EUROPEAN COMMISSION

European Research Area

CArbon-14 Source Term

CAST

Advisory Group Review of WP 2 Final Synthesis Report (D1.10)

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Date of issue of this report: 08/06/2018

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.

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 release 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		
Work Package: 1	CAST Document no. :	Document type: R
Task: 1.1	CAST-2018-D1.10	R = report, O = other
Issued by:		Document status:
Internal no. : number		Draft/Review/Final

Document title
Advisory Group Review of WP 3 Final Synthesis Report

Executive Summary

One of the tasks of the CAST Advisory Group is to review the final synthesis reports from the different Work Packages. This report represents the review of the final synthesis report from WP 2 on the inventory and release of C-14 from irradiated steels [MIBUS ET AL. 2018]. Where necessary, information in this report has been supplemented by review of the final reports for the individual WP tasks [BOTTOMLEY ET AL. 2018; DE VISSER-TÝNOVÁ ET AL. 2017; DRUYTS ET AL. 2017; HEIKOLA AND OLLILA 2018; HERM ET AL. 2017a,b; RODRIGUEZ ALCALÁ AND GASCÓN 2018; RODRIGUEZ ALCALÁ ET AL. 2017; SAKURAGI 2017; WIELAND AND CVETKOVIC 2018].

Significant progress was made during the CAST project on the inventory and distribution of C-14 in irradiated steels and on the rate and speciation of release under simulated waste disposal conditions. Many technical and experimental challenges were overcome in advancing the state of knowledge of C-14 release from irradiated steels. The C-14 inventory in irradiated steels can be estimated within a factor of three by various activation models. A range of gaseous and dissolved organic species was observed from active leaching tests and there is evidence that C-14 release is congruent with corrosion of the steel.

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1 Introduction

The focus of Work Package 2 was the behaviour of C-14 in irradiated steels. Stainless steels are extensively used as the material of choice for reactor internals and fuel assembly components, as well as other Ni-Cr-based alloys, and carbon steel (C-steel) is typically used as either the primary containment barrier or as a liner for a concrete radiological shield. Activation of N-14 impurities is the most common route for the generation of C-14, although activation of O-17 and C-13 are also possible routes.

Prior to the CAST project, little was known about the release and speciation of C-14 from irradiated steels and, as a consequence, a conservative approach was taken in safety assessments [SWANTON ET AL. 2015]. There is a good database of corrosion rates for stainless and carbon steels in alkaline solutions representative of cement pore waters, as well as some information on the effects of radiolysis products. In-reactor service will also lead to radiation damage, although such damage typically affects the localised corrosion behaviour of the materials and, as such, should not impact C-14 release unless it is concentrated at a pit or crevice site. Carbon is generally present in steels as carbide or carbonitride inclusions and some work has been published on the dissolution of such phases when exposed to aqueous environments. There is a range of reactivities depending on the nature of the cation, with some carbides highly reactive and others relatively stable. A range of gaseous and dissolved, organic and inorganic dissolution products have been reported. However, it is not apparent that the behaviour of carbides in inactive materials will necessarily be the same as the behaviour C-14, presumably in solid solution, in irradiated steels.

There is a limited amount of existing information on the behaviour of C-14 in irradiated steels [SWANTON ET AL. 2015]. Both gaseous and dissolved C-14 species have been reported, with somewhat more organic than inorganic species. Interestingly, there is some evidence for the congruent release of C-14 with corrosion of the metal.

Four tasks were defined for WP 2, namely:

- Task 2.1 – Current status review;

- Task 2.2 –Development of analytical methods for measuring C-14 speciation;
- Task 2.3 –Corrosion experiments and measurement of released C-14;
- Task 2.4 – Interpretation of the results and synthesis in final report.

A total of twelve different partners undertook activities in one or more of these tasks (NAGRA, PSI, SCK-CEN, KIT, RWMC, JRC, ENRESA, VTT, ARMINES, NRG, AMEC, CIEMAT). Here the focus is on the outcomes of Tasks 2.3 (Section 2) and the significance of the new data in terms of the safety assessment and safety case (Section 3).

2 Characterization of C-14 released from irradiated steels

2.1 *Carbon-14 inventory*

Various CAST partners either measured the C-14 inventory of irradiated steels directly or estimated the inventory based on known or assumed N contents and suitable activation codes (Table 1). Compared with Zr alloys [NECIB ET AL. 2018], there is a relatively large range of specific activities of C-14 in stainless and C-steels reflecting the range of materials and their irradiation histories. Therefore, it is not feasible to define a generic range for use in safety assessment. KIT [HERM ET AL. 2017a] measured the C-14 inventory of a stainless steel plenum spring by acid dissolution and calculated the inventory using two different activation models. The calculated and measured inventories agreed within a factor of three, with the measured value being higher. The authors suggested that the assumed N content of 80 wppm used for the activation calculations was too low and again highlights the relatively poor understanding of the composition of the unirradiated material compared with that for the Zr wastes for which excellent agreement was found between measurement and calculation [NECIB ET AL. 2018]

There is relatively little information about the chemical form of the C-14 in irradiated steels. Comparing the microstructure of irradiated and non-irradiated reactor pressure vessel (RPV) steels, DRYUTS ET AL. [2017] found an increase in iron carbide upon irradiation. Whether this was due to radiation-induced migration of stable carbon or whether it reflects the formation of $Fe_3{}^{14}C$ is not clear but, if it was caused by the latter, there is a relatively good database on the dissolution behaviour of carbides that could be useful for estimating the rate and speciation of C-14 release. Dissolution of carbide phases, however, is unlikely to be congruent with corrosion of the steel matrix.

Table 1: Summary of measured and calculated C-14 inventories in steels carried out in CAST WP2 (from RODRIGUEZ ALCALÁ AND GASCÓN [2018]).

Participant	Steel type	^{14}C Determination	^{14}C Activity (Bq/g)
AMEC/NRG	Stainless Steel 316 L(N) (0.0238% C)	Computer modelling calculation	2.2E5
CIEMAT	Stainless Steel 304/316	Wet chemistry digestion technique	4.0E0
ENRESA	Stainless Steel 304/316	Computer modelling calculation	1.8E1
KIT	Alloy X7CrNiAl17-7	Wet chemistry digestion technique	2.8E5
PSI	One of the following alloys (0.08%C): X6CrNiTi18-10; X6CrNiNb18-10 or X6CrNiMoTi17-12-2	Wet chemistry digestion technique	1.78E4
SCK·CEN	JRQ Carbon Steel (0.1-0.7% C)	Computer modelling calculation	1.75E2
VTT	Ti_Austenitic Stainless Steel (0.023% C)	Computer modelling calculation	2.0E3

2.2 Corrosion and leaching experiments

Various corrosion and leaching experiments were conducted on irradiated and unirradiated steels as part of WP2 (Table 2). SAKURAGI [2017] reported the results of long-term corrosion rate measurements on unirradiated stainless steel in anoxic alkaline solution (NaOH, pH 12.5) based on the amount of H_2 evolved. Long-term rates as low as 0.4 nm/yr after 6.5 years exposure were reported at a temperature of 30°C. The corrosion rate was observed to increase with increasing temperature, with an activation energy of 83 kJ/mol.

The majority of the tests, however, were conducted on various irradiated stainless steels, with one partner investigating C-steel [DRUYTS ET AL. 2017]. The majority of investigators used anoxic alkaline leachates to represent deep geological disposal environments with cementitious materials, although some experiments were also conducted in aerated environments to simulate conditions during long-term storage. The aims of these experiments were to measure the rate and speciation of C-14 release and to demonstrate whether that release is congruent with the corrosion rate. Because the amount of stable carbon (in the form of C-12) is so much higher than that of C-14, the rate of release and speciation of C-12 was also considered by some partners, as an analogue for C-14. The results of these experiments are discussed in some detail by MIBUS ET AL. [2018] and RODRIGUEZ ALCALÁ AND GASCÓN [2018] and are summarised here in Table 3.

A great many experimental challenges were encountered, and overcome, in these studies. In addition to the difficulties of obtaining and handling active samples, the amounts of C-14 released were small making sampling and analysis very difficult. A number of CAST partners struggled to determine release rates or speciation.

Nevertheless, progress was made in a number of areas, including C-14 release kinetics and the speciation of dissolved and gaseous products (Table 3). Different methods were used to estimate the corrosion rate of irradiated steels. There was contradictory evidence regarding whether the release of Co-60 can be used as a surrogate for the corrosion rate, with CIEMAT suggesting that it could be under some circumstances [RODRIGUEZ ALCALÁ ET AL. 2017], but NRG observing a decrease in Co-60 activity with time [DE VISSER-TÝNOVÁ ET AL. 2017].

Table 2: Summary of corrosion and leaching experiments carried out in CAST WP2 (from RODRIGUEZ ALCALÁ AND GASCÓN [2018]).

Participant	Steel type (Active/Inactive material)	Leachant	O_2	Duration
AMEC/NRG	Stainless Steel 316 L(N) (0.0238% C) (Active)	NaOH pH = 13	NO	5 months
CIEMAT	Stainless Steel 304/316 (Active)	NaOH pH =12 1M H_3PO_4	YES	281 days 263 days
ENRESA	Stainless Steel 304/316 (Active)	Deionised water pH =7	YES	455 days
PSI	One of the following alloys (0.08%C): X6CrNiTi18-10; X6CrNiNb18-10 or X6CrNiMoTi17-12-2 (Active)	$Ca(OH)_2$ pH = 12.5	NO	412 days
RWMC	18Cr-8Ni Austenitic Stainless Steel (0.07% C) (Active)	NaOH pH = 12.5 Deionised water	NO	6.5 years 3 years
SCK·CEN	JRQ Carbon Steel (0.1-0.7% C) (Active)	$Ca(OH)_2$ pH = 12.5	NO	231 days
VTT	Ti_Austenitic Stainless Steel (0.023% C) (Active) AISI316Ti Steel (0.3% C) (Inactive) Iron Carbide (Inactive)	Simulated groundwater pH = 8.5 NaOH pH = 12	NO	133 days

Table 3: Summary of corrosion rates and the release rate and speciation of C-12 and C-14 from corrosion and leaching experiments carried out in CAST WP2 (from RODRIGUEZ ALCALÁ AND GASCÓN [2018]).

Participant	Corrosion Rate (nm/y) (Determined by)	Release Rate (fraction/y) (Determined by)	Compounds Gas Phase	Compounds Liquid Phase
AMEC/NRG	1 week: 520 (^{14}C) 22 weeks: 3 (^{14}C)	Not determined	^{14}CO, $^{14}CH_4$	Not determined
CIEMAT	2 weeks: 3580 (^{60}Co) in NaOH pH = 12 40 weeks: 274 (^{60}Co) in NaOH pH = 12	40 weeks: 1.55E-4 (^{60}Co) in NaOH pH=12	^{12}CO	Not detected
	2 weeks: 206000 (^{60}Co) in 1M H_3PO_4 38 weeks: 20100 (^{60}Co) in 1M H_3PO_4	38 weeks: 1.14E-2 (^{60}Co) in 1M H_3PO_4	^{12}CO	$^{12}C_2O_4^{2-}$
ENRESA	65 weeks: 4390 (^{60}Co)	65 weeks: 1.10E-3 (^{60}Co) pH=7	Not determined	Not determined
PSI	Not determined	Not determined	$^{12}CH_4$, $^{12}C_2H_4$,	^{14}Formic acid, ^{14}acetic acid, oxalic acid, malonic acid, glycolic acid and ^{14}l-lactic acid.
RWMC	13 weeks: 1.5 (H_2) 338 weeks: 0.4 (H_2)	Not determined	Not determined	Not determined

Table 3 (continued): Summary of corrosion rates and the release rate and speciation of C-12 and C-14 from corrosion and leaching experiments carried out in CAST WP2 (from RODRIGUEZ ALCALÁ AND GASCÓN [2018]).

Participant	Corrosion Rate (nm/y) (Determined by)	Release Rate (fraction/y) (Determined by)	Compounds Gas Phase	Compounds Liquid Phase
SCK·CEN	33 weeks: 68-117 (Carbon in gas phase)	Not determined	$^{12}CH_4$, $^{12}C_2H_6$, $^{12}C_2H_4$, H_2	Not detected
VTT	No data in active/inactive material	*Data Inactive AISI316Ti Steel (0.3% C):* 90 weeks: 2.9E-3 pH = 8.5 (total C) 90 weeks: 3.7E-3 pH = 12.5 (total C)	Not detected	Total ^{12}C measured in inactive material
		Data Inactive Fe_3C: 90 weeks: 4.8E-4 pH = 8.5 (total C) 90 weeks: 8.4E-4 pH = 12.5 (total C)	*pH = 8.5:* $^{12}C_2H_6$, $^{12}C_3H_8$, $^{12}C_4H_{10}$, $^{12}C_5H_{12}$ *pH = 12.5:* $^{12}C_2H_6$, $^{12}C_3H_8$, $^{12}C_3H_4$, $^{12}C_4H_{10}$, $^{12}C_4H_8$, $^{12}C_5H_{12}$, $^{12}C_5H_{10}$, $^{12}C_6H_{14}$	

Both NRG [DE VISSER-TÝNOVÁ ET AL. 2017] and PSI [WIELAND AND CVETKOVIC 2018] estimated corrosion rates based on the assumption of congruent C-14 release and derived rates that the authors suggested were consistent with rates independently measured for stainless steels in similar anoxic alkaline environments.

In terms of the speciation of released C-14, NRG observed primarily dissolved species although there was an initial release of gaseous C-14 amounting to 1-12% of the released activity [DE VISSER-TÝNOVÁ ET AL. 2017]. Focussing on the total organic fraction of dissolved C-14, WIELAND AND CVETKOVIC [2018] were able to positively identify the presence of formate, acetate, and lactate.

A wider range of stable C-12 species was reported by a number of CAST partners (Table 3). While this is useful evidence, presumably much of this stable carbon would have been in the form of carbides which might behave differently from C-14 present in solid solution.

2.3 *IRF*

Various groups reported a rapid initial release of C-14 followed by a slower long-term release [DE VISSER-TÝNOVÁ ET AL. 2017, RODRIGUEZ ALCALÁ ET AL. 2017]. RODRIGUEZ ALCALÁ ET AL. [2017] reported the release of 3.6% of the inventory within the first 15 days exposure to the leachate. Unlike the situation with irradiated Zr alloys [NECIB ET AL. 2018], neither group referred to this rapidly released component as an instant release fraction. It is not clear whether this initial rapid release is due to surface contamination or other experimental artifacts or whether it in fact represents an initial release of C-14 from the oxide.

3 Significance of the Outcomes of Work Package 2

Based on the comparison of measured and predicted inventories, activation models can estimate the C-14 inventory to within a factor of three. Given the magnitude of other uncertainties, this margin is probably acceptable for safety assessment purposes. Better agreement may be possible if conservative assumptions regarding the original N content of the alloy are made. However, uncertainties associated with an understanding of the local flux will remain.

A range of gaseous and dissolved organic C-14 species have been detected during the leaching of irradiated stainless steel. This observation should help inform the choice of transport properties and retardation factors used for safety assessment.

There is evidence for a fast initial release of C-14, but it is unclear whether this is a true IRF or an experimental artifact due to surface contamination.

Although there were indications from the CAST project of congruent release, these were not based on direct measurement of the corrosion rate but rather on a comparison of the inferred corrosion rate on the basis of congruent C-14 release and the generally expected corrosion rate under the given experimental conditions. In one case, the inferred corrosion rate was 3 nm/yr [DE VISSER-TÝNOVÁ ET AL. 2017], whereas in another it was 20-100 nm/yr [WIELAND AND CVETKOVIC 2018]. Because the corrosion rate of stainless steel in alkaline solution changes with exposure time (especially over the period 1-12 months typical of the experimental times considered here) the use of this inferred corrosion rate to demonstrate congruent release should be treated with caution. Furthermore, WIELAND AND CVETKOVIC [2018] observed that the total organic C-14 content of the leachate decreased with time after approximately 3 months exposure which further complicates the estimation of corrosion rates based on C-14 release. A more-robust demonstration of congruent release would be based on a comparison of the directly measured corrosion rate (measured by mass-loss, electrochemical, electrical resistance or (in the absence of radiolysis) H_2 evolution) and the rate of release of C-14.

MIBUS ET AL. [2018] considered the implications from the work carried out in WP 2 for the long-term evolution of the release and speciation of C-14 in the repository. Three main factors were considered; the time-dependent saturation of the repository, the build-up and possible release of H_2 (and gas more generally) as a consequence of the corrosion of ferrous materials (and of microbial processes), and the impact of radiolysis and evolving redox conditions. The degree of oxidation of the C-14 may well be expected to be influenced by whether conditions are oxic or anoxic and the presence of radiolysis products, and there are some insights into the effect of radiolysis from the CAST studies. The presence of H_2 will also influence the redox conditions and, possibly, the C-14 speciation. Perhaps the more important consequence of gas build-up, however, is the possibility of rapid transport of C-14 as gaseous species. This will be impacted, in part, by the time dependence of the saturation of the repository since an unsaturated near field has a larger storage capacity for gaseous species than a completely saturated one. The logical consequence of the scenario(s) developed by MIBUS ET AL. [2018] would be that the speciation of C-14 would be time dependent and that the transport mechanisms should be linked to the time-dependent saturation behaviour. Some of the inferred behaviour, for example, the effect of radiolysis, is consistent with observations from the CAST project but perhaps need further experimental validation before implementation. Furthermore, depending upon the level of sophistication of the safety assessment models, not all national programmes will be able to handle the proposed time-dependent C-14 speciation and transport. Regardless, the proposed evolution of the C-14 speciation and release is a useful build on the information included in the safety case.

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