EUROPEAN COMMISSION
European Research Area

CArbon-14 Source Term

CAST

Advisory Group Review of WP 4 Final Synthesis Report (D1.12)

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Date of issue of this report: 19/05/2018

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

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(D1.12)

CAST		
Work Package: 1	CAST Document no. :	Document type: R
Task: 1.1	CAST-2018-D1.12	R = report, O = other
Issued by:		Document status:
Internal no. : number		Draft/Review/Final

Document title
Advisory Group Review of WP 4 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 4 on the inventory and release of C-14 from spent ion-exchange resins (SIERs) [REILLER 2018] and the supporting final reports of the various WP tasks [BUCUR ET AL. 2017, RIZZATO ET AL. 2017, RIZZO ET AL. 2017, and VECERNÍK ET AL. 2018].

A wide range of operational factors determine the C-14 inventory of SIERs and a dedicated sampling and analytical campaign is required by each country to characterise their wastes. Carbon-14 is predominantly present in inorganic form and can be released both as gaseous and as dissolved species in concentrated alkaline conditions, but not in dilute alkali or in synthetic ground water. Immobilisation of the SIERs in a cement matrix also appears to inhibit C-14 release.

The work in CAST WP 4 has contributed to improved understanding of the inventory and release mechanism of C-14 in SIERs and should result in reduced uncertainty in the associated national safety assessments.

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1 Introduction

The focus of Work Package 4 was the behaviour of C-14 in spent ion-exchange resins (SIERs). Ion-exchange resins are used to purify various process streams at nuclear power plants and research reactors and will contain a range of radionuclides, including C-14.

A number of challenges to the proper treatment of SIERs in performance assessment (PA) were recognised from the outset of the work, including:

- The differences in reactor type, operating history, storage conditions, and other factors, resulting in a wide range in the C-14 inventory. As a consequence, it will be difficult to define a common inventory for use in PA and each programme will need to conduct their own sampling and analysis campaign.
- Part of the inventory may be lost during storage, further complicating the definition of the source term.
- The resin matrix may undergo degradation during storage due to gamma irradiation, resulting in loss of C-14 and/or alteration of the release characteristics after disposal, further complicating the definition of the source term.
- In some programmes, the SIERs will be immobilised in a cementitious or other matrix material, which will further impact the C-14 release characteristics.

It is interesting to note the range of experience with, and confidence in, the treatment of C-14 in PA at the outset of CAST [KENDALL ET AL. 2015]. For example, SKB have historically made many measurements on the C-14 inventory of SIERs and consider the uncertainty to be low (±20%). Other organizations have less experience, with some expressing an uncertainty in the C-14 of greater than one order of magnitude.

Within this context, four tasks were defined for WP 4, including:

- Task 4.1 – Current status review of C-14 and its release from SIERs;
- Task 4.2 –C-14 inventory and speciation in SIERs;
- Task 4.3 –C-14 release from SIERs and its speciation;
- Task 4.5 – Synthesis of experimental data and interpretation – final report.

A total of seven different partners undertook activities in one or more of these tasks (CEA-EDF, ENEA, FZJ, RATEN-ICN, SKB, and ÚJV. Here the focus is on the outcomes of Tasks 4.2 (Section 2) and 4.3 (Section 3), and the significance in terms of the safety assessment and safety case (Section 4).

2 Carbon-14 Inventory and Speciation in SIERs

2.1 *Carbon-14 inventory*

Six CAST participants reported on the C-14 inventory of SIERs from their respective national programmes [RIZZO ET AL. 2017]. As noted above, the variation in reactor type and resin operating history results in a wide range of C-14 inventory (Table 1, modified from Table 4 of RIZZO ET AL. 2017). Among the factors that will determine the C-14 inventory are:

- The type of reactor (pressurized water versus boiling water);
- The degree of saturation (loading factor) of the SIERs, which may be limited by radiological considerations;
- Premature removal of the bed from service due to unacceptable pressure drop;
- Mixing of SIERs from different beds for storage.

Regardless of the reason(s) for the variability, the important conclusion is that each national programme will need to institute a focussed sampling and analysis campaign in order to properly characterise the C-14 inventory. It is noteworthy that SKB have analysed many hundreds of SIERs samples over the past decade or so, and this accounts for their relatively high level of confidence in the C-14 inventory [KENDALL ET AL. 2015].

Another important conclusion from the measurements in Table 1 is that a substantial fraction of the C-14 may be lost during storage and handling of the SIERs. The resins are stored under water after being taken out of service until such time that the short-lived radionuclides have decayed. The resins are then dried to remove water, during which C-14 is lost, as much as 99% based on the SKB measurements on wet and dried PWR resin samples (highlighted in yellow in Table 1). This apparent loss of C-14 on drying could clearly have a significant impact on the estimated inventory for disposal if it is representative of the behaviour elsewhere.

Table 1: Carbon-14 inventories reported by various WP 4 participants [RIZZO ET AL. 2017].

CAST partner	Type of SIER	^{14}C total inventory
CEA	PWR (EDF-A) wet resins	5630 ± 325 Bq/g (wet mass basis)
CEA	PWR (EDF-A) dry resins	10754± 680 Bq/g (dry) (H_2O 40%) 10930 ±760 Bq/g (dry) (H_2O 57%)
CEA	PWR (EDF-B) wet resins	2125 ± 200 Bq/g (wet)
SKB	CCU PWR wet resins	1470 Bq/g (dry)
SKB	CCU PWR dried resins	7.9 -21 Bq/g (dry)
SKB	BWR	2200 - 6200 Bq/g (dry)
RATEN	CANDU SIERs wet	36500 ± 2220 Bq/g (wet)
UJV	PWR SIERs	45 ±5 Bq/g (wet)
UJV	Research Reactor SIERS	2000 ± 280 Bq/g (wet)

2.2 *Carbon-14 speciation*

In contrast to the high degree of variability in the inventory, there is a high degree of consensus regarding the speciation of C-14 in SIERs. In “as-received” (i.e., in resins that have not undergone drying), the C-14 is largely in the form of inorganic carbon, presumably as carbonate (Table 2, modified from Table 10 of RIZZO ET AL. [2017]). There are differences in speciation between PWR (70-80% inorganic) and BWR (90% inorganic). Furthermore, although not shown in Table 2, the inorganic fraction from CANDU reactors is predominantly in the anionic form [RIZZO ET AL. 2017]. The small amount of organics are present in the form of short-chain acids (formate, acetate).

Interestingly, the speciation changes completely upon drying. Whereas inorganic C-14 is predominant in wet samples, organic C-14 predominates in dried resins (see the speciation for wet and dry SKB samples highlighted in yellow in Table 2). This change in speciation implies that the loss of C-14 observed upon drying is likely due to the loss of $^{14}CO_2$, and results in a change in the predominant speciation of the C-14 that would actually be disposed of in the repository.

Table 2: Carbon-14 speciation (inorganic vs. organic) in SIERs samples analysed by CAST WP 4 partners [RIZZO ET AL. 2017].

CAST partner	Type of SIER	State	C-14 form	C-14 activcity (% of total)
CEA	EDF–A PWR	Wet sample	Inorganic	77
			Organic	23
RATEN-ICN	CANDU	Wet samples	Inorganic	93
			Organic	7
SKB	CCU BWR	Wet samples	Inorganic	95-99
			Organic	1-5
SKB	CCU BWR	Dried samples	Inorganic	8
			Organic	92
SKB	RWCU PWR	Wet samples	Inorganic	70
			Organic	30
UJV	EDU-PWR	Wet samples	Inorganic	29
			Organic	71
UJV	ETE-PWR	Wet samples	Inorganic	37
			Organic	63
UJV	UJV-PWR	Wet samples	Inorganic	96-100
			Organic	4-0

3 Carbon-14 Release from SIERs and its Speciation

In addition to the summary report, three reports present data on the release of C-14 from SIERs; namely BUCUR ET AL. [2017], RIZZATO ET AL. [2017], and VECERNÍK ET AL. [2018]. Some of the studies are reported in more than one of these reports, but here the results from all three reports are discussed collectively. In general, C-14 release from SIERs was widely observed, which lead RIZZATO ET AL. [2017] to conclude that "^{14}C in SIERs is rather labile …". While this may be the case for many of the systems studied, it is not necessarily true of conditioned wastes under disposal conditions.

3.1 *Release of gaseous carbon-14*

Gaseous release of C-14 from SIERs occurs under both storage and disposal conditions. The former is important for operational safety and for developing suitable storage and conditioning strategies, as well as for defining the C-14 inventory to be disposed. Gaseous C-14 release under disposal conditions (simulated here by alkaline solution) is important for post-closure safety assessment.

FZJ studied the release of gaseous C-14 in atmospheric conditions representative of interim storage [BUCUR ET AL. 2017, RIZZATO ET AL. 2017, RIZZO ET AL. 2017]. No release was observed from dry resins under vacuum, but significant gaseous release was observed in closed air systems with wet resins. The fact that the presence of moisture is necessary for C-14 release led the investigators to suggest that the mechanism involves ion exchange or isotopic exchange with CO_2 in the atmosphere. Regardless, rapid equilibration between wet SIERs and the gas phase was observed within 20 days, with between 1-2% of the inventory released at room temperature and as much as 8% at 50°C. The higher amount at the higher temperature was explained in terms of temperature-dependent degradation of the resin rather than an effect of temperature on the equilibrium. If this is a true equilibrium process and desorption is rapid, it suggests that in a continuously vented system and/or in a closed system with a larger headspace:SIERs volume ratio than that used experimentally, a much greater fraction of the C-14 inventory could be lost. This conclusion is consistent with the apparent loss of 99% of the C-14 inventory upon drying of wet PWR resins (Table

1). To control this gaseous release, it seems that drying under vacuum could be a potential strategy, since FZJ observed no release from dry resins under these conditions.

Dissolved C-14 is the primary release path under aqueous alkaline conditions (see Section 3.2), but RATEN-ICN reported some gaseous release from solution [BUCUR ET AL. 2017, RIZZATO ET AL. 2017, RIZZO ET AL. 2017]. Approximately 7% of the C-14 inventory was released as CO_2 and was associated with a pH excursion. A further 6% of the inventory could not be accounted for in either the inorganic gaseous release, the dissolved component, or that remaining on the SIERs, prompting speculation that this missing fraction might have been released in gaseous organic form. The implications for safety assessment of this 7% gaseous release of inorganic C-14 under alkaline conditions is unclear since it was associated with a pH excursion and it is uncertain whether a similar such excursion would occur under repository conditions, although the system should be buffered by the presence of calcite.

3.2 *Release of carbon-14 in solution*

A number of CAST partners conducted leaching tests in alkaline solutions designed to simulate the water in equilibrium within a near-field environment of a cementitious backfill [BUCUR ET AL. 2017, RIZZATO ET AL. 2017, RIZZO ET AL. 2017]. RATEN-ICN studied the rate of release and speciation of C-14 from CANDU SIERs in alkaline solution and found only 8% of the inventory remained associated with the SIERs after 174 days exposure. Of the initial inventory, 79% was released in dissolved form, 7% as gaseous CO_2 (during a pH excursion), 8% remained, and 6% was unaccounted for. The dissolved component was predominantly inorganic (>99%) in the first 2 days, but approximately 8% of the total was present in organic form after a further 22 days leaching.

CEA also report the leaching of C-14 from SIERs in alkaline solution [VECERNÍK ET AL. 2018]. Repeatedly contacting SIERs with 1 mol/L LiOH solution released C-14 with the amount decreasing with increased exposure, but none was released using either 0.001 mol/L LiOH or deionized water. Similarly, VECERNÍK ET AL. [2018] also report little release of C-14 (maximum 1-2% of the inventory) from SIERs exposed to either 0.02 mol/L NaOH or a near-neutral pH synthetic granitic ground water solution.

3.3 *Release of carbon-14 from conditioned waste*

Some national programmes are proposing to condition or immobilise SIERs for disposal using a matrix material, such as epoxy, bitumen, or cementitious grout. While a number of CAST partners considered the effect of the alkaline pH characteristic of immobilisation in cement, only one partner (ÚJV) actually studied the release of C-14 from resins embedded in cement [VECERNÍK ET AL. 2018]. Artificially produced C-14 containing IER samples were prepared for this study, but regardless of the sample surface area:leachate volume ratio or the nature of the leachate (distilled water, synthetic ground water, or 0.02 mol/L NaOH solution), minimal release of C-14 was observed.

This is a potentially important observation since it implies that conditioning of the SIERs could lead to a slower release of C-14. One question is whether, over repository timescales, the release of C-14 could be significant. Based on the limited current data set, it is not possible to predict the behaviour over a period of 60,000 years (ten half-lives of C-14), but it may be possible to take some credit in the safety assessment for the slow release of C-14 from immobilised SIERs waste forms.

4 Significance of the Outcomes of Work Package 4

In this section, the significance of the WP 4 outcomes for the safety case and safety assessment are considered. In general, quantitative information relating to the inventory or rate of release of C-14 can be used directly for the safety assessment. Mechanistic information and more-qualitative observations are useful for supporting the overall safety case. Figure 1 summarises some of the achievements from WP 4 towards the improved understanding of the inventory and release mechanism of C-14 from SIERs.

As noted in the Introduction, at the start of the CAST project, some national programmes reported a large degree of uncertainty in the treatment of C-14 from SIERs in their safety assessments. This uncertainty was largely associated with the inventory and, to some degree, this level of uncertainty has been significantly reduced by the ensuing studies. Although a dedicated sampling and analytical programme may be required because of the wide range of operational factors that determine the C-14 inventory, the "order of magnitude or more" uncertainty initially reported by some participants should have been significantly reduced. There is also consensus on the speciation of C-14 in SIERs, with the majority being present in inorganic form as carbonate. There is still some uncertainty, however, as to how much of the initial inventory may be lost during handling and storage (either due to drying of the SIERs or by exposure of wet resins to the atmosphere). These observations are also important for developing proper handling and conditioning strategies.

There have also been interesting developments in the area of the release of C-14 under disposal conditions. When exposed to aqueous environments, the release of C-14 is only observed in concentrated alkaline solutions (of the order of 1 mol/L), and not from either synthetic ground water or from more-dilute alkaline solutions. However, when immobilised in a cement matrix, no measurable C-14 release was observed over laboratory timescales. Thus, whatever effect of pH there might be, there is also considerable transport resistance to C-14 release from cemented resins. Whether this transport resistance is significant over repository timescales has yet to be determined.

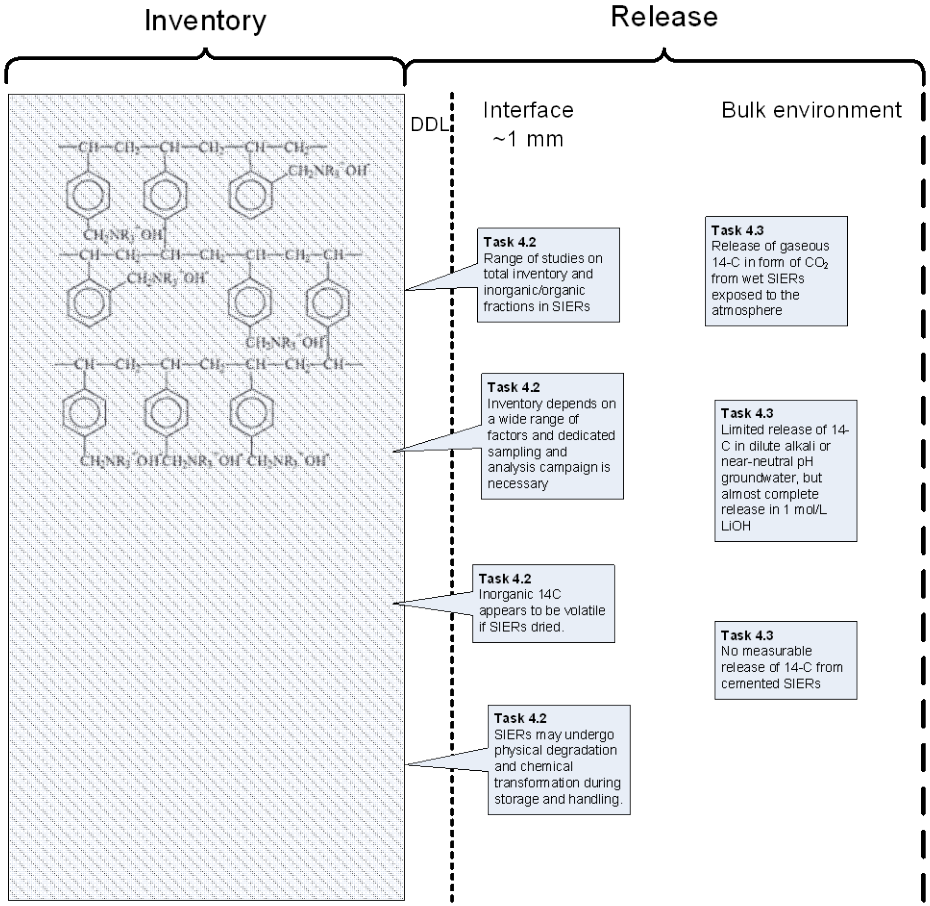

Figure 1: Summary of contributions from WP 4 to improved understanding of the inventory and speciation of C-14 in spent ion-exchange resins and the associated release mechanisms.

Overall, there has been considerable progress in the understanding of the behaviour of SIERs as a waste form as a result of the work done in the CAST project which should result in improved treatment of C-14 in national safety assessments.

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