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Final report on C-14 release from steels under low pH and acidic conditions (D2.16)

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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, Zircalloys), 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 Zircalloys 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>

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Final report on C-14 release from steels under low pH and acidic conditions (D2.16)

Executive Summary

In this report, the influence of pH on the release of ^{14}C as well as the influence of pH on the chemical form of ^{14}C released from activated stainless steels is discussed using experimentally obtained results from KIT, VTT, and NRG within the CAST project.

Acidic digestion experiments performed by KIT show that about 99% of the ^{14}C inventory present in steel is released as gaseous or dissolved organic ^{14}C bearing compounds. The majority of ^{14}C is found in the acidic digestion liquor.

In leaching experiments (pH 8.5 and 12) performed by VTT, ^{54}Mn , ^{58}Co , ^{60}Co , ^{125}Sb , ^{124}Sb , and $^{110\text{m}}\text{Ag}$ were determined. However, ^{14}C was not analysed yet due to delays caused by the relocation of the laboratories to new buildings. However, the work will continue within the Finnish national research programme.

An initial fast release of ^{14}C during the first week of leaching (pH 13) is seen by NRG. The release of ^{14}C is primarily to the aqueous phase. However, 1 to 12% of released ^{14}C is present in the gaseous phase as organic ^{14}C -bearing compounds.

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1 Introduction

During reactor operation the activation product ^{14}C is produced by neutron capture reactions, mainly from ^{14}N impurities present in metallic components of the reactor and fuel assemblies.

In assessments of the long-term safety of a repository for nuclear waste, ^{14}C is one of the key radionuclides with respect to estimated doses arising upon release due to its long half-life and assumed mobility. Corrosion of the emplaced waste possibly releases ^{14}C -bearing volatile and/or dissolved compounds. Organic ^{14}C -bearing compounds reveal a high mobility either in the aqueous or in the gaseous phase and, once released, are potentially transported into the biosphere. On the contrary, volatile/dissolved inorganic ^{14}C -bearing compounds are affected by various retention and potential transformation processes in the near-field of a repository and the geosphere. However, ^{14}C is a difficult radionuclide to measure (soft β^- -emitter and no γ -rays). Therefore, an elaborate and robust extraction and analysis technique is required. Details about the ^{14}C extraction set-up can be found elsewhere [HERM *et al.*, 2015; HERM, 2015].

Only few studies are available dealing with radiocarbon quantification in irradiated steels [SCHUMANN *et al.*, 2014; SWANTON *et al.*, 2014]. Also the number of studies dealing with speciation of ^{14}C after release from irradiated stainless steels is very limited [SCHUMANN *et al.*, 2014; SWANTON *et al.*, 2014].

In this report, the influence of pH on the release of ^{14}C as well as the influence of pH on the chemical form of ^{14}C released from activated stainless steels is discussed using experimental results obtained by KIT, VTT, and NRG.

2 Materials and irradiation characteristics

The irradiated stainless steel samples used in experiments performed by KIT were taken from the plenum spring of a UO₂ fuel rod segment, irradiated in the pressurized water reactor (PWR) Gösgen in Switzerland. Activated stainless steel samples used in experiments performed by VTT were obtained from a reactor vessel surveillance capsule (the chain with capsules was mounted between reactor vessel and core barrel) irradiated in the Loviisa PWR in Finland, whereas compact tension (CT) stainless steel specimens, irradiated in the high flux reactor (HFR) at Petten (Netherlands), were used in experiments performed by NRG. Relevant characteristic parameters of the samples are given in table 1.

Table 1: Features of the stainless steel samples studied by KIT, VTT, and NRG.

	KIT	VTT	NRG
Reactor:	Gösgen PWR	Loviisa PWR (WVER-40)	Petten HFR
Material data:	X7CrNiAl17-7 stainless steel ¹⁾	stainless steel ²⁾	316L(N) EHRII-type austenitic stainless steel ³⁾
Irradiation data:			
average burn-up:	50.4 GWd/t _{HM}		
number of cycles:	4		
average linear power rate:	260 W/cm		
maximal linear power rate:	340 W/cm		
irradiation duration:	1985–1989	2011–2015	1996–1997
effective full power days:	1226 days		
radiation damage in the material:			2 dpa

¹⁾ only nominal chemical composition known [MIBUS *et al.*, 2015].

²⁾ measured chemical composition of stainless steel available elsewhere [HEIKOLA AND OLLILA, 2017].

³⁾ measured chemical composition provided by manufacturer [DE VISSER-TYNOVA, 2017].

3 Preparation of samples for dissolution experiments

Samples prepared by KIT for dissolution experiments were dry cut using an IsoMet® low speed saw (11-1180, Buehler Ltd.) equipped with an IsoMet® diamond wafering blade (11-4254, Buehler Ltd.). Cutting was very slow (ca. 5-10 hours per sample) to prevent overheating of the material. The three cut subsamples were used in three digestion experiments without any further pre-treatment. Two subsamples were cut from a reactor vessel surveillance capsule and used in two leaching experiments after rinsing with ethanol by VTT. Six CT specimens were directly used in two leaching experiments (three subsamples per experiment) performed by NRG. Characteristics of the subsamples are given in table 2.

Table 2: Characteristic data of the irradiated steel subsamples.

	KIT	VTT	NRG
mass [g]	#1: 0.283 #2: 0.356 #3: 0.047	#1: 2.975 #2: 9.211	#1: 73 #2: 74 #3: 74 #4: 74 #5: 74 #6: 74

4 Inventory calculations

The ^{14}C inventory of the steel studied by KIT was obtained by means of MCNP/CINDER as well as SCALE/TRITON/ORIGEN-S calculations [WILSON *et al.*, 2008; GAULD *et al.*, 2009; ORNL, 2011; PELOWITZ, 2011]. Also the inventory of the samples used by VTT was calculated based on the irradiation history. NRG calculated the amount of ^{14}C and other radionuclides present in each of the activated steel subsamples, taking into account the irradiation history, using ORIGEN. The results of the inventory calculations are shown in table 3.

Table 3: Calculated inventory of the steel samples used by KIT, VTT, and NRG.

KIT [Bq/g]	VTT [Bq/g]	NRG [Bq/g]
MCNP/CINDER: 8.5×10^4 *	2×10^3	#1: 1.55×10^5
SCALE/TRITON/ORIGEN-S: 9.5×10^4 *		#2: 2.87×10^5
		#3: 2.21×10^5
		#4: 1.81×10^5
		#5: 2.85×10^5
		#6: 2.01×10^5

* The results of the two independent theoretical approaches, performed assuming 80 ppm ^{14}N impurity in the steel, are in very good agreement with each other but clearly underestimate the experimentally determined ^{14}C inventory ($2.8 (\pm 0.3) \times 10^5$) obtained by KIT.

5 Dissolution experiments

Digestion of stainless steel specimens at KIT was performed inside the KIT-INE shielded box-line. Therefore a subsample was placed in an autoclave equipped with a double ended gas collecting cylinder and flushed with argon. A mixture of dilute $\text{H}_2\text{SO}_4/\text{HF}$ was added and all valves in the lid of the autoclave were closed. The sample was digested within a day at ambient temperature. Subsequently, the gas phase and digestion liquor was sampled. Aliquots of the digestion liquor as well as the gas phase in the gas collecting cylinder were analysed for ^{14}C in the extraction and analysis system. Details can be found elsewhere [HERM *et al.*, 2015; HERM, 2015].

VTT performed two leaching experiments in an argon glove-box. The samples were placed in a zirconia crucible inside a 500 mL glass bottle, respectively. Sample #1 was immersed in simulated groundwater (pH 8.5) whereas sample #2 was immersed in 0.01 M NaOH (pH 12.0) [HEIKOLA AND OLLILA, 2017]. First sampling of the liquid phase (gas phase was not analysed) was performed after 133 days of leaching and analysed, without any pre-treatment, by liquid scintillation counting (LSC) and gamma spectroscopy.

Two leaching experiments, performed by NRG, were conducted in a shielded-box with nitrogen atmosphere. The two leaching containers were made of borosilicate glass with a zirconia crucible inside containing three subsamples and 600 mL leaching solution (0.1 M NaOH, pH 13), respectively. Gas phase and about 7 mL of the liquid phase were sampled periodically. Gas sampling was performed by purging the container with nitrogen and

passing the gas through sampling rigs to capture ^{14}C on soda lime columns [DE VISSER-TYNOVA, 2017]. An aliquot of the sampled liquid phase (~ 0.4 mL) was used for gamma spectroscopy whereas about 5.5 mL were used for analysing ^{14}C after separation. For details see [DE VISSER-TYNOVA, 2017].

6 Results and discussion

6.1 Inventory of ^{14}C in activated steels

In table 4, the ^{14}C inventory experimentally determined by KIT is shown and compared to inventory calculations performed within this study. For more details see elsewhere [HERM *et al.*, 2017]. Neither VTT nor NRG determined experimentally the ^{14}C inventory in their samples.

Table 4: Mean values of the experimentally determined inventory of ^{14}C in comparison with results from the activation calculations performed in the present study.

	total ^{14}C [Bq/g steel]
experimentally determined inventory	$2.8(\pm 0.3)\times 10^5$
calculated inventory (MCNP/CINDER)	$8.5(\pm 0.9)\times 10^4$
calculated inventory (SCALE/TRITON/ORIGEN-S)	$9.5(\pm 1.0)\times 10^4$

6.2 Release of ^{14}C from activated steels and chemical form of ^{14}C released

Dissolution experiments performed by KIT in an autoclave equipped with gas collecting cylinder provided information about the distribution of the released inorganic/organic ^{14}C -bearing compounds into the aqueous and gaseous phase. However, acidic digestion experiments performed by KIT do not allow to the determination of corrosion rates or release rates of ^{14}C from the activated material.

Figure 1 shows the partitioning of ^{14}C -bearing compounds in inorganic/organic fractions and their distribution into the aqueous and/or gaseous phase. About $(70 \pm 10)\%$ of the ^{14}C inventory present in the studied steel is released as dissolved organic ^{14}C -bearing compounds into the acidic digestion liquor and about $(29 \pm 10)\%$ of the inventory is released as gaseous organic ^{14}C -bearing compounds into the gas phase. A very low content of inorganic ^{14}C -bearing compounds ($< 1\%$) are found in all experiments both in the gaseous and in the aqueous phase.

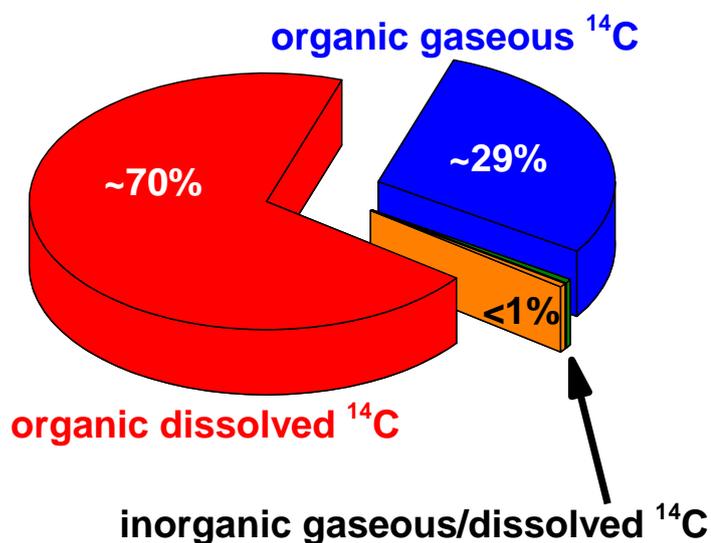


Figure 1: Partitioning of ^{14}C -bearing compounds in inorganic/organic fractions and their distribution into the aqueous and/or gaseous phase.

Five millilitre samples were obtained during the first sampling of the leaching experiments performed by VTT, respectively. An aliquot of 1 mL was used for gamma- and an aliquot of 4 mL was used for LSC-measurements. For details see elsewhere [HEIKOLA AND OLLILA, 2017].

Since LSC measurements were performed without chemical separation of ^{14}C (or other radionuclides), it was not possible to identify or quantify ^{14}C (or other radionuclides) in the leaching solution.

In gamma measurements ^{54}Mn , ^{58}Co , ^{60}Co , ^{125}Sb , ^{124}Sb , and $^{110\text{m}}\text{Ag}$ nuclides were identified and their measured activities are shown in table 4. Clearly higher activities were detected in the leaching experiment performed with synthetic groundwater at pH 8.5 (CA85). This could be due to the higher chloride concentration in the simulated groundwater solutions and pH. Corrosion rate of steel materials is increased in lower pH and higher chloride content.

Table 4: Activities of the measured radionuclides in sample solutions using gamma spectroscopy.

Bq/g	^{54}Mn	^{58}Co	^{60}Co	^{125}Sb	^{124}Sb	$^{110\text{m}}\text{Ag}$
Specimen #2 in NaOH	0.4	–	1.2	2.0	0.7	0.4
Specimen #1 in CA85	23.0	2.2	328.9	16.0	4.9	–

The two leaching experiments with activated steel performed by NRG were sampled after 1, 3, 6, 13, and 22 weeks and compared to an inactive experiment. ^{14}C release to the aqueous as well as to the gaseous phase was analysed. For further details see elsewhere [DE VISSER-TYNOVA, 2017].

The cumulative releases of ^{14}C to the gas phase is shown in figure 2 and the cumulative ^{14}C activity released to solution is shown in figure 3 for the two leaching experiments performed with activated steel. An initial fast release of ^{14}C from the steel is seen during the first week of leaching, followed by a drop in the rate of release at longer times. ^{14}C released during the first week of leaching corresponds to a release fraction of about 4×10^{-6} of the estimated ^{14}C inventory. ^{14}C is primarily released to the aqueous phase, but 1 to 12% of released ^{14}C is present in the gaseous phase. The chemical form of ^{14}C released to the gas phase is mainly organic (methane), while no $^{14}\text{CO}_2$ is found. The data presented regarding ^{14}C release into solution are valid only for inorganic ^{14}C species since the separation method used is not effective for collecting ^{14}C present as water-soluble organic species (e.g. carboxylic acids).

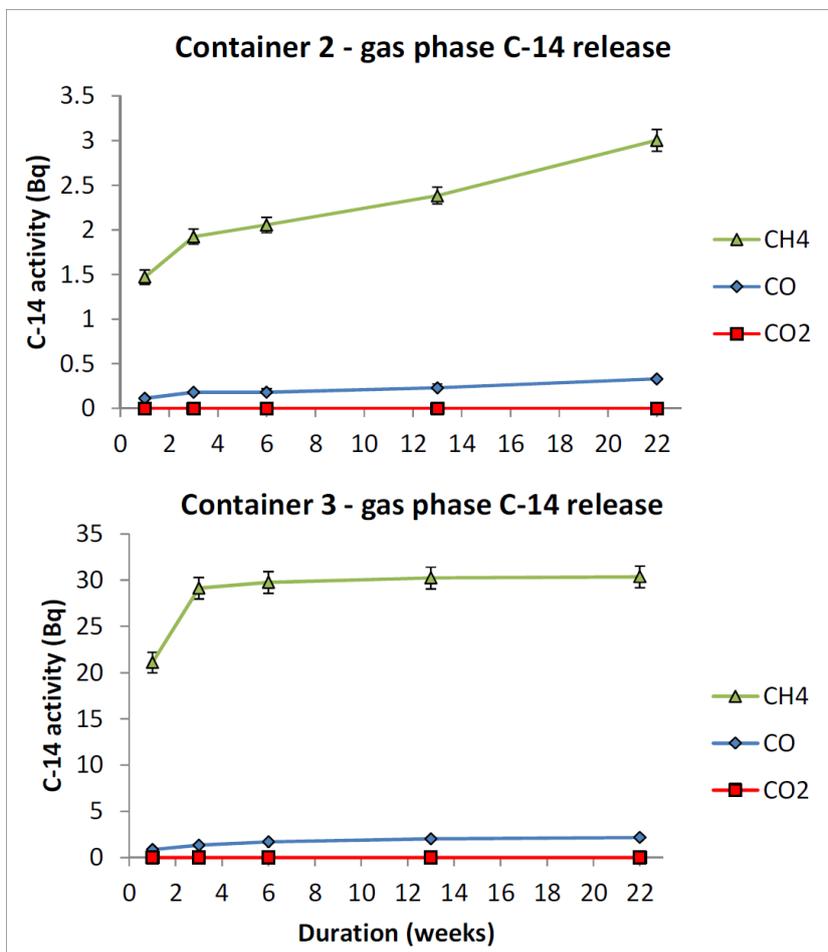


Figure 2: Cumulative releases of ¹⁴C to the gas phase.

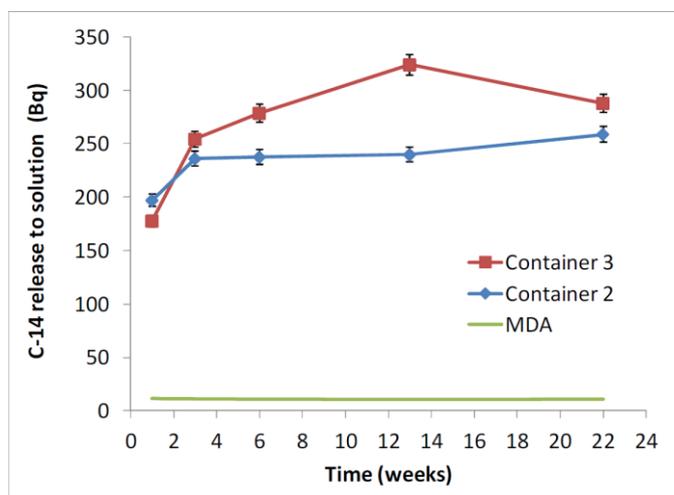


Figure 3: Cumulative ¹⁴C activity released to solution over time during leaching of irradiated steel samples in 0.1 M NaOH solution.

7 Summary and conclusions

About 99% of the ^{14}C inventory present in steel is released as gaseous or dissolved organic ^{14}C bearing compounds from steel in experiments performed by KIT. These results are in accordance with results obtained on the chemical form of ^{14}C after release from irradiated Zircaloy-4 cladding within CAST WP3 [NECIB *et al.*, 2016].

In experiments performed by VTT, ^{14}C was not analysed yet due to delays caused by the relocation of the laboratories to new buildings. However, the work will continue within the Finnish national research programme.

In the two experiments, performed by NRG, containing irradiated steel specimens, a relatively fast initial release of accessible ^{14}C 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 ^{14}C is released into the solution, but about 1% to 12% of the ^{14}C releases are to the gas phase.

Although the digestion experiments of KIT were performed under acidic conditions, clearly outside of repository-relevant conditions, little impact on the chemical form of ^{14}C released into the gaseous phase under repository relevant conditions is expected. This assumption is further supported by the results obtained by NRG where the release of ^{14}C into the gas phase is mainly as organic ^{14}C -bearing compounds in leaching experiments performed under anaerobic conditions and pH 13.

The majority of ^{14}C is found as dissolved hydrocarbons in experiments performed by KIT and almost no dependency on the pH is expected for the organic compounds. This assumption is further supported by experiments performed by NRG, where also the majority of ^{14}C -bearing compounds is released into the aqueous phase at pH 13. Moreover, inactive leaching experiments performed by VTT at pH 8.5 and 12 show that the content of organic carbon leached into solution was always higher compared to inorganic carbon at both investigated pH-values [HEIKOLA AND OLLILA, 2017]. Also the corrosion rate at lower pH potentially increases and leads to an enhanced release of radionuclides and in particular ^{14}C -bearing compounds to the aqueous and gaseous phase.

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