The drop in cobalt-60 activity in the solution phase with time indicates that the cobalt is being removed from solution either by a precipitation process, due to solubility limitation, and/or a sorption process (e.g. to the vessel walls or onto the surface of the steel samples themselves). As a result, cobalt-60 is not a suitable marker of the corrosion rate of the steel in this set of experiments.

The fractional release of the Co-60 content of the steels during week one is $8.4 \pm 1.2 \times 0^{-7}$ for Container 2 and $1.2 \pm 0.1 \times 10^{-6}$ for Container 3. This is somewhat lower than the fractional release of carbon-14 during the same period. This does not necessarily mean that the release of carbon-14 is not congruent with the corrosion of the steel; in the case of cobalt-60, precipitation and/or sorption processes may already be significant in the first week of leaching.

4.2.1 Additional test of Co-60 sorption

To help discriminate between the possible mechanisms of Co-60 loss from the solutions, an additional experiment was set up to investigate the removal of Co-60 from the solution in the absence of steel. A spare leaching container with a zirconia insert was set up and was filled with 601.8g of 0.1 mol dm^{-3} NaOH solution prepared in the same way as that used in the leaching experiments. 0.1004 g of a Co-60 solution with a specific activity of 112 kB g^{-1} was added to the solution. This gave an initial specific activity in solution of 18.7 Bq g^{-1}, comparable with that measured in Container 2 after 1 week. Once the sample had been well-mixed a sample (Co-T0) was taken for analysis by gamma spectroscopy. The experiment was then kept under a nitrogen atmosphere at room temperature for 6 weeks before a second sample (Co-T6) was taken for analysis.

The gamma spectroscopy results are presented in Table10. There is no evidence for any change in the cobalt-60 concentration over six weeks. This rules out sorption to the zirconia container as the mechanism of cobalt-60 loss from the experiments. In this case, it also indicates that the cobalt-60 was not being precipitated due to cobalt concentrations exceeding the solubility limit. However, this depends both on the total cobalt concentration in the cobalt-60 solution and the solubility limiting phase for cobalt. The possibility that cobalt and cobalt-60 concentrations are solubility-limited in the experiments is discussed in the next section.

Table10 Cobalt-60 activity in the solution phase samples from periodic sampling of each experiment

Sample	Mass (g)	Co-60 corrected activity (Bq)	Uncertainty in activity, 1σ, (%)	Specific Activity ^{60}Co (Bq g^{-1})
Co-T0	0.4048	7.78	6.5	19.2 ± 1.3
Co-T6	0.3968	8.82	6.7	22.2 ± 1.5

4.2.2 Are the experiments solubility-limited with respect to cobalt?

The activity of Co-60 in the solution after one week can be used to estimate the concentration of cobalt in the leachate, if it assumed that the cobalt-60 and cobalt are both uniformly distributed through the steel. Given that the steel contains 0.08 wt% cobalt, the equivalent dissolved amounts of cobalt in the two leachate solutions after 1 week are about 0.15 µg and 0.21 µg, respectively. These correspond to 4.2×10^{-9} mol dm^{-3} of cobalt in Container 2 and 5.9×10^{-9} mol dm^{-3} in Container 3.

The solubility of cobalt with respect to cobalt (II) hydroxide at pH 13 is about 2×10^{-6} mol dm^{-3} [3]. Therefore, cobalt does not appear to be solubility limited with respect to its hydroxide in the leachate solutions. Alternatively, the solubility could be controlled by the solid solution of cobalt in the steel.

An approach for evaluating the dissolved activity release from irradiated steels was put forward by Hooper [4]. Hooper recognised that the solubility of activation products in a matrix is dependent not only on the solubility of the element, but also on their concentration in the matrix. Hooper proposed an ideal solid solution model for evaluating dissolved release. If a steel surface is allowed to equilibrate with a volume of water, the solution concentration, C_i, of the dissolved forms of each component element, *i*, will become:

$$C_i = S_i X_i \gamma_i \quad (1)$$

Here S_i is the solubility of the solubility-limiting phase of element *i*, X_i is the mole fraction of the element in the steel of interest and γ_i is the activity coefficient for the element in solid solution in the corrosion product. For the purposes of modelling, Hooper assumed ideal solution behaviour for each component of the solid solution such that for all elements, γ is one. In addition, it was assumed that the steel components are uniformly distributed throughout the steel. Using this approach, the predicted solubility limit for cobalt in the 316L(N) steel (0.0755% mol fraction) is about 1.5×10^{-9} mol dm^{-3}. This would be equivalent to about 13.5 kBq dm^{-3} in terms of the activity content of cobalt 60 in the experiments or about 8.1 KBq of cobalt-60 in the 600 cm^{3} of each leachate.

It is interesting to note that the estimated total activities of cobalt-60 in the leachates from the measurements after three and six weeks leaching are similar to the above figure, as shown in Figure 9. This suggests that the observed drop in measured cobalt-60 activities beyond one week may be due to solubility control with the steel corrosion products acting as the solubility limiting phase for cobalt. The drop in measured cobalt concentrations after 3 months may be due to additional processes, such as sorption to the steel or the vessel walls. Between 3 and 5 months the cobalt-60 concentration in Container 3 has dropped only a small amount. The results after one year will show whether the drop in cobalt-60 concentration continues.

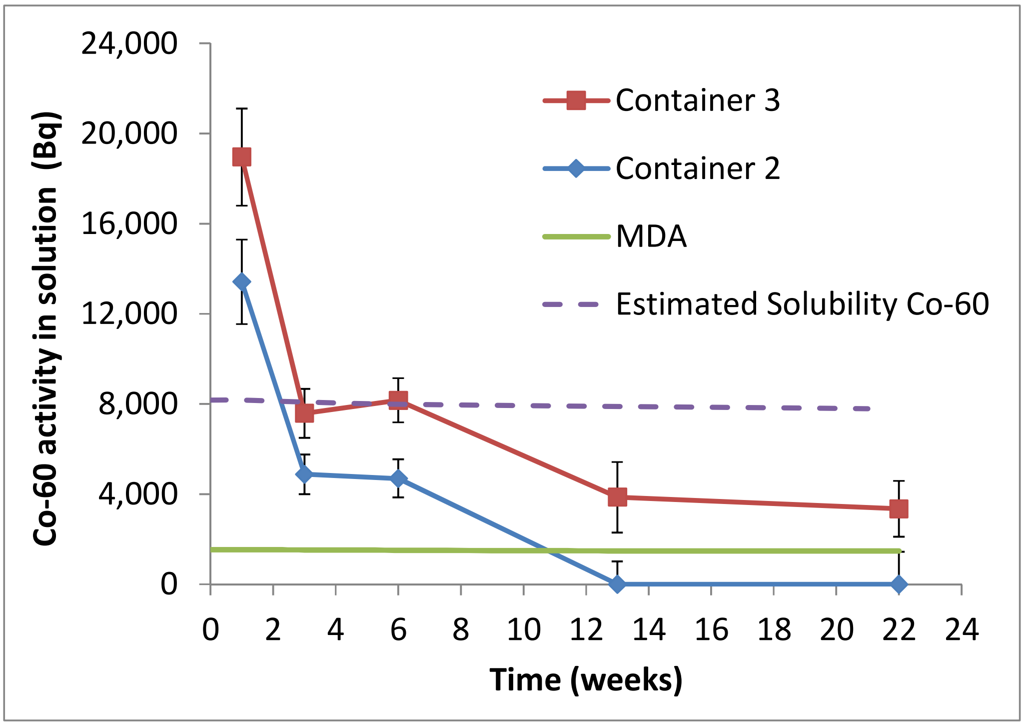


Figure 9 Cobalt-60 activity measured in solution with time during leaching of irradiated stainless steel samples in 0.1 mol dm^{-3} NaOH solution; the dashed line shows the estimated solubility limit for the experiment in terms of cobalt-60 activity assuming that the steel corrosion products act as the solubility limiting phase for cobalt

5 Conclusions

Experiments to study the rate and speciation of carbon-14 from irradiated stainless steel under high pH, anaerobic conditions have been in progress in NRG's Hot Cell Laboratory at Petten for a period of ten months. The three experiments have been sampled five times to date and analytical data are now available for the carbon-14 releases to the gas phase and solution and cobalt-60 releases to solution up to five months leaching.

In the two experiments containing irradiated steel specimens, a relatively fast initial release of accessible carbon-14 species from the surface of the steel is observed within the first week of leaching, followed by a drop in the rate of release at longer times. Most of the carbon-14 is released into the solution, but about 1% and 12% of the carbon-14 releases are to the gas phase in Containers 2 and 3, respectively. Not only are the proportions of gas phase releases different between Containers 2 and 3 but also the rates and speciation of gas phase release after the first week.

Although the total amount of gas phase release from Container 3 is larger than that from Container 2, the rate of release decreases more rapidly in Container 3 so that by five months a faster rate of gas phase release is recorded from Container 2. In addition, the speciation changes from predominantly hydrocarbons to a 4:5 mix of hydrocarbons to CO by 5 months in Container 3. In contrast, the gas phase speciation from Container 2 remains at about 6:1 hydrocarbons to CO from one week up to five months.

For Container 2, the total carbon-14 releases decrease after the first week and have decreased to about 0.17 ±0.07 Bq day^{-1} between three weeks and five months leaching. If it is assumed that the release of carbon-14 over this period was congruent with the corrosion of the steel surface, this would be equivalent to a corrosion rate of about 3 nm yr^{-1}. For Container 3, the total carbon-14 releases continue at a higher rate than in Container 2 at about 1.0 Bq day^{-1} between three weeks and three months leaching. After five months, a drop in the Container 3 solution activity of carbon 14 has been recorded. The reason for this is unclear at present.

The data presented regarding carbon-14 release into solution are valid only for inorganic carbon -14 species. Measurements of total carbon -14 (including any organic carbon – 14 species) will be made using a pyrolysis method on solution samples collected after 1 year.

There is uncertainty concerning the speciation and quantification of the dissolved release and whether the separation method used is effective in collecting carbon-14 present as water-soluble organic species (e.g. carboxylic acids), as well as carbonate (for which the method has been validated). Therefore, it is possible that the dissolved releases discussed above may be underestimated.

Measurement of the release of cobalt-60 into solution has been undertaken as a possible analogue for the corrosion of the stainless steel, on the assumption that cobalt-60 release would be congruent with respect to the corrosion of the steel surface. However, after a fast initial release of cobalt-60 during the first week of leaching, a drop has been observed in the cobalt-60 activity in solution at longer times. Further tests at NRG have demonstrated that the cobalt-60 loss is not due to sorption to the walls of the zirconia inner container.

Some initial scoping calculations suggest that the loss of cobalt-60 could result from precipitation of cobalt associated with the formation of steel corrosion products; the total cobalt concentrations in solution initially may exceed an estimated solubility limit for cobalt controlled by the corrosion products of the steel. It is possible also that cobalt-60 may be sorbing onto the steel specimens themselves.

It is concluded that cobalt-60 release is not a suitable analogue for measuring the corrosion rate of the irradiated steel in these experiments.

The three experiments are planned to continue for a minimum period of one year with further sampling scheduled at the beginning of June 2017. Prior to that, a decision will need to made as to whether the experiments are to be terminated at that point or extended for additional sample collection at longer time intervals.

References

[1] G.M.N. Baston, T.A. Marshall, R.L. Otlet, A.J. Walker, I.D. Mather and S.J. Williams, Rate and speciation of volatile carbon-14 and tritium releases from irradiated graphite, Mineralogical Magazine 76(8), 3293-3302, 2012.

[2] G. Baston , S. Preston, R. Otlet, J. Walker, A. Clacher, M. Kirkham and B. Swift, Carbon-14 release from Oldbury Graphite, AMEC Report AMEC/5352/002 Issue 3, 2014.

[3] C.F. Baes and R.E. Mesmer, The hydrolysis of cations, pp. 238-242, John Wiley and Sons, New York, 1976.

[4] A.J. Hooper, The behaviour of radionuclides in radioactive steel waste contacted by water: the Trawsfynydd absorber bar vaults – a case study, CEGB Report TPRB/B/0782/R86, February 1986.

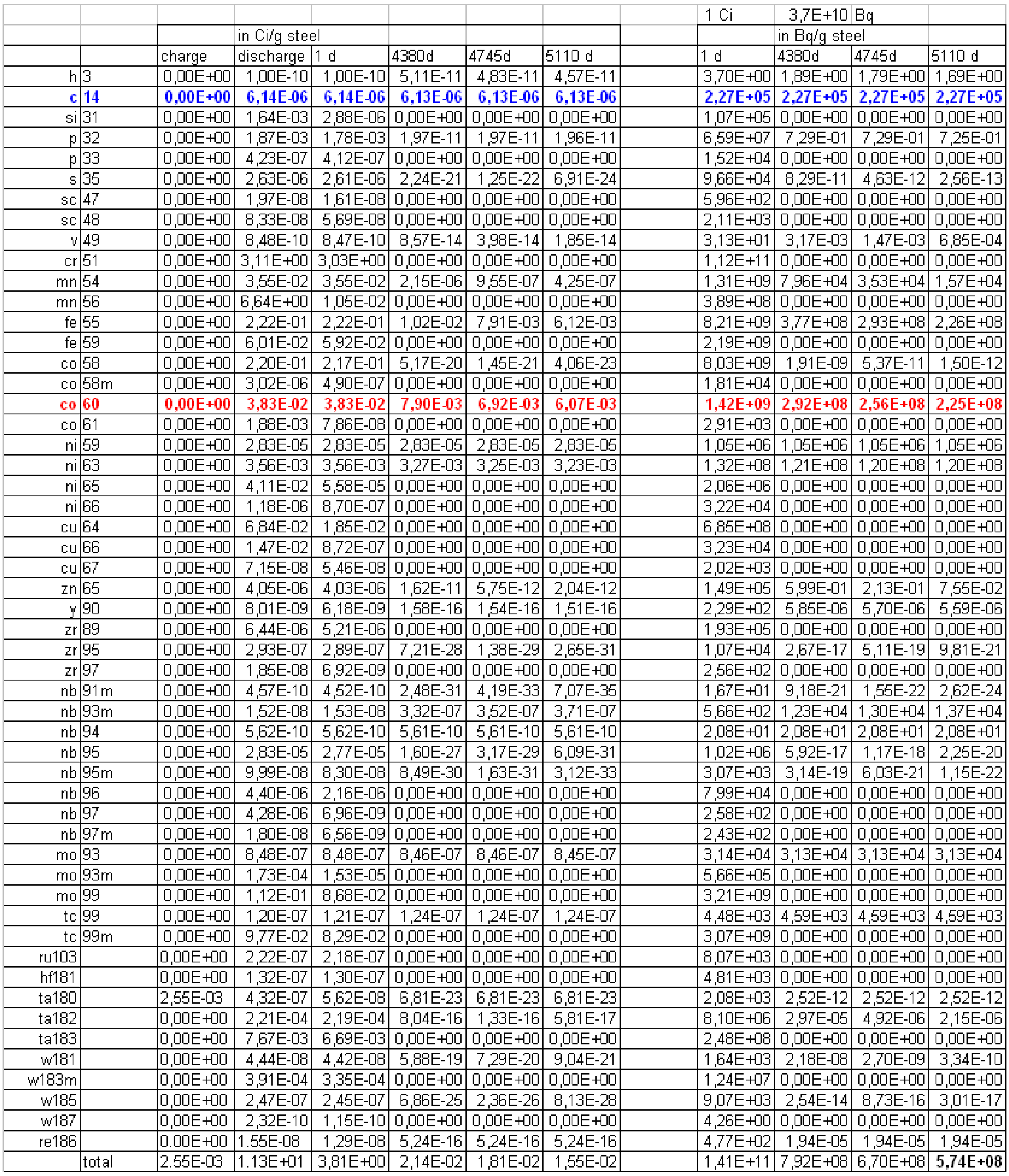
List of tables

List of figures

Appendix 1 Activation calculation

In Table11, an example of the activation calculation results for the irradiated stainless steel is presented.

Table11 An example of the activation calculation results for irradiated stainless steel, in this case for the sample b107



									1 Ci	3,7E+10	Bq	
			in Ci/g steel							in Bq/g steel		
		charge	discharge	1 d	4380d	4745d	5110 d		1 d	4380d	4745d	5110 d
h	3	0,00E+00	1,00E-10	1,00E-10	5,11E-11	4,83E-11	4,57E-11		3,70E+00	1,89E+00	1,79E+00	1,69E+00
c	**14**	**0,00E+00**	**6,14E-06**	**6,14E-06**	**6,13E-06**	**6,13E-06**	**6,13E-06**		**2,27E+05**	**2,27E+05**	**2,27E+05**	**2,27E+05**
si	31	0,00E+00	1,64E-03	2,88E-06	0,00E+00	0,00E+00	0,00E+00		1,07E+05	0,00E+00	0,00E+00	0,00E+00
p	32	0,00E+00	1,87E-03	1,78E-03	1,97E-11	1,97E-11	1,96E-11		6,59E+07	7,29E-01	7,29E-01	7,25E-01
p	33	0,00E+00	4,23E-07	4,12E-07	0,00E+00	0,00E+00	0,00E+00		1,52E+04	0,00E+00	0,00E+00	0,00E+00
s	35	0,00E+00	2,63E-06	2,61E-06	2,24E-21	1,25E-22	6,91E-24		9,66E+04	8,29E-11	4,63E-12	2,56E-13
sc	47	0,00E+00	1,97E-08	1,61E-08	0,00E+00	0,00E+00	0,00E+00		5,96E+02	0,00E+00	0,00E+00	0,00E+00
sc	48	0,00E+00	8,33E-08	5,69E-08	0,00E+00	0,00E+00	0,00E+00		2,11E+03	0,00E+00	0,00E+00	0,00E+00
v	49	0,00E+00	8,48E-10	8,47E-10	8,57E-14	3,98E-14	1,85E-14		3,13E+01	3,17E-03	1,47E-03	6,85E-04
cr	51	0,00E+00	3,11E+00	3,03E+00	0,00E+00	0,00E+00	0,00E+00		1,12E+11	0,00E+00	0,00E+00	0,00E+00
mn	54	0,00E+00	3,55E-02	3,55E-02	2,15E-06	9,55E-07	4,25E-07		1,31E+09	7,96E+04	3,53E+04	1,57E+04
mn	56	0,00E+00	6,64E+00	1,05E-02	0,00E+00	0,00E+00	0,00E+00		3,89E+08	0,00E+00	0,00E+00	0,00E+00
fe	55	0,00E+00	2,22E-01	2,22E-01	1,02E-02	7,91E-03	6,12E-03		8,21E+09	3,77E+08	2,93E+08	2,26E+08
fe	59	0,00E+00	6,01E-02	5,92E-02	0,00E+00	0,00E+00	0,00E+00		2,19E+09	0,00E+00	0,00E+00	0,00E+00
co	58	0,00E+00	2,20E-01	2,17E-01	5,17E-20	1,45E-21	4,06E-23		8,03E+09	1,91E-09	5,37E-11	1,50E-12
co	58m	0,00E+00	3,02E-06	4,90E-07	0,00E+00	0,00E+00	0,00E+00		1,81E+04	0,00E+00	0,00E+00	0,00E+00
co	**60**	**0,00E+00**	**3,83E-02**	**3,83E-02**	**7,90E-03**	**6,92E-03**	**6,07E-03**		**1,42E+09**	**2,92E+08**	**2,56E+08**	**2,25E+08**
co	61	0,00E+00	1,88E-03	7,86E-08	0,00E+00	0,00E+00	0,00E+00		2,91E+03	0,00E+00	0,00E+00	0,00E+00
ni	59	0,00E+00	2,83E-05	2,83E-05	2,83E-05	2,83E-05	2,83E-05		1,05E+06	1,05E+06	1,05E+06	1,05E+06
ni	63	0,00E+00	3,56E-03	3,56E-03	3,27E-03	3,25E-03	3,23E-03		1,32E+08	1,21E+08	1,20E+08	1,20E+08
ni	65	0,00E+00	4,11E-02	5,58E-05	0,00E+00	0,00E+00	0,00E+00		2,06E+06	0,00E+00	0,00E+00	0,00E+00
ni	66	0,00E+00	1,18E-06	8,70E-07	0,00E+00	0,00E+00	0,00E+00		3,22E+04	0,00E+00	0,00E+00	0,00E+00
cu	64	0,00E+00	6,84E-02	1,85E-02	0,00E+00	0,00E+00	0,00E+00		6,85E+08	0,00E+00	0,00E+00	0,00E+00
cu	66	0,00E+00	1,47E-02	8,72E-07	0,00E+00	0,00E+00	0,00E+00		3,23E+04	0,00E+00	0,00E+00	0,00E+00
cu	67	0,00E+00	7,15E-08	5,46E-08	0,00E+00	0,00E+00	0,00E+00		2,02E+03	0,00E+00	0,00E+00	0,00E+00
zn	65	0,00E+00	4,05E-06	4,03E-06	1,62E-11	5,75E-12	2,04E-12		1,49E+05	5,99E-01	2,13E-01	7,55E-02
y	90	0,00E+00	8,01E-09	6,18E-09	1,58E-16	1,54E-16	1,51E-16		2,29E+02	5,85E-06	5,70E-06	5,59E-06
zr	89	0,00E+00	6,44E-06	5,21E-06	0,00E+00	0,00E+00	0,00E+00		1,93E+05	0,00E+00	0,00E+00	0,00E+00
zr	95	0,00E+00	2,93E-07	2,89E-07	7,21E-28	1,38E-29	2,65E-31		1,07E+04	2,67E-17	5,11E-19	9,81E-21
zr	97	0,00E+00	1,85E-08	6,92E-09	0,00E+00	0,00E+00	0,00E+00		2,56E+02	0,00E+00	0,00E+00	0,00E+00
nb	91m	0,00E+00	4,57E-10	4,52E-10	2,48E-31	4,19E-33	7,07E-35		1,67E+01	9,18E-21	1,55E-22	2,62E-24
nb	93m	0,00E+00	1,52E-08	1,53E-08	3,32E-07	3,52E-07	3,71E-07		5,66E+02	1,23E+04	1,30E+04	1,37E+04
nb	94	0,00E+00	5,62E-10	5,62E-10	5,61E-10	5,61E-10	5,61E-10		2,08E+01	2,08E+01	2,08E+01	2,08E+01
nb	95	0,00E+00	2,83E-05	2,77E-05	1,60E-27	3,17E-29	6,09E-31		1,02E+06	5,92E-17	1,17E-18	2,25E-20
nb	95m	0,00E+00	9,99E-08	8,30E-08	8,49E-30	1,63E-31	3,12E-33		3,07E+03	3,14E-19	6,03E-21	1,15E-22
nb	96	0,00E+00	4,40E-06	2,16E-06	0,00E+00	0,00E+00	0,00E+00		7,99E+04	0,00E+00	0,00E+00	0,00E+00
nb	97	0,00E+00	4,28E-06	6,96E-09	0,00E+00	0,00E+00	0,00E+00		2,58E+02	0,00E+00	0,00E+00	0,00E+00
nb	97m	0,00E+00	1,80E-08	6,56E-09	0,00E+00	0,00E+00	0,00E+00		2,43E+02	0,00E+00	0,00E+00	0,00E+00
mo	93	0,00E+00	8,48E-07	8,48E-07	8,46E-07	8,46E-07	8,45E-07		3,14E+04	3,13E+04	3,13E+04	3,13E+04
mo	93m	0,00E+00	1,73E-04	1,53E-05	0,00E+00	0,00E+00	0,00E+00		5,66E+05	0,00E+00	0,00E+00	0,00E+00
mo	99	0,00E+00	1,12E-01	8,68E-02	0,00E+00	0,00E+00	0,00E+00		3,21E+09	0,00E+00	0,00E+00	0,00E+00
tc	99	0,00E+00	1,20E-07	1,21E-07	1,24E-07	1,24E-07	1,24E-07		4,48E+03	4,59E+03	4,59E+03	4,59E+03
tc	99m	0,00E+00	9,77E-02	8,29E-02	0,00E+00	0,00E+00	0,00E+00		3,07E+09	0,00E+00	0,00E+00	0,00E+00
ru103		0,00E+00	2,22E-07	2,18E-07	0,00E+00	0,00E+00	0,00E+00		8,07E+03	0,00E+00	0,00E+00	0,00E+00
hf181		0,00E+00	1,32E-07	1,30E-07	0,00E+00	0,00E+00	0,00E+00		4,81E+03	0,00E+00	0,00E+00	0,00E+00
ta180		2,55E-03	4,32E-07	5,62E-08	6,81E-23	6,81E-23	6,81E-23		2,08E+03	2,52E-12	2,52E-12	2,52E-12
ta182		0,00E+00	2,21E-04	2,19E-04	8,04E-16	1,33E-16	5,81E-17		8,10E+06	2,97E-05	4,92E-06	2,15E-06
ta183		0,00E+00	7,67E-03	6,69E-03	0,00E+00	0,00E+00	0,00E+00		2,48E+08	0,00E+00	0,00E+00	0,00E+00
w181		0,00E+00	4,44E-08	4,42E-08	5,88E-19	7,29E-20	9,04E-21		1,64E+03	2,18E-08	2,70E-09	3,34E-10
w183m		0,00E+00	3,91E-04	3,35E-04	0,00E+00	0,00E+00	0,00E+00		1,24E+07	0,00E+00	0,00E+00	0,00E+00
w185		0,00E+00	2,47E-07	2,45E-07	6,86E-25	2,36E-26	8,13E-28		9,07E+03	2,54E-14	8,73E-16	3,01E-17
w187		0,00E+00	2,32E-10	1,15E-10	0,00E+00	0,00E+00	0,00E+00		4,26E+00	0,00E+00	0,00E+00	0,00E+00
re186		0.00E+00	1.55E-08	1,29E-08	5,24E-16	5,24E-16	5,24E-16		4,77E+02	1,94E-05	1,94E-05	1,94E-05
	total	2.55E-03	1.13E+01	3,81E+00	2,14E-02	1,81E-02	1,55E-02		1,41E+11	7,92E+08	6,70E+08	**5,74E+08**

Appendix 2 Experimental results up to 13 months experiments

In this appendix the progress of the experimental work up to 13 months leaching is presented.

The liquid and gas sampling has been done in the same way as described in previous chapters of the deliverable D2.8.

Additionally, the Co-60 measurements have been repeated; it was done because of the unexpected low ^{60}Co activity of the 3 months, 5 months and 1 year samples, all measurements have been carried out both on the detector surface and on a distance of 10 cm of the detector.

The method of C-14 release form the liquid sampling was proven only for determination of inorganic C-14 in the solution. Additional liquid samples have been taken to by analyzed for total C-14 by pyrolysis. The samples of 13 months sampling have been sent to Wood for this analysis. The results are presented in de related chapter. The other samples will be analyzed by NRG in the coming period.

Gas sampling and results

In Table A2. 1 measured carbon-14 content of soda lime columns from sampling after 13 months is presented. The cumulative activities of carbon-14 captured in each chemical form from each experiment with time are given in Table A2. 2 and shown in Figure A.2 1-Figure A.2 3.

The uncertainties in the measured activities are based on the counting errors for carbon-14 analysis by LSC. In deriving uncertainties in the cumulative activities of carbon-14, where a result has been recorded as below the limit of detection (LoD), the LoD itself has been used as an upper limit for the positive uncertainty on a zero measurement (the negative uncertainty is zero).

Table A2. 1 Measured carbon-14 content of soda lime columns from sampling after 13 months

Sampling date	**RCD reference No.**	**Total carbon-14 activity in sample (Bq)**			**Experiment**
		CO	**CO$_2$**	**CH$_4$**	
12/13 months					
29/05/17	RCD-8746 – CO RCD-8747 – CO$_2$ RCD-8748 – CH$_4$	< 0.04	< 0.04	< 0.04	Container 1
19/07/17	RCD-8749 – CO RCD-8750 – CO$_2$ RCD-8751 – CH$_4$	0.09 ± 0.01	< 0.04	1.09 ± 0.06	Container 2
24/07/17	RCD-8752 – CO RCD-8753 – CO$_2$ RCD-8754 – CH$_4$	0.16± 0.01	< 0.04	0.38 ± 0.02	Container 3

Table A2. 2 Cumulative releases of carbon-14 to the gas phase by chemical form from each experiment with leaching time; the evaluation of uncertainties has taken account of the limit of detection (LoD) as an upper limit for the carbon-14 activity in those samples where the activity is below LoD

Leaching time (weeks)	**Cumulative carbon-14 release to the gas phase in each experiment (Bq)**		
	CO_2	CO	CH_4
Container 1			
1	<0.040	<0.040	0.158 ± 0.009
3	<0.057	$0.070^{+0.040}_{-0.004}$	$0.158^{+0.041}_{-0.009}$
6	<0.069	$0.070^{+0.057}_{-0.004}$	$0.158^{+0.057}_{-0.009}$
13	<0.080	$0.070^{+0.069}_{-0.004}$	$0.158^{+0.070}_{-0.009}$
22	<0.089	$0.070^{+0.080}_{-0.004}$	$0.158^{+0.081}_{-0.009}$
52	<0.098	$0.070^{+0.090}_{-0.004}$	$0.158^{+0.090}_{-0.009}$
Container 2			
1	<0.040	0.111 ± 0.007	1.470 ± 0.080
3	<0.057	0.180 ± 0.008	1.923 ± 0.085
6	<0.069	$0.180^{+0.041}_{-0.008}$	2.054 ± 0.086
13	<0.080	$0.230^{+0.041}_{-0.011}$	2.384 ± 0.095
22	<0.080	$0.330^{+0.043}_{-0.015}$	3.004 ± 0.124

Leaching time (weeks)	Cumulative carbon-14 release to the gas phase in each experiment (Bq)		
59	<0.098	0.420 + 0.044 - 0.018	4.094 ± 0.138
Container 3			
1	<0.040	0.865 ± 0.050	21.10 ± 1.10
3	<0.057	1.343 ± 0.058	29.13 ± 1.17
6	<0.069	1.692 ± 0.062	29.75 ± 1.17
13	<0.080	2.022 ± 0.073	30.23 ± 1.17
22	<0.089	2.172 ± 0.076	30.35 ± 1.17
59	<0.098	2.332 ± 0.077	30.73 ± 1.17

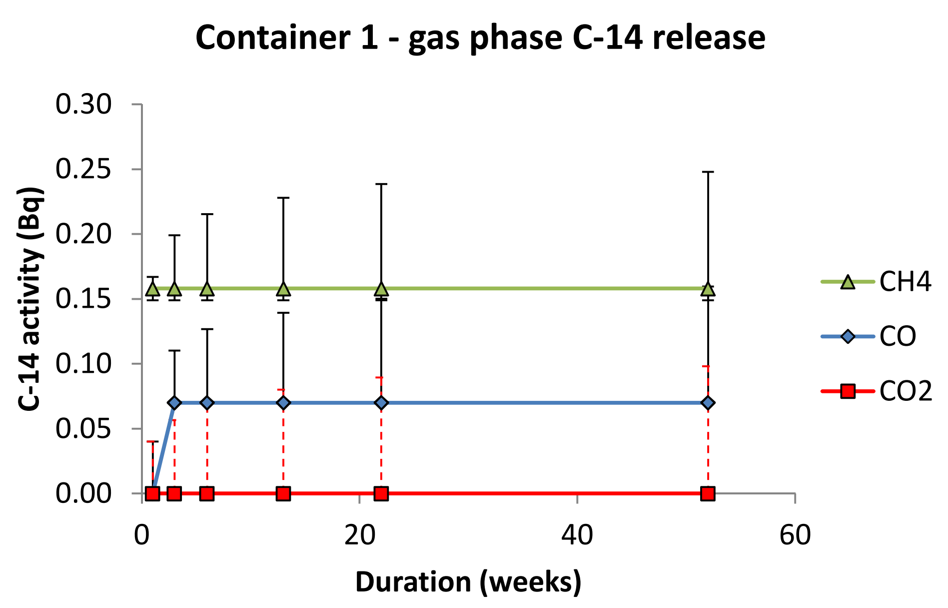


Figure A.2 1 Cumulative release of carbon-14 to the gas phase from the container 1 (unirradiated material)

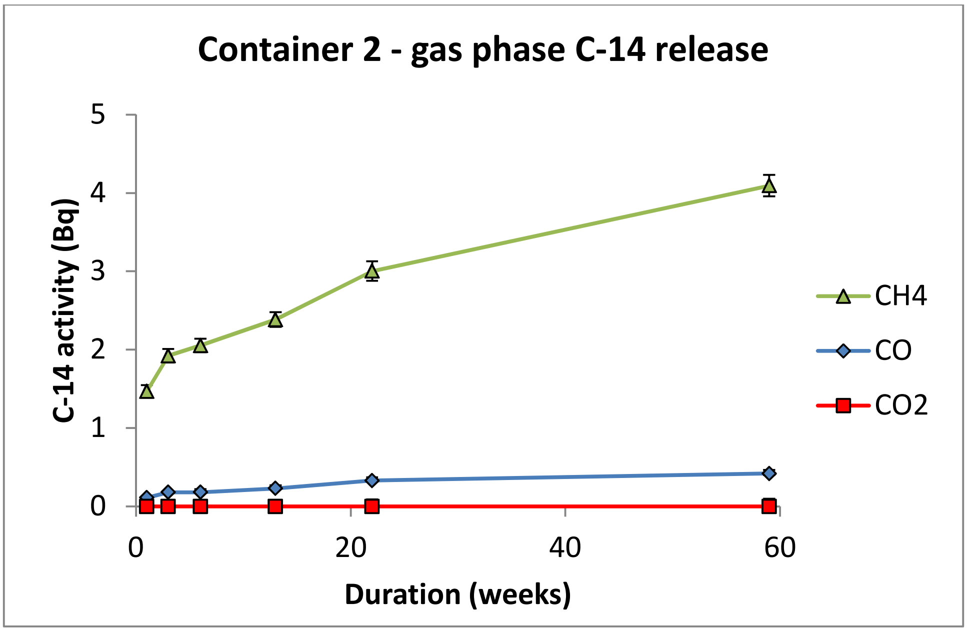


Figure A.2 2 Cumulative release of carbon-14 to the gas phase from the container 2

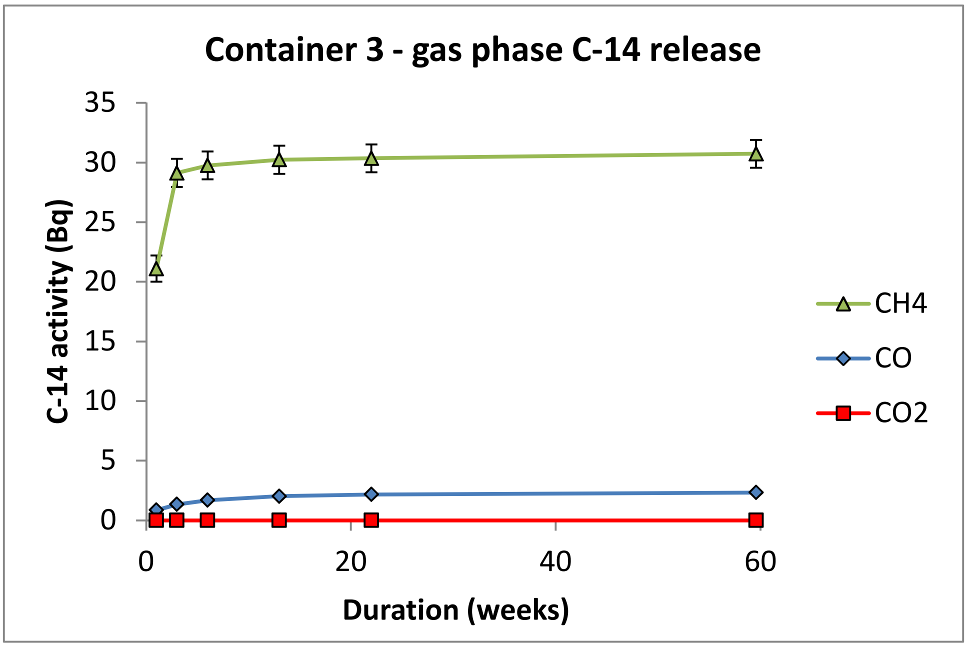


Figure A.2 3 Cumulative release of carbon-14 to the gas phase from the container 3

Liquid sampling and results

The liquid sampling has followed the standard procedure as described in the previous chapters of the report.

The results of carbon-14 measurements on sub-samples of the leachate solutions to date are provided in Table A2. 3 . These results provide the specific activities of carbon-14 in the solution phase at the time of each measurement. The total carbon-14 activities in the solution phase at the time of each sampling, based on the residual volumes of the leaching solution, are presented inTable A2. 8. The removed volumes are calculated from the weight of the removed leachant during each sampling from each container. This gives slightly different values compared to the data presented in the deliverable (see Table 8) where it was assumed that a constant volume of 7.0 cm^3 of solution is removed during each sampling.

The estimated total activity of carbon-14 released to the solution phase with time is given in Table A2. 9. The removed volumes are again calculated from the weight of the removed leachant during each sampling.

It should be noted that separation procedure (acidification with nitric acid and capture of the released CO_2 in Carbosorb) has been verified for the quantification of carbon-14 as carbonate, but not in organic forms (e.g. as small carboxylic acids). Additional tests have been performed to establish its effectiveness in separating and capturing water-soluble organic carbon-14 species in addition to carbonate; these tests have shown that this method measures inorganic carbon-14 only.

Table A2. 3 Results of carbon-14 activity measurements for leachate samples after applying the separation procedure – 13 months sampling

Leaching time (weeks)	**Sample code** †	**Sample weight (g)**	**Carbon-14 activity (Bq)**				**Carbon-14 specific activity (Bq g^{-1})**
			Carbosorb trap 1	**Carbosorb trap 2**	**Total**	**Uncertainties 2σ, trap 1, 2 (%)**	
59	C1Y1	4.8785	<0.1	<0.1	<0.1	-	<0.02
	C2Y1	5.4664	2.69	<0.1	2.69	3	0.492 ± 0.015
	C3Y1	4.9743	2.34	<0.1	2.34	3	0.470 ± 0.014

† The sample codes are based on the container (C) and the week, months of year (W , M or y) at which the sample was taken, so, C1Y1 is the year 1 sample from Container 1, for example.

Table A2. 4 Total carbon-14 activity in the solution phase in each experiment with time

Leaching time (weeks)	**Total carbon-14 activity in the solution phase in each experiment (Bq)**		
	Container 1	**Container 2**	**Container 3**
1	<11.2	197 ± 6	178 ± 5
3	<10.8	232 ± 7	250 ± 8
6	<10.5	230 ± 7	272 ± 8
13	<10.0	225 ± 7	307 ± 9
22	<10.0	237 ± 7	260 ± 8
59	<11.0	260 ± 8	248 ± 7

Table A2. 5 Estimated total carbon-14 activity released to the solution phase in each experiment with time

Leaching time (weeks)	**Estimated total carbon-14 activity released to the solution phase in each experiment (Bq)**		
	Container 1	**Container 2**	**Container 3**
1	<11.2	197 ± 6	178 ± 5
3	<10.8	236 ± 7	254 ± 8
6	<10.5	237 ± 7	278 ± 8
13	<10.0	239 ± 7	324 ± 9
22	<10.0	258 ± 7	288 ± 8
59	<11.0	290 ± 8	283 ± 7

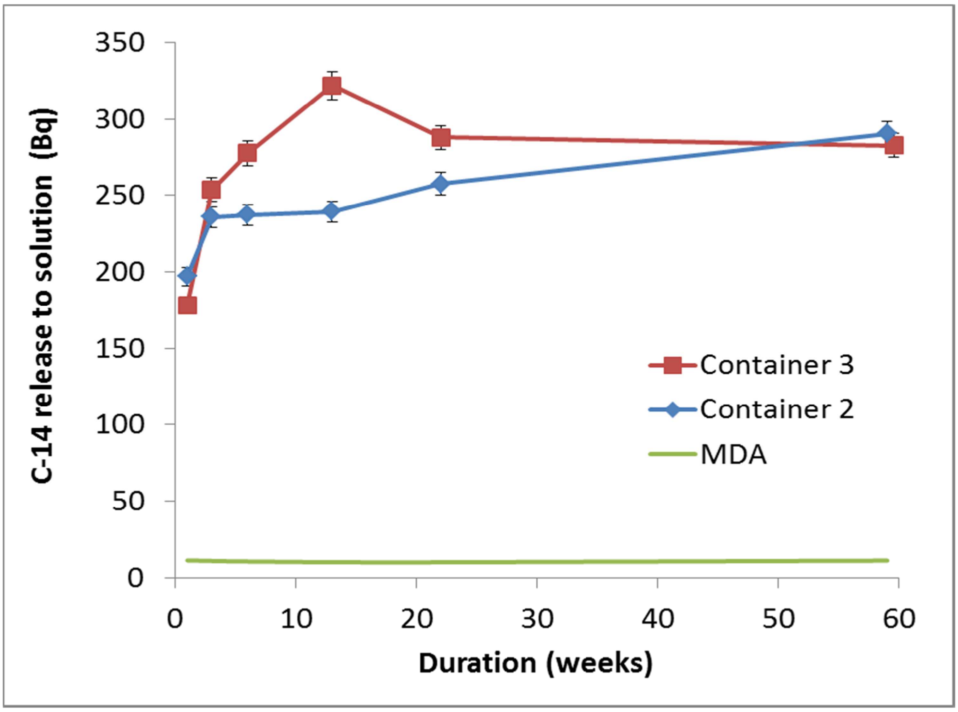


Figure A.2 4 Cumulative release of inorganic carbon-14 to the liquid phase from all three experiments

Analysis of total C-14 in solution

During the liquid sampling since 6 weeks sampling, additional samples were taken for total C-14 analysis. The samples of 13 months sampling has been transported to Wood for total C-14 determination in the solution by pyrolysis. Samples from the other sampling are planned to be analysed by NRG in the coming period.

Sample solution were combusted in a glass boat containing cellulose powder in a two-stage pyrolyser (RADDEC Ltd. – Catalytic pyrolyser-6 Trio).

Table A2. 6 Results (as obtained) of the total C-14 determined by pyrolysis

Sample code †	**Carbon-14 specific activity (Bq g^{-1})**
C1Y1	0.0097 ± 0.084
C2Y1a	0.539 ± 0.046
C2Y1b	0.529 ± 0.045
C3Y1a	0.740 ± 0.061
C3Y1b	0.762 ± 0.063
45 ml demi water + 5 ml $NaCO_3$	< 0.0086

These total C-14 measurements indicate organic carbon-14 fractions: 18±7% in Container 2 and 43±5% in Container 3 (see Table A2. 7).

Table A2. 7 Overview of distribution of inorganic and organic C-14 in the leachant after 1 year sampling

Sample	Total C-14 (Bq/g)	Inorganic C-14 (Bq/g)	% Inorganic C-14	% Organic C-14	Ratio Inor/Org
1	0.0112 ± 0.01	< 0.02	-	-	-
2	0.60 ± 0.05 0.59 ± 0.05	0.49 ± 0.01	82% ± 7%	18% ± 7%	4.59
3	0.82 ± 0.07 0.84 ± 0.07	0.47 ± 0.01	57% ± 5%	43% ± 5%	1.32

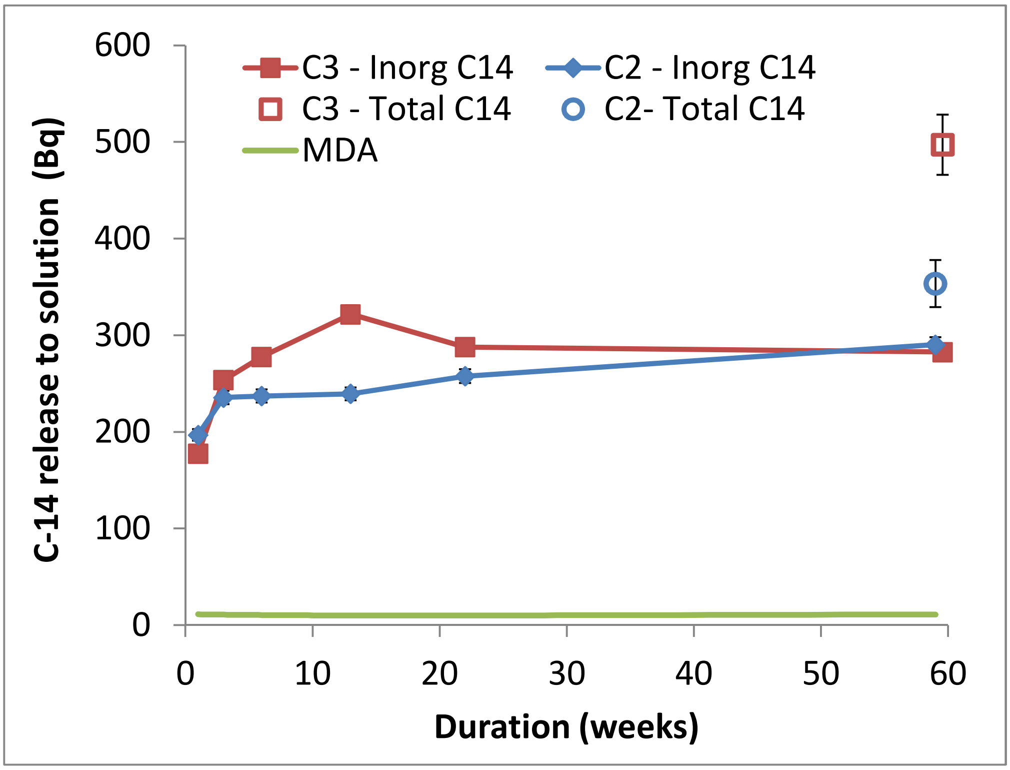


Figure A.2 5 Cumulative release of inorganic carbon-14 to the liquid phase from all three experiments, including total C-14 values for 13 months sampling

Co-60 measurements

The results of cobalt-60 measurements on sub-samples of the leachate solutions to date are provided in Table A2. 8. These results provide the specific activities of cobalt-60 in the solution phase at the time of each measurement. The total cobalt-60 activities in solution at the time of each sampling, based on the estimated volume of the leaching solution, are presented in Table A2. 9 and are shown in Figure A.2 6.

Because of the unexpected low ^{60}Co activity of the 3 months, 5 months and 1 year samples, all measurements have been carried out both on the detector surface and on a distance of 10cm of the detector. The surface measurements including their geometry uncertainties sometimes showed smaller uncertainties than in the deliverable D2.8 presented 10 cm results (see Table 9). The activities with the smallest uncertainties are presented, i.e. for the 3 months, 5 months and 1 year samples the results of the surface measurements are presented.

Table A2. 8 Cobalt-60 activity in the solution phase samples from periodic sampling of each experiment

Sample	**Leaching time (weeks)**	**Mass (g)**	**Co-60 corrected activity (Bq)**	**Uncertainty in activity, 1σ, (%)**	**Specific Activity ^{60}Co (Bq g^{-1})**	**Uncertainty in specific activity, 1σ, (%)**
C1W1	1 week	0.400	0.1	–	–	–
C2W1		0.399	8.86	6.9	22.19	7.0
C3W1		0.400	12.60	5.6	31.49	5.7
C1W3	3 weeks	0.397	0.1	–	–	–
C2W3		0.396	3.23	9.0	8.16	9.0
C3W3		0.400	5.10	7.1	12.75	7.2
C1W6	6 weeks	0.394	0.1	–	–	–
C2W6		0.399	3.17	9.0	7.96	9.1
C3W6		0.398	5.53	5.9	13.89	6.0
C1M3	3 months	0.400	< 0.1	–	–	–

Sample	Leaching time (weeks)	Mass (g)	Co-60 corrected activity (Bq)	Uncertainty in activity, 1σ, (%)	Specific Activity ^{60}Co (Bq g^{-1})	Uncertainty in specific activity, 1σ, (%)
C2M3		0.395	1.39	11.6	3.53	11.6
C3M3		0.400	3.28	11.1	8.19	11.2
C1M5	5 months	0.396	< 0.1	–	–	–
C2M5		0.400	0.50	12.9	1.24	13.0
C3M5		0.399	1.54	11.4	3.86	11.5
C1Y1	1 year	0.396	< 0.1	–	–	–
C2Y1		0.392	0.19	19.9	0.49	19.9
C3Y1		0.395	3.27	11.1	8.27	11.2

Table A2. 9 Total cobalt-60 activity in the solution phase in each experiment with time

Leaching time (weeks)	Cobalt-60 activity in the solution phase in each experiment (kBq)		
	Container 1	Container 2	Container 3
1	<0.2	13.4 ± 1.9	19.0 ± 2.2
3	<0.2	4.9 ± 0.9	7.6 ± 1.1
6	<0.2	4.7± 0.9	8.2 ± 1.0
13	<0.2	2.0± 0.5	4.6 ± 1.1
22	<0.2	0.7± 0.2	2.1 ± 0.5
59	<0.2	0.3± 0.1	4.4 ± 1.0

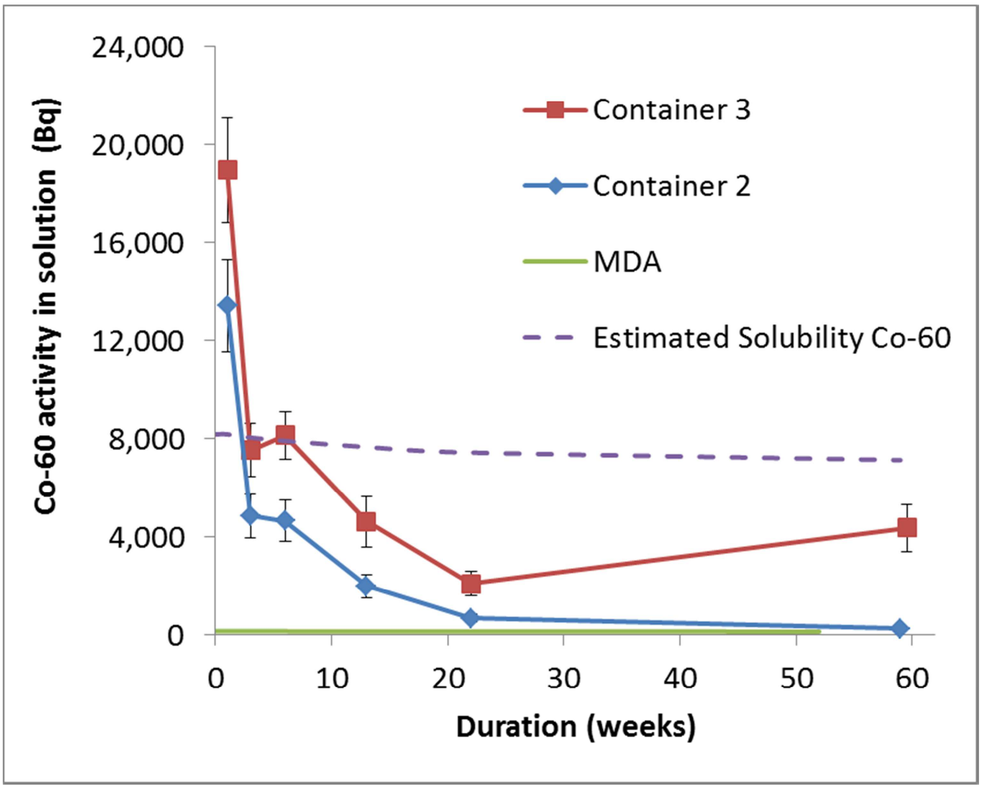


Figure A.2 6 Co-60 activity measured in the liquid phase from all three experiments

Additional tests of Co-60 sorption

The first additional test is described in 4.2.1. This test did not show any changes in the Co-60 concentration after 6 weeks sampling, so it could be concluded that there is no absorption on the zirconia insert walls. New test has been done in the same way as the first test, this time with addition of stainless steel material to the solution to study the influence of the stainless steel.

Table A2. 10 Overview of distribution of inorganic and organic C-14 in the leachant after 1 year sampling

Period (weeks)	**Cobalt-60 activity (Bq/g solution)**	
	Exp. without steel	**Exp. with steel**
T0	19.22 ± 0.51	21.26 ± 0.53
T6	22.33 ± 0.59	20.92 ± 0.55

These data show no significant dissolution limitation of Co- compounds nor sorption in the walls of the zirconia insert or on the steel surfaces at this conditions. These tests are done without any radiation source which is the case of the experiments with irradiated steels. There is a possibility the e.g. radiolysis could affect the chemical behavior of the present ions or chemical compounds.

After finishing the experiments of Container 2 & 3, these will be visually inspected and acid washed to determine if there is any Co-60 present.

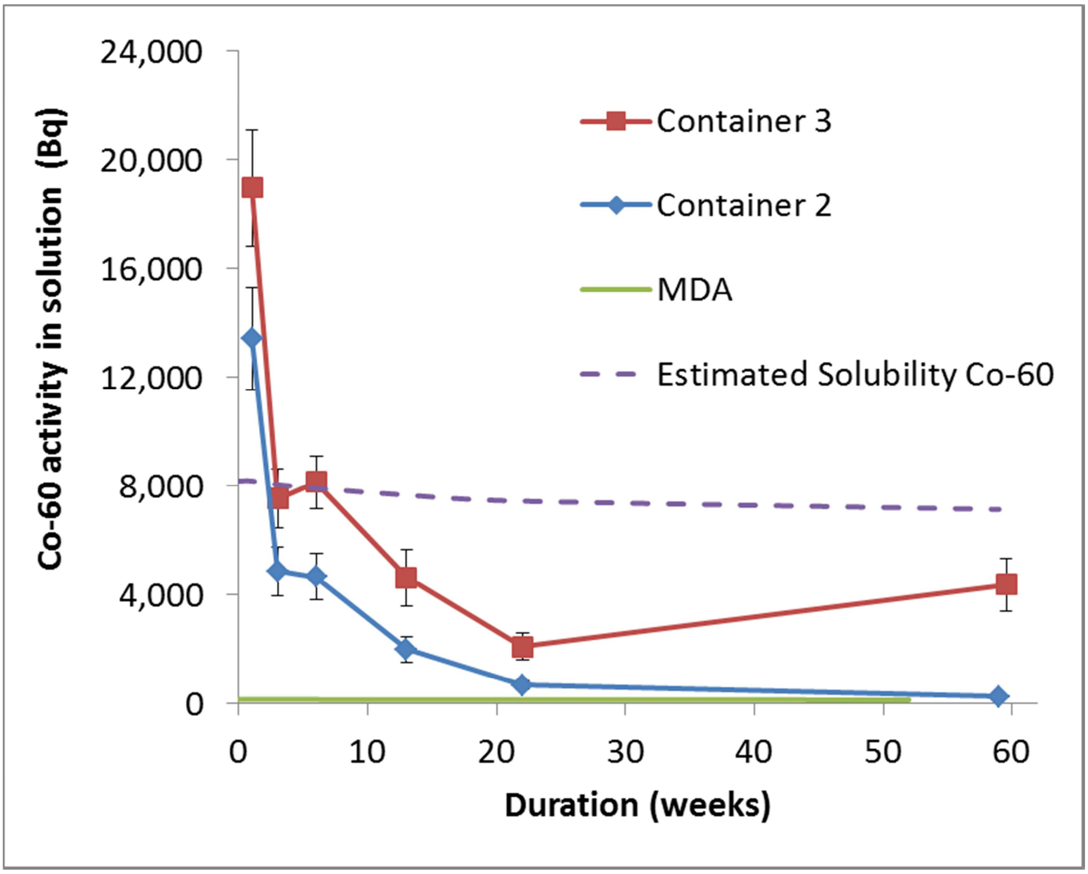


Figure A.2 7 Cumulative release of inorganic carbon-14 to the liquid phase from all three experiments, including total C-14 values for 13 months sampling

Discussion and conclusions

Experiments to study the rate and speciation of carbon-14 from irradiated stainless steel under high pH, anaerobic conditions have been in progress in NRG's Hot Cell Laboratory at Petten for a period of twenty months. The three experiments have been sampled six times to date and analytical data are now available for the carbon-14 releases to the gas phase and solution and cobalt-60 releases to solution up to 13 months leaching.

Further to the results presented in this report, the behaviour of C-14 release in gas observed during five months sampling is confirmed during 13 months sampling. The total amount of gas phase release from Container 3 is larger than that from Container 2, the rate of release decreases more rapidly in Container 3 so that from five months a faster rate of gas phase release is recorded from Container 2.

The C-14 release in the solution as inorganic carbon -14 in Container 2 is still increasing in steady rate, in contrast to Container 3 where the C-14 activity changes are negligible.

Based on the results of total C-14, there seems to be significantly higher dissolved organic carbon release in Container 3 than in Container 2 by a factor of nearly 4 which mirrors the larger initial gas phase release from that container. However, the way in which the release of carbon-14 as dissolved organic species has changed over the course of the experiments is not yet known.. The retained solution samples from 6 weeks, 3 months and 5 months will be analysed at NRG in the coming period.

Clearly, the presence of an organic fraction also affects the release rate estimate in Container 2 and the evaluation of an equivalent corrosion rate (2.8±0.4 nm/y). The effect of dissolved organic carbon release may increase the equivalent corrosion rate by about 20% to 3.4±0.5 nm/yr.

Measurement of the release of cobalt-60 into solution has been undertaken as a possible analogue for the corrosion of the stainless steel, on the assumption that cobalt-60 release would be congruent with respect to the corrosion of the steel surface. However, after a fast initial release of cobalt-60 during the first week of leaching, a drop has been observed in the cobalt-60 activity in solution at longer times. Further tests at NRG have demonstrated that the cobalt-60 loss is not due to sorption to the walls of the zirconia inner container nor to the stainless steel samples.

Some initial scoping calculations suggest that the loss of cobalt-60 could result from precipitation of cobalt associated with the formation of steel corrosion products; the total cobalt concentrations in solution initially may exceed an estimated solubility limit for cobalt controlled by the corrosion products of the steel. It is concluded that cobalt-60 release is not a suitable analogue for measuring the corrosion rate of the irradiated steel in these experiments.

The three experiments are planned to continue for a minimum period of two years with further sampling scheduled at the beginning of June 2018.