CArbon-14 Source Term

CAST

Overview of achievements on technical results for regulators for Workshop 1 (D7.7)

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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, 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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Executive Summary

One of the aims of the CAST project is dissemination of the results of the performed research in the project and transmission of the developed knowledge. This report presents an overview of the work, already performed under the CAST project and activities planned in the future. The information presented in the report serves as a basis material for a Workshop 1, which is dedicated to the various stakeholders. The aim of the report is to make the regulators familiar with the research being performed in the framework of CAST in advance, in order they can make an effective contribution to CAST during their attendance at workshops.

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1 Introduction

The CAST project (CArbon-14 Source Term) aims to develop understanding of the potential release mechanisms of ^{14}C from radioactive waste materials. The investigations on ^{14}C releases are shared between four Work Packages.

Work Package 2 (WP2) in the CAST project is dedicated to the identification and quantification of ^{14}C species formed during corrosion of irradiated steels.

Work Package 3 (WP3) is related to Zircaloy and Zr alloys in the CAST project. It aims to obtain a better understanding of ^{14}C behaviour in waste Zr fuel claddings under disposal conditions.

Work Package 4 (WP4) is dedicated to the study of speciation, source term, leaching, and gaseous release of ^{14}C from spent ion exchange resins (SIERs).

Work Package 5 (WP5) of the EC CAST project considers irradiated graphite and related ^{14}C behaviour.

In addition, Work Package 6 (WP6) is established to evaluate the results from WPs 2 to 5 in the context of national safety assessments.

One of the aims of the CAST project is dissemination of the results of the performed research in the project and transmission of the developed knowledge. This report presents the work already performed under the CAST project and activities planned in the future. The information focuses on the data and processes relevant for safety assessments and substantiation of assumptions, which need to be considered.

2 WP2: Release of ^{14}C from irradiated steels

Irradiated steel wastes comprise the irradiated ferrous metal components of nuclear reactor structures and nuclear fuel assemblies, which have been made from low-carbon steel, stainless steel and/or nickel alloys. ^{14}C is formed in steels primarily by the thermal neutron activation of ^{14}N that is present in all steels as a trace component.

The investigations and activities, which are performed under the CAST project in WP2 are related to the release of ^{14}C from irradiated steels and comprise:

- State of the art review of steel corrosion and ^{14}C release;
- Development of analytical techniques for identification and quantification of aqueous and gaseous ^{14}C species formed during corrosion of irradiated steels under conditions relevant to cement-based repositories;
- Validation of existing activation models by measuring ^{14}C inventories in irradiated steel;
- Carrying out experiments and modelling to further our understanding of the speciation and rate of $^{12}C/^{13}C$ and ^{14}C release from corrosion of irradiated and unirradiated steels under conditions relevant to deep geological repositories.

The status of the tasks and available outcomes are presented below.

2.1 *State of the art review of steel corrosion and ^{14}C release*

The literature review on steel corrosion and ^{14}C release has already been completed and the report [SWANTON, 2015] has been released. The review presents the current state of understanding of steel corrosion rates and ^{14}C releases from irradiated steels under conditions relevant to the storage and long-term disposal of radioactive wastes.

It should be noted that the corrosion data compiled in the review were obtained for unirradiated materials. It is known that neutron irradiation can change the microstructure of steels; however, the overall impact of irradiation on the long-term corrosion rates of waste steels is unknown.

2.1.1 Corrosion of carbon steel

Two phases of corrosion of carbon steel can be distinguished with the different corrosion rates: acute phase and long-term chronic corrosion.

For carbon steels treated to remove the passivating layer before encapsulation in cement, the acute phase under aerobic conditions is short-lived (order of days) with the corrosion rate of the order of 200 μm/y, which decreases to <1 μm/y. The corrosion rate increases at higher temperatures. The long-term corrosion rate of carbon steel in cementitious environments is very low because of the protection offered by the passive film formed under alkaline conditions. In the absence of chloride and carbonation effects, corrosion rates as low as 0.08 μm/y have been measured. Higher values in the range of 10-50 μm/y have been reported for the case where carbonation may be important. The actual corrosion rates of cemented carbon steel wastes, prior to closure of a disposal facility, are likely to depend on the specific cement types and waste stream and the environmental conditions (in particular the relative humidity).

Under anaerobic alkaline conditions the acute corrosion rate of carbon steel is reduced to <5 μm/y; however, the duration of the acute phase is longer (up to 5 years before longer-term rates are achieved). The acute corrosion rate increases with temperature, but the rate of passivation is also increased. Long-term anaerobic corrosion rates in the range 0.04-0.11 μm/y have been measured. It was found that there was little effect of γ-irradiation, chloride or sulphur species on anaerobic corrosion under alkaline conditions and little effect of temperature on the long-term rates.

2.1.2 Corrosion of stainless steel

Stainless steels undergo very rapid passivation if the oxide layer is disrupted and there is not expected to be a distinct period of acute corrosion. Under alkaline conditions, the aerobic corrosion rate of stainless steel is in the range 0.01 to 0.04 μm/y. Aerobic corrosion rate increases with temperature.

Anaerobic corrosion rates of stainless steel in alkaline solutions are below 0.01 μm/y. The newest data indicate a mean anaerobic corrosion rate of 0.0008 μm/y for 18/8 stainless steel. Anaerobic corrosion rate under alkaline conditions decreases with time and increases with temperature.

2.1.3 C and ^{14}C releases from steels

Upon the slow corrosion of irradiated steel, different forms of ^{14}C may be expected to be released. The speciation of carbon released from steels is likely to be determined both by the chemical form of the carbon in the steel and the corrosion conditions, in particular the availability of oxygen.

Current understanding on the release of carbon from iron and steels is rather limited. Experiments on non-irradiated iron-water systems as well as corrosion experiments with carbon and stainless steel have shown clear evidence for the release of carbon as hydrocarbon species. A variety of hydrocarbons have been identified in the gas phase.

On the other hand, there are experiments on non-irradiated carbon steel and iron carbide, where carbon releases were presented as arising primarily as soluble organic species, with some of the dissolved carbon being inorganic. Carbon releases from iron carbide were identified as both inorganic and organic. However, these findings have to be corroborated.

It should be noted, that there is considerable uncertainty concerning whether ^{14}C produced by activation of ^{14}N will be present in the same chemical form in irradiated steels as the carbon present in the steels at the time of their production; radiation-induced segregation of alloying components of steel may also contribute to a redistribution of the carbon species.

There are no reported studies on the release of ^{14}C from irradiated carbon steels to date and only limited information is available on the studies of ^{14}C release from irradiated stainless steel. The findings of these studies are outlined below, but again require corroboration:

- ^{14}C is released from irradiated stainless steel into solution at rates that are consistent with metal corrosion rates.
- Experiment on ^{14}C releases from irradiated stainless steel leached in a pH 10 cement-equilibrated water showed that ^{14}C is released as a mixture of inorganic (25-34%) and organic (66-75%) species.
- In the most recent leaching experiment a small amount of ^{14}C was reported to be released; the distribution of the released ^{14}C was reported to be 25% to the gas phase

with a ratio of organic to inorganic ^{14}C of nearly one in the solution phase. Organic species in solution were reported to be predominantly in anionic forms [Y. Miyauchi et al., Nuclide Release Behaviour from Activated Stainless and Measurement of Kd-value, Atomic Energy Society of Japan Autumn Meeting, B23 (2011) cited in NDA, 2012].

Summary of information on the corrosion rate of the steels and release of ^{14}C is presented in Table 1 below.

Table 1: Summary of information on the corrosion rate of the steels and release of ^{14}C in alkaline environment

	Carbon steel		**Stainless steel**	
	Aerobic cond.	**Anaerobic cond.**	**Aerobic cond.**	**Anaerobic cond.**
Acute corrosion phase*	order of days	up to 5 years	no distinct period of acute corrosion	
Corrosion rate in acute phase*	200 µm/y	<5 µm/y		
Long-term corrosion rate, µm/y*	0.08-50	0.04-0.11	0.01-0.04	0.01-0.0008
Factors and their influence on corrosion rate*	Increases with temperature	Depends on cement types, waste stream, environmental conditions	Increases with temperature	Decreases with time and increases with temperature
^{14}C release rate	No information on irradiated carbon steel. Hydrocarbons in gas phase, soluble organic species, with some of the dissolved carbon being inorganic.*		Consistent with metal corrosion rates	
Speciation of released ^{14}C in solution			Inorganic species: 25-34%; Organic species: 66-75%. Recent experiments: organic / inorganic ≈ 1; Organic species in anionic forms	
Release in gas phase			25%	
* Data are obtained for unirradiated materials.				

2.2 *Experimental set-up*

The literature review has highlighted that:

- A lot of work has been undertaken on the corrosion of steels relevant to disposal conditions although most of this relates to unirradiated steels.
- There is little, and somewhat contradictory, published information on carbon release from unirradiated steels.
- There is almost no information on ^{14}C release from irradiated steels.

Therefore, under WP2, it is planned to undertake both experimental and modelling studies to develop further understanding of the speciation and rate of both ^{14}C and stable carbon release from the corrosion of irradiated and unirradiated steels under conditions relevant to deep geological repositories. It is possible that the experiments performed under WP2 may provide some insight on the relative corrosion rates of irradiated compared to unirradiated steels.

A comparison is planned for WP2 on activation calculations of ^{14}C in steels. This test allows the comparison of modelling capabilities and, after measurement of the real concentrations, the assessment of model validity.

The current status of the experimental work is as follows:

- Analytical development is making good progress, even presenting first speciation results;
- Experiments are planned, the approaches to the corrosion experiments among WP2 participants were agreed and represent a good selection of relevant conditions.

The details of the work planned for the participants of the WP2 are summarized in Table 2 below.

Table 2: Summary of the experimental work planned in WP2

Organization	**Steel**	**Experiment/ Method**	**Aim and outcomes**
AMEC/NRG (UK/Netherlands)	Stainless steel (irradiated/ non-irradiated)	Leaching experiment (anoxic and alkaline conditions), corrosion rate	Aim: ^{14}C release; ^{14}C speciation; ^{14}C in gaseous phase
Ciemat, Enresa (Spain)	Activated stainless steel	Leaching experiment, oxic conditions, neutral and alkaline pH, corrosion rate	Aim: characterisation of the initial samples; speciation of ^{14}C in gaseous and aqueous phase
JRC (EU)	Stainless steel (irradiated)	Corrosion experiment, leaching test (at room temperature and 80°C), anoxic, neutral and alkaline conditions	Aim: speciation of ^{14}C in gaseous and aqueous phase
KIT (Germany)	Stainless steel (irradiated)	Digestion in H_2SO_4-HF, surface analytical methods	Aim: organic/inorganic ^{14}C
RWMC (Japan)	Stainless steel (non-irradiated)	Corrosion test on non-irradiated stainless steel, hydrogen measurements; analytical methods	Aim: impact of key parameters (materials and environmental factors) on corrosion processes; speciation of stable carbon in gaseous/liquid phases
SCK.CEN (Belgium)	Carbon steel (irradiated)	Electrochemical corrosion test; leaching test (at room temperature)	Aim: total ^{14}C, ^{14}C speciation (gas phase and liquid phase)
VTT (Finland)	Stainless steel (irradiated)	Leaching experiment, synthetic ground waters, two different pH (8 and 12)	Aim: ^{14}C speciation in gaseous and aqueous phase
PSI (Switzerland)	Stainless steel (irradiated)	Corrosion experiment (anoxic conditions), analytical methods, corrosion rate	Aim: ^{14}C in activated steels, ^{14}C speciation in gaseous and aqueous phase

3 WP3: Release of ^{14}C from Zircaloy and Zr alloys

In zirconium alloy claddings, the neutron activation of ^{14}N, impurity element of these alloys, is the main source of ^{14}C. ^{17}O coming from the UO_2 (or $(U\text{-}Pu)O_2$) oxide fuel and from water coolant is also a significant precursor of ^{14}C in the zirconia oxide layers formed in reactor on the internal and external sides of cladding respectively.

The objective of WP3 is to obtain a better understanding of ^{14}C behaviour in waste Zr fuel claddings under disposal conditions with regard to ^{14}C inventory (and origins), release from waste packages and speciation of released ^{14}C. To achieve this, the following tasks for WP3 are defined:

- Current status review of Zircaloy corrosion and ^{14}C release;
- Development of analytical methods for measuring ^{14}C speciation;
- Characterization of ^{14}C released from irradiated zirconium fuel clad wastes.

The status of the tasks and available outcomes are presented below.

3.1 *State of the art review of Zircaloy corrosion and ^{14}C release*

The literature review on Zircaloy corrosion and ^{14}C release has already been completed and the report [GRAS, 2014] has been released. The report provides a review of the current status of knowledge on various aspects related to the release of ^{14}C from zirconium alloys waste (hulls), which is of importance for long-term safety analyses of final repositories for long-lived intermediate level waste.

3.1.1 Inventory and distribution of ^{14}C in Zircaloy cladding

Inventories of ^{14}C in hulls have been determined either by calculation or more rarely by direct measurement. For a fuel irradiated at ~ 45 GWd/t_U, the production of ^{14}C in cladding is 30 ± 10 kBq/g. The analysis of the collected data shows that the power-related ^{14}C production amounts to 1.9 ± 0.4 GBq/GWyr.ppm N. Japanese experience suggests that the calculation overestimates the inventory, even when the calculation is carried out with the actual value of the nitrogen content in alloy.

Distribution of ^{14}C between the metal cladding and the zirconia oxide layer depends on the thickness of the oxide. On PWR fuels irradiated at burn-up ≥ 45 GWd/t_U, the external oxide layer contains ≤ 20 % of the ^{14}C inventory. On BWR fuels, the thinner external oxide layer contains a lower inventory.

There is a lack of reliable data on the chemical state of ^{14}C in the metal and in the zirconium oxide layer. A modelling approach at the atomic scale would be needed to identify the ^{14}C insertion sites in the metal and in the oxide.

3.1.2 Release rates of ^{14}C from Zircaloy hulls

The mechanisms and the rate of ^{14}C release from hulls are expected to be controlled in large part by:

- The uniform corrosion rate of Zircaloy.
- The diffusion rate of ^{14}C from zirconia oxide layers.
- The dissolution rate of zirconia oxide layers, at the time of the contact between hulls and the infiltrated water

In addition, questions arise regarding the physical condition of the hulls. It should be taken into account that the bulk Zircaloy of hulls is hydrided in reactor, linked to the burn-up, which makes the metal brittle and probably more or less fragmented if they are press compacted during waste processing.

3.1.2.1 Corrosion rates of zirconium alloys

Zirconium alloys are highly resistant to uniform corrosion at low or moderate temperatures, and their susceptibility to localized corrosion (pitting or crevice corrosion and stress corrosion cracking) appears unlikely in anaerobic groundwater. However, as mentioned above, considerable uncertainties remain regarding the possibility of hydrogen-induced cracking of press compacted hulls under repository conditions.

Nevertheless, regardless of the degree of division of hulls, it can be considered that ^{14}C in the bulk metal of hulls is released congruently with corrosion of zirconium alloy. During the corrosion of Zircaloy, there is a possibility of a mechanism in which ^{14}C is not released immediately by corrosion but is incorporated into the oxide film and then released by diffusion or during the zirconia dissolution. It is supported by the fact that measured ^{14}C specific concentrations in zirconia oxide layers are about twice of that of Zircaloy metal after irradiation in a reactor.

Various studies show that the uniform corrosion rates of zirconium alloys are very low in anaerobic neutral or alkaline waters at low temperature. The envelope value of 20 nm/y, which was sometimes adopted in assessment models, seems excessively conservative. The most recent results lead to corrosion rates of 1 to 2 nm/y. It means that the thickness of metal corroded on each side of hull for 10 half-lives of ^{14}C would be only of ~ 60 µm. Such low corrosion rates will lead to decay of much of the inventory of ^{14}C before release can occur.

However it should be noted that the knowledge on the corrosion resistance of zirconium alloys at low temperature regards the very beginning of the corrosion regime (Figure 1). Now the study of the corrosion behaviour of Zircaloy in high temperature water has shown that, when the zirconia oxide layer reaches a critical thickness of ~ 2.5 µm (corresponding to a weight gain of 30 to 40 mg/dm^2), there is a change of the corrosion regime: the corrosion kinetics firstly follows a cubic law and after the break-away point a pseudo-linear law. It is not possible from a practical point of view, at low temperature, to explore the corrosion regime which is beyond a possible phenomenon of break-away, where the corrosion kinetics could be pseudo-linear. Corrosion tests on pre-oxidized samples (oxide thickness > 10 µm) or hulls should complete the range of tests already performed.

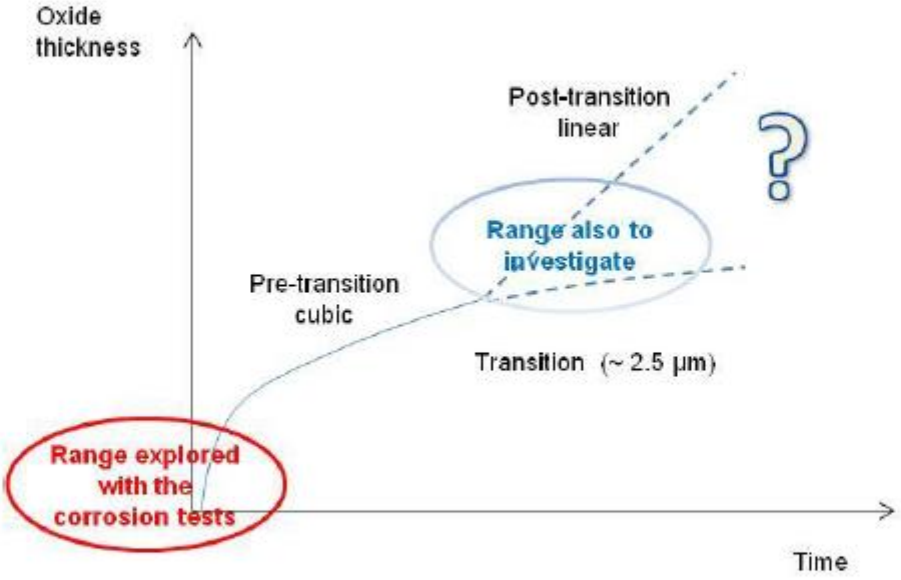

Figure 1: Typical corrosion-time curve of Zircaloy in neutral and alkaline waters

It should be noted that the hydrogen pick-up ratio for Zircaloy reaches values of about 90 % in alkaline and in pure water between 30 and 50 °C. So attention should be given to the fact that the non-corroded metal of hulls will be gradually transformed into brittle zirconium hydride, as it will corrode. This will generate on the external surface of hulls a high-density region of hydrides, acting as a brittle layer, and presumably having a corrosion behaviour different from that of zirconium metal.

3.1.2.2 Dissolution rates of zirconia oxide layer

The zirconia oxide layer formed on spent fuel rod cladding is chemically very stable in pure water (a solubility of 10^{-9} M can be considered as a conservative and realistic estimate). The solubility increases with increasing alkaline concentrations, and reaches values of the order of 10^{-6} M at pH 12.5 at ambient temperature. The zirconia solubility remains very low for carbonate concentrations lower than 10^{-2} M. At low to moderate concentrations, chloride ions do not seem to have any significant effect on the zirconia solubility. The exception is $CaCl_2$ solutions of concentration higher than 0.05 M at pH > 10, when the formation of a highly soluble complex with calcium takes place.

It is not known if the release of radionuclides can be considered as congruent with the dissolution of zirconia. This has led to the conservative assumption in performance assessment studies that the oxide layer provides no delay to the release of radionuclides. However, in light of some recent results, a realistic value, but possibly not conservative, of the dissolution rate of zirconia in neutral groundwaters or in cementitious environments, weakly carbonated (< 0.01 M) and fluoride-free, could be very low (order of magnitude: 1 nm/y).

The recent Japanese experiments of leaching in alkaline solutions at pH 12.5 at room temperature suggest that ^{14}C release would be congruent with the oxide layer dissolution and metal corrosion.

3.1.3 Chemical forms of released ^{14}C

Both dissolved organic and inorganic forms of carbon have been identified in leaching experiments with irradiated hulls or no-activated (non-irradiated) Zr-based materials (powder of Zr, ZrC), although a higher proportion was clearly released as small organic molecules. The origin of these compounds and their reaction mechanisms are not fully understood. The finding that small organic molecules such as short-chain carboxylic acids, alcohols and aldehydes are dominant species raises many questions regarding the ultimate fate of such molecules. Therefore, some significant uncertainties remain with respect to speciation of ^{14}C (inorganic vs. organic), as well as the nature of the organic ^{14}C.

The main findings of the literature survey are summarized in Table 3 below.

Table 3: Summary of information on the ^{14}C release from Zr waste

	Metal	**Oxide layer**
^{14}C activity	30 ± 10 kBq/g at burn-up 45 GWd/$t_{U;}$ 1.9 ± 0.4 GBq/GWyr.ppm N	
^{14}C activity distribution*	PWR, at burn-up ≥ 45 GWd/t_U: ≥ 80 %	PWR at burn-up ≥ 45 GWd/t_U: ≤ 20 %
^{14}C release mechanism	Corrosion; Possibility to be incorporated in the oxide layer; Potential fragmentation due to hydriding in reactor	Diffusion; Dissolution
Release rate	Congruent with corrosion	Possibly congruent with dissolution
	Low temperature, anaerobic neutral	

	Metal	**Oxide layer**
	or alkaline waters: 1-2 nm/y **	
	High temperature: follows power law up to thickness of 2.5 µm, then linear	
Solubility limit		Pure water: 10^{-9} M; pH 12.5, ambient temp.: 10^{-6} M
Impact of Cl to solubility		No significant impact at low to moderate concentrations.***
Dissolution rate		Neutral or alkaline environment: order of 1 nm/y
Chemical form of released ^{14}C	Organic and inorganic, with higher proportion as small organic molecules	

* Depends on the thickness of the oxide layer.
** Envelope value of 20 nm/y was sometimes adopted in assessment models.
*** Exception is $CaCl_2$ solutions of concentration higher than 0.05 M at pH > 10, when the formation of a highly soluble complex with calcium takes place.

3.2 *Experimental set-up*

The literature review has highlighted that:

- There is a lack of reliable data on the chemical state of ^{14}C in the metal and in the zirconium oxide layer.
- Significant uncertainties remain with respect to speciation of the released ^{14}C (inorganic vs. organic), as well as the nature of the organic ^{14}C.
- Corrosion tests on pre-oxidized samples (oxide thickness > 10 µm) or hulls would complete the range of tests already performed.

Therefore, the objectives of WP3 are to determine the forms of released ^{14}C organic/inorganic, the partitioning between solution and gas, and to characterise ^{14}C release from irradiated Zr fuel cladding wastes sampled from different BWRs and PWRs. This will be determined from corrosion of activated materials in experiments under conditions relevant to deep geological disposal (i.e. cementitious or argillaceous media). The results will lead to an assessment of release rates of ^{14}C from zirconium alloys (from metal corrosion and oxide dissolution) and a better understanding of ^{14}C release mechanisms.

Development of analytical methods for measuring ^{14}C inventory and speciation is being done. Experimental methodologies have been agreed, including: characterisation of samples; oxide thickness; and cleaning of samples but with no polishing. Experiments will be conducted with both non-irradiated and irradiated Zr alloys.

The main technique envisaged is LSC (Liquid Scintillation Counting). If this is not sufficiently accurate, AMS (Accelerated Mass Spectrometer) will be used as it has a lower detection limit. Spectroscopic methods such as Infra-red will be used to identify the main families of chemical functions (carboxylic acids, aromatic compounds, ketones, alcohols...). Chromatographic techniques will be used to detect and quantify families of molecules.

Corrosion experiments will be performed on both non-irradiated and irradiated Zr, in the reference solution.

The details of the work planned for the participants of the WP3, the progress and available outcomes are summarized in Table 4 below.

Table 4: Summary of the experimental work planned in WP3

Organi-zation	Zr alloys	Experiment/ Method	Aim and outcomes
Armines/ Subatech (France)	Hulls from PWR reactors	Analysis on liquid samples taken from CEA's leaching experiment	Aim: ^{14}C content in liquid phase, organic, inorganic fractions
CEA (France)	Hulls from PWR reactors: M5, Zircaloy 4, Zr-0,8% Sn	Leaching experiment with NaOH, pH12 at room temperature	Aim: characterisation of the ^{14}C release
INR (Romania)	Zircaloy 4 from a CANDU spent fuel bundle	Corrosion experiment on non-irradiated and irradiated samples, analytical measurements	Aim: total ^{14}C content, organic/inorganic ^{14}C fraction

Organi-zation	**Zr alloys**	**Experiment/ Method**	**Aim and outcomes**
ITU/JRC (EU)	Zircaloy 4 claddings from a high burn-up (>70 GWd/t_U) commercial LWR fuel	Metallography, leach testing in the autoclave	Aim: total ^{14}C content
KIT-INE (Germany)	Zircaloy 4 cladding from the fuel rod segment, irradiated at PWR	Dissolution experiments	Aim: separation and quantification of inorganic and organic/CO ^{14}C species in gaseous and aqueous samples
SCK-CEN (Belgium)	Zircaloy 4 from two Belgian nuclear reactors (burnup 50-60 MWd/kgHM)	Inert gas fusion, static leaching, polarised corrosion test for both, non-irradiated and irradiated samples (NaOH solution, pH ~12.5), metallographic examination	Aim: initial nitrogen content; released ^{14}C; organic/inorganic ratio
RWMC (Japan)	BWR cladding materials (irradiated and non-irradiated)	Corrosion test, hydrogen measurements; leaching tests (base case conditions – solution of NaOH at pH 12.5 degassed with N_2); analytical methods	Aim: ^{14}C content, inorganic/organic ^{14}C in liquid phase; ^{14}C content in gaseous phase; parameters influencing corrosion rate. Available results for irradiated cladding: ^{14}C inventory in: metal – (1.74-2.48)E+4 Bq/g; oxide film – 5.68E+4 Bq/g*. Calculated ^{14}C inventory in metal: 96.3% (PWR case – 83%). ^{14}C in gaseous form: 50% for t<1y. ^{14}C in liquid phase: amount of organic ^{14}C higher than that of inorganic (the same for PWR case). BWR samples showed a lower ^{14}C release fraction than that of the PWR (t up to 1y). Available results for un-irradiated Zircaloy 4:

Organi-zation	Zr alloys	Experiment/ Method	Aim and outcomes
			Corrosion rate in pure water: 8E-3 µm/y (at 303 K); increases with temperature, pH, in SGW. Hydrogen pick-up ratio: 80-95% (at 303 K); decreases with temperature. Material type (Zircaloy 4 and Zircaloy 2) has not significant difference on corrosion rate.
* Amount of oxide film is converted into the equivalent amount of Zr metal.			

4 WP4: Release of ^{14}C from spent ion exchange resins

Ion exchange resins (IER) are widely used in nuclear facilities for the purification of liquid processes or wastes streams. The main contribution to ^{14}C in PWR resins comes from the clean-up of coolant circuits. In BWR resins it comes from condensate treatment.

The aim of WP4 is to obtain a better understanding of the ^{14}C source term from spent ion exchange resins (SIERs) of different origins (BWR or PWR), under different storage strategies and likely release and chemical species under geological disposal conditions. In order to achieve this, the following tasks for WP4 are defined:

- Current status review of ^{14}C and its release from SIERs;
- Identification of the ^{14}C inventory, its speciation and distribution in SIERs;
- Investigation of ^{14}C release from SIERs and its speciation.

The current status of the tasks and available outcomes are presented below.

4.1 *Current status review of ^{14}C and its release from SIERs*

The review of the available information on ^{14}C and its release from SIERs has been completed and released [RIZZATO, 2015]. Only very limited information is available on ^{14}C in SIERs. Most of the existing ^{14}C determinations for SIERs deal with the maximum activity determination, percentage of recovery, and differentiation between organic and inorganic fractions. Several authors have studied the acidic release of $H^{14}CO_3^-$ from inactive IERs – which implied the hypothesis that inorganic ^{14}C is adsorbed on the resins – for subsequent gasification. However, this does not bring any information about the actual speciation of ^{14}C in the SIERs.

Available results on the speciation of ^{14}C originated from SIERs – partition between inorganic (carbonate) and organic fractions – seem to show that the majority of the ^{14}C activity comes from the inorganic part. In particular, for CANDU reactors, the major part is retained in anionic exchange resins in an inorganic form. A minor fraction of ^{14}C-containing species were found in cation-exchange resins and were probably in the form of metal carbonates. However, results on the partition of inorganic and organic molecules are contrasting. For SIERs from PWRs and CANDU, between 5% and 20% was in the form of organic molecules. More recently, the inorganic vs. organic partition in two actual cemented SIERs from RMBK graphite-moderated reactors has been measured. An almost equal partition (48/52) of inorganic vs. organic ^{14}C was found for the first sample and slightly more inorganic than organic (59/41) ^{14}C was found in the second sample.

At present no determination of organic molecules in leachates from SIERs has been published. It has been hypothesized that acetate and formate are the possible organic forms of ^{14}C since they are expected in the reactor coolant of PWRs and BWRs. However, no direct measurements have been reported. In addition, the conditions of the coolant water going through the resins are different from near-ambient conditions and lead to different redox potentials and, accordingly, potentially different speciation. Finally, the storage conditions for the SIERs are expected to affect the amount of ^{14}C released and its speciation depending on, for example, pH, temperature, microbial activity and radiolysis.

No published investigations on the release of gaseous ^{14}C from SIERs have been found. In general, inorganic releases in the gas phase are expected to be in form of $^{14}CO_2$. When a factor affecting the bicarbonate-loaded resin or the acid-base equilibria in the solution occurs bicarbonate will be released leading to the formation of $^{14}CO_{2(g)}$. However, ^{14}CO cannot be excluded at present and $^{14}CH_{4(g)}$ and, more generally, volatile organic ^{14}C-species could be released. In the gas phase one could expect to measure organic radiocarbon, coming directly from the degradation (of different nature) of the resin or from secondary reactions due to the concomitant presence of H_2 and other gases.

In general, a disturbance of the acid-base equilibrium of the solution in contact with the resins will result, directly or indirectly, in a release of ^{14}C present in the form of carbonate. This could also arise through the ingress of foreign anions with selectivity on the resin higher than HCO_3^-, e.g. as chloride, nitrate, or hydrogenosulphate anions. Other less known effects leading to ^{14}C release from SIERs are the effects of service/storage temperatures and strong oxidants (thermal and chemical degradation), that could affect resin equilibrium and capacity. Microbial growth, which could convert some inorganic ^{14}C into an organic form or produce anions that may displace the ^{14}C from the resins; however, highly alkaline media ($pH > 12$) are not favourable for microbial activity.

Radiolysis could represent an important variable affecting the release and possibly the speciation of the released radionuclides. IERs are in most of the cases divinylbenzene (DVB)-based resins, i.e., they are particularly sensitive to radiation damage during and even after operation, compared to other materials like inorganic IERs or cement. Effects on the speciation of radionuclides due to the degradation of mixed bed IERs have been reported with releases of trimethylamine (TMA), $H_{2(g)}$ and $CO_{2(g)}$ from anion exchange resins due to γ-irradiation. A distinction between anaerobic and aerobic conditions was made with $CO_{2(g)}$ detected only in the presence of oxygen. Studies on radiolytic and chemical degradation of strong acidic IERs underlined the formation of mainly sulphate and dissolved organic carbon in solution. Among these, only oxalate was identified, constituting 10-20% of the organic fraction. Other degradation products were CO_2 and H_2.

The main findings of the literature survey are summarized in Table 5 below.

Table 5: Summary of information on the ^{14}C release from SIERs

Parameter	Value	Comment
Partition between organic and inorganic ^{14}C originated from SIERs	Organic fraction in SIERs from reactor: PWR, CANDU – 5% to 20%, RBMK – 40-50%.	

^{14}C organic form in leachate from SIERs	Acetate and formate	Hypothesis, no direct measurements
Gaseous ^{14}C from SIERs	Inorganic in form of $^{14}CO_2$.	Hypothesis, no published investigations; ^{14}CO, $^{14}CH_{4(g)}$ and, more generally, volatile organic ^{14}C-species cannot be excluded
Factors influencing ^{14}C release	disturbance of the acid-base equilibrium	Increased CO_2 partial pressure, ingress of foreign anions
	service/storage temperatures and strong oxidants	Thermal and chemical degradation
	bacterial growth	However, high alkaline media (pH > 12) are not favourable for microorganisms
	radiolysis	Can affect the release and the speciation of the released ^{14}C

4.2 *Experimental set-up*

Based on the literature review and in the framework of their national constraints, the WP4 partners have defined on which relevant ion exchange resin samples they will construct their program. Most of the partners are studying SIERs from pressurised water reactors (including CANDU reactors) and two partners are studying resins taken from boiling water reactors. It is to be noticed that SIERs provided by EDF to CEA do not represent the final waste, as it is to be encapsulated in an epoxy matrix.

The details of the work planned for the participants of the WP4, the progress and available outcomes are summarized in Table 6 below.

Table 6: Summary of the experimental work planned in WP4

Organi-zation	SIER	Experiment/ Method	Aim and outcomes
EDF-CEA (France)	From 5 different EDF nuclear reactors (PWR)	Trials performed and reliable technique developed for total ^{14}C determination; the method for ^{14}C distribution is under optimization.	Aim: total activity of ^{14}C; distribution among mineral and organic forms
	Non-irradiated and irradiated IER	Leaching experiments (leachates are	Aim: source term of ^{14}C and its speciation from resins leaching

		prepared in simulated cementitious environment)	
ENEA (Italy)	PWR Trino NPP in granulometric particles	Measurement analysis and morphological characterizations; stepped combustion	Aim: inventory of ^{14}C, presence of volatile/non-volatile fractions.
	Fresh IER stored for 10 y and of recent production	Scanning electron microscopy (SEM) analyses; degradation experiment under investigations	Aim: morphology of IER, origin of mechanical degradation of samples
FZJ (Germany)	BWR (S)IERs	Morphological characterization; leaching experiments on BWR resins and powder IER	Aim: morphology of IER; ^{14}C on/released by BWR (S)IERs in different conditions (total, organic and inorganic) and evaluation of the influencing parameters; generation of gases during storage and degradation of SIERs
INR (Romania)	SIERs from Cernavoda NPP storage tanks or non-fuel contact purification system	Acid stripping/wet oxidation technique	Aim: total ^{14}C, organic/inorganic ^{14}C fraction
SKB (Sweden)	Condensate Clean-up (BWR)	Analytical methods	Aim: total ^{14}C, organic/inorganic ^{14}C Available results: ^{14}C activity in wet resins: total – 103-905 Bq/MWh$_{th}$, organic fraction – 1.1-29 %; ^{14}C activity in dried resins: total – 1.26-4.52 Bq/MWh$_{th}$, organic fraction – 91-93 %. Organic species: most likely simple organic acids; Inorganic species: species in the carbonate system, mainly, hydrogen carbonate.
	Reactor Water Clean-up (PWR)		
UJV (Czech Republic)	SIERs from Temelín NPP	Laboratory analysis (activity of ^{14}C samples was	Aim: total ^{14}C, organic/inorganic ^{14}C

		determined by Liquid Scintillation Counting (LSC))	Available results: ^{14}C activities: for organic form – 27 ± 4 kBq/kg; for inorganic form – 16 ± 2 kBq/kg

It can be seen from the table above that the experimental work related to ^{14}C inventory in, and release from, SIERs is progressing. The choices of samples have been done – and received whenever available – and analytical techniques are under optimization. Some results of the investigations are already available. All the experimental results obtained in WP4 will be synthesised and presented in the final report.

5 WP5: Release of ^{14}C from irradiated graphite

The major contamination sources for the graphite are: neutron activation of raw graphite material – carbon; impurities activation in the graphite matrix and within the pore space; activation of reactor coolant gases; and technological incidents during the reactor operation.

The objective of WP5 is to understand the factors determining release of ^{14}C from irradiated graphite (i-graphite) under geological disposal conditions. To achieve this, the following tasks for WP5 are defined:

- Review of CARBOWASTE and other relevant R&D activities to establish the current understanding of inventory and release of ^{14}C from i-graphites;
- Characterisation of the ^{14}C inventory in i-graphites;
- Measurement of release of ^{14}C inventory from i-graphites;
- Consideration of new wasteforms and ^{14}C decontamination techniques for i-graphites.

When completed, the tasks identified above will provide information on the ^{14}C inventory and concentration distribution in i-graphites and factors that may control these; the rate and speciation of ^{14}C release to solution and gas from i-graphites in contact with aqueous solutions; and the impact of selected waste treatment options on ^{14}C release and relating this to the nature of ^{14}C in i-graphite.

The current status of the tasks and available outcomes are presented below.

5.1 *Review of current understanding of inventory and release of ^{14}C from i-graphites*

In order to establish the current understanding of inventory and release of ^{14}C from i-graphites, review of CARBOWASTE and other relevant R&D activities has been performed and released [TOULHOUT, 2015]. It includes a review of public available results on ^{14}C compounds released from irradiated graphite in alkaline environment, which is performed by INR (Romania), a review on ^{14}C leaching data in French irradiated graphite and a review of ^{14}C release from Oldbury Reactor graphite. The main conclusions of the reviews are presented below.

5.1.1 ^{14}C compounds released from irradiated graphite in alkaline environment

The review of public available results on ^{14}C compounds released from irradiated graphite in alkaline environment (specific to a cement-based geological disposal) confirms the CARBOWASTE achievements and showed a large agreement on the following:

- Only a very small fraction of the ^{14}C is released (less than 1%), which can be correlated with the ^{14}C activated from the nitrogen adsorbed on the surface of the graphite.

- Both organic and inorganic ^{14}C species are released in alkaline solutions, their amounts depending on the irradiation history and graphite properties.

- ^{14}C amount released in solution seems to be larger than ^{14}C amount released in gas phase under alkaline conditions.

- CO_2/carbonate dominates the ^{14}C release in solution, while CO and CH_4 are considered the major compounds released in gas phase.

- Either in liquid or gas, ^{14}C leaching rate decreases in time with 1-2 orders of magnitude, trending to establish a very slow release rate; the process could be quite well described by a first-order kinetics function.

- Chemical mechanisms leading to CO_2, CO, CH_4 formation are not clearly understood.

- Canadian studies on the CANDU filling gas (N_2) pointed out that the ^{14}C atoms created in graphite can be chemically bound with hydrogen, nitrogen or oxygen. They revealed the formation of ^{14}C atoms which have been quickly converted to simple hydrocarbons or carbon-nitrogen compounds.

5.1.2 ^{14}C leaching data in French irradiated graphite

^{14}C leaching behaviour has been studied on French irradiated graphite samples from different origins. It was indicated that ^{14}C leaching rate is very slow for the stack graphite. In most of cases, a quasi-steady state leach rate appears to be achieved after the elapse of around 100 to 200 days (which is achieved before retrieval of the graphite when the reactor is decommissioned underwater).

The measured ^{14}C release rate depends on the shape of the samples (block and powder samples were analysed). Therefore, the mean ^{14}C leaching rate was calculated taking into account the geometric volume ratio on geometric surface of the sample. The calculated mean ^{14}C leaching rate lies between 10^{-11} and 10^{-8} m/day. The both values correspond to two types of UNGG reactors with different operational history.

A faster ^{14}C leach rate seems to be observed for the sleeve graphite (operational waste). However, more investigations are needed to clarify this behaviour.

For the experiments reviewed, the nature of the leaching liquid (deionised or lime or soda water) does not evidence any clear impact on the ^{14}C leaching behaviour.

Concerning the implications of these studies for other i-graphite, it seems important to remind that the results obtained on the radionuclide behaviour might depend on the history and on the background behind the used i-graphite. The results obtained on the studied French i-graphite cannot be directly and simply extended to other i-graphite.

5.1.3 ^{14}C release from Oldbury Graphite

In initial experimental studies in the UK, small releases of gaseous ^{14}C were measured from samples of irradiated graphites from the Windscale Advanced Gas-cooled Reactor (WAGR) and the British Experimental Pile 0 reactor (BEP0) on immersion in alkaline solutions. The majority of the ^{14}C remained in the graphite although there was also some release of ^{14}C in a form that was retained in the liquid phase. In the measurements on BEP0 graphite, gaseous ^{14}CO and $^{14}CO_2$ were not distinguished, but the fraction of CO_2 in the gas phases was assumed to be negligible, due to its high solubility in alkaline solution. All of these studies were performed under oxic conditions and the impact of anoxic conditions (which are expected to form in the post-closure period) on the speciation of released ^{14}C was not known.

The examination of the release of gaseous ^{14}C from irradiated graphite from Oldbury Magnox power station was performed in order to:

- Determine the speciation and rate of gaseous release of ^{14}C from irradiated Oldbury graphite when in contact with alkaline solution under anoxic conditions and compare this to the release under oxic conditions;
- Scope the effects of changes in pH, particle size and temperature on ^{14}C speciation and rate of release under anoxic conditions; and
- Provide data and understanding for a possible update to the treatment of the releases of ^{14}C from irradiated graphite in assessment models.

The main conclusions from the study are:

- Under baseline conditions (anoxic, under pH 13 solution, ambient temperature), the predominant ^{14}C release was to the solution phase, with about 0.07% of the ^{14}C inventory being released into solution in one year. About 1% of the released ^{14}C was released to the gas phase.
- In all gas-phase release experiments under high-pH conditions, broadly similar levels of total ^{14}C release were observed to the gas phase from each of the five graphite segments on comparable timescales.
- In all experiments, for both gaseous and solution-phase release, an initial phase of rapid ^{14}C release was observed, which was followed (beyond about 28 days) by a longer term phase of slower release.

- For single piece graphite sample, under baseline conditions an initial rapid release of ^{14}C to the gas phase was observed in the first week, which represents ~ 10^{-6} of the ^{14}C in the graphite.

- For single piece graphite sample, the gaseous ^{14}C was predominantly in the form of hydrocarbons and other volatile organic compounds and CO. The ratio of ^{14}C in hydrocarbons / organic compounds to CO was approximately 2:1. Less than 2% of the gas-phase release under alkaline conditions was in the form of $^{14}CO_2$.

- When the graphite was powdered, the rapidly releasable fraction of ^{14}C to the gas phase was found to be lower (by a factor of ~2) than from leaching intact segments, whereas the total solution phase release after 91 days was higher (by about 65%). This contrasting behaviour is most likely due to a loss of loosely-bound volatile ^{14}C species during the powdering process and an overall increase in release rate, primarily to solution, due to the increased surface area of the sample.

- At pH 7, levels of ^{14}CO and ^{14}C bearing volatile organic compounds were similar to the baseline values. However, the overall gaseous ^{14}C release was at least an order of magnitude higher than the baseline, due to significantly more $^{14}CO_2$ being released as gas from solution rather than being retained as dissolved carbonate.

- There is some evidence that increased temperature increases the release rate of ^{14}C, but this observation is from a limited set of data.

- Under oxic conditions the total carbon-14 gaseous release rate was similar to the baseline condition values but the ratio of organic compounds to CO was closer to 1:1. The rates of ^{14}C release from Oldbury graphite were significantly lower than those measured previously from irradiated BEP0 graphite under oxic conditions, but the ratio of hydrocarbon / organic species to CO was higher.

The differences between the fractional releases of ^{14}C from Oldbury and BEP0 graphites are likely to be due to differences between the original graphites, their irradiation histories, operating temperatures and coolant gases (CO_2 and air respectively). However, the results of this study do not allow to determine whether any one of these differences is a dominant effect although a wider comparison of irradiated graphites might.

Main outcomes from the experimental work with irradiated graphite performed in the UK are summarized in Table 7 below.

Table 7: Main outcomes from the experimental work with irradiated graphite performed in the UK

Graphite	**Oldbury graphite**			**BEP0 graphite**
Conditions	Baseline*	pH 7	Oxic	Oxic
^{14}C release to solution	Single piece sample: 0.07% from total inventory (in one year) Powdered: higher by ~65% than from single piece (after 91 days)			Rates of release significantly higher than for Oldbury graphite
^{14}C release to gas phase	1% from the released ^{14}C (in one year)	At least an order of magnitude higher than the baseline**	Similar to baseline case	
Release phases	Initial rapid (~28 days) followed by a longer term phase of slower release			
^{14}C gaseous release during rapid release phase	Single piece sample: ~ 10^{-6} from total inventory (in one week) Powdered: lower by a factor of ~2 than from single piece			
^{14}C form in the released gas	Hydrocarbons (possibly, other volatile organic compounds) and CO	Hydrocarbons (possibly, other volatile organic compounds), CO and CO_2	Hydrocarbons (possibly, other volatile organic compounds) and CO	
Ratio of ^{14}C in hydrocarbons to CO	2:1	Similar to the baseline values	Closer to 1:1	Lower than for Oldbury graphite
$^{14}CO_2$ in gas-phase release	<2%			

* Baseline conditions: anoxic, under pH 13 NaOH solution, laboratory ambient temperature.
** Due to significantly more $^{14}CO_2$ being released as gas from solution rather than being retained as dissolved carbonate.

5.2 *Experimental set-up*

The literature review and a range of national approaches to i-graphite management that affects research requirements and prioritisation of i-graphite studies within national programmes are the basis for the experimental work foreseen in CAST WP5. The details of the work planned for the participants of WP5, the progress and available outcomes are summarized in Table 8 below.

Table 8: Summary of the experimental work planned in WP5

Organi-zation	**Graphite**	**Experiment/ Method**	**Aim and outcomes**
IPNL (France)	Virgin SLA2 moderator graphite (open pores – 19-25 %, closed pores – 6-7 %)	Implantation of ^{13}C and ^{14}N, annealing	Aim: Inventory of ^{14}C, behaviour of ^{14}C during reactor operation. Available results: Thermal annealing in inert atmosphere does not induce any migration of ^{13}C up to 1600°C, at 1600°C a slight diffusion occurs. Highly probable that the implanted ^{13}C rearranges into new carbon structures as for example clusters.
	Virgin model HOPG graphite (no pores)	Implantation of ^{13}C, annealing	
IGNS (Ukraine)	Graphite from the RBMK reactor	Removing graphite material layer by layer by polishing-out and measuring of activity after each treatment	Aim: effect of etching and removing the surface layer of graphite; long–term behaviour of ^{14}C in concrete waste packages.
INR (Romania)	i-graphite from TRIGA 14MW thermal column	Leaching test in environments simulating cement-based and bentonite-based repository	Aim: leaching rate; inventory of ^{14}C; inorganic/organic ratio.
ENEA (Italy)	i-graphite from Latina NPP (powdered)	Exfoliation/ decontamination in organic solvent	Aim: inventory of ^{14}C, chemical and structural properties of the treated graphite.
FZJ (Germany)	i-graphite from research reactors AVR and RFR	Leaching samples (decontaminated and untreated)	Aim: investigate impact of treatment on leaching; to confirm a labile ^{14}C fraction, rather than slow diffusion of ^{14}C from within the graphite.

Organi-zation	Graphite	Experiment/ Method	Aim and outcomes
CIEMAT (Spain)	i-graphite from Vandellós I NPP (powdered)	Leaching test in pure water and in granite-bentonitic water at pH=7	Aim: gaseous and liquid phase originated during leaching; total ^{14}C and organic/inorganic compounds.
	Graphite Glass Coating Waste Form, IGM		
IFIN-HH (Romania)	i-graphite from thermal column of VVR-S research reactor	Accelerator mass spectrometry; developed separation technique for release of ^{14}C from crushed and intact i-graphite	Aim: inventory of ^{14}C and its distribution, release to solution and gas form

It can be seen from the table that a wide range of experiments are planned regarding the better understanding of the ^{14}C inventory in the irradiated graphite, its distribution, leaching, distribution between organic and inorganic species, release to solution and in gas form. In addition, different options of treatment of the i-graphite are analysed and chemical and structural properties of the treated graphite are investigated.

6 WP6: Relevance of results in national contexts and safety assessments

WP6 acts as an integration exercise to ensure that the results from WP2 to 5 are as relevant to the safety cases for the end-users as possible. Therefore, the objective of WP6 is to combine the results of WP 2 - 5 to deliver sound scientific basis and safety relevant information; to consider the CAST results in the context of safety cases; to identify the commonalities and differences between national programmes; and to provide conclusions and recommendations over possible future studies and orientations to waste.

Three tasks for WP6 are defined:

- Handling of ^{14}C in current safety assessments;
- Knowledge base contextualisation in light of safety assessment (SA) hypothesis;
- Integration of the CAST results to SA.

The first phase of WP6, prior the analysis of the experimental results delivered by the project, aims at taking stock of the ^{14}C knowledge from the angle of safety assessments. For this purpose the report on handling of ^{14}C in safety assessments – state of the art – was published [KENDALL H., 2015]. This report, D6.1, provides a compilation of national reports on C-14 treatment in respective waste management programs. Based on this report, the commonalities and differences between disposal concepts regarding the impact of the uncertainties linked to ^{14}C release from radioactive waste disposal will be identified and discussed in the next deliverable. The topics tackled are the following: (a) the ^{14}C inventories, (b) source terms used in safety assessments and (c) the ^{14}C transport though different host rock formations.

The CAST project is an opportunity to present an overview of the ^{14}C inventory for the most relevant waste families. These are spent fuel assemblies, vitrified waste, activated metals (compacted waste from spent fuel reprocessing, core internals, pressure vessels, assembly structural parts), graphite and ion-exchange resins. This summarizing exercise has several objectives. Firstly, it allows for a consistency check of the inventories for CAST participants and end-users. Secondly, it provides a comparison between measured and calculated inventories in function of impurities (e.g. zircaloy claddings and spent fuel matrix) as basis for the development of different approaches in SA: from covering/highly conservative to more realistic (measured based) inventories. In addition, it is a basis for agreement on the methodology to estimate ^{14}C inventory and source term (including instant release fraction, IRF) of waste originating from spent fuel reprocessing.

The task of knowledge base contextualisation in the light of SA hypotheses is ongoing. However, some preliminary findings are drawn and presented below.

6.1 *Source term*

The release is specified through source terms for SA, either as instant release fraction (IRF) or as congruent release. For UOx, a conservative IRF of 10% to 15% (if accounting for alpha-self irradiation enhanced diffusion) is usually used.

^{14}C activity in Zr claddings depends on many factors such as burn-ups, operating conditions and cladding types. Different approaches are possible in safety assessment when considering the ^{14}C inventory of Zircaloy. The usual cautious approach is to consider 80 ppm of N impurity and a conservative thickness of the oxide layer to account for the ^{17}O(n,alpha)^{14}C reaction. These conservatisms can be reduced in calculations aiming at more realism (e.g. when assessing safety margins) by assuming, for example an inventory closer to the measurements (40 ppm maximum of N for common burn-ups) and function of the cladding type or the cladding heterogeneity (what results in a more limited oxide layer thickness). As an example, ^{14}C inventory in the Zircaloy material of the spent fuel assembly is presented in Figure 2.

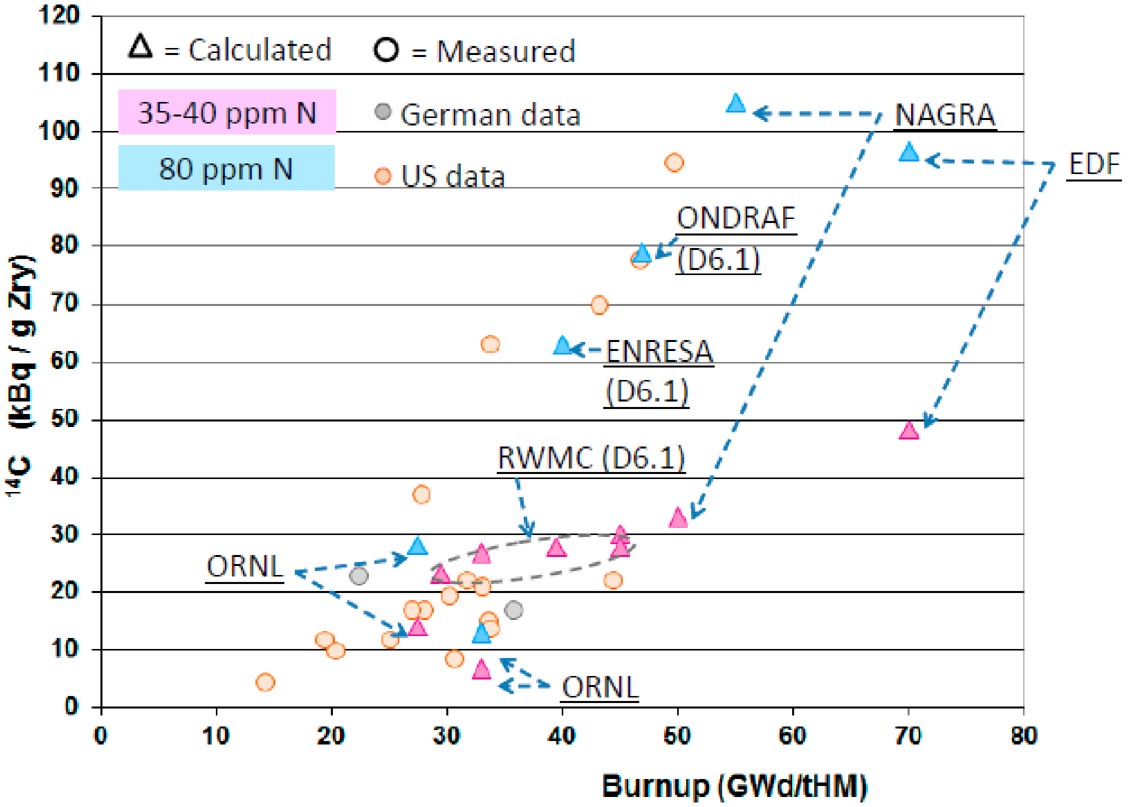

Figure 2: ^{14}C inventory in Zry material of the spent fuel assembly (LWR data) (adapted from [Gras, 2014])

Due to the large uncertainties regarding the ^{14}C speciation in clay and crystalline systems, release from activated metals is conservatively considered as aqueous organics or as methane.

Specific activity of SIERs as a waste depends on type of resins (anionic, cationic, mixed); reactor type and power, storage/handling and conditioning; and varies between 0.1 and 10 MBq/kg (see Figure 3).

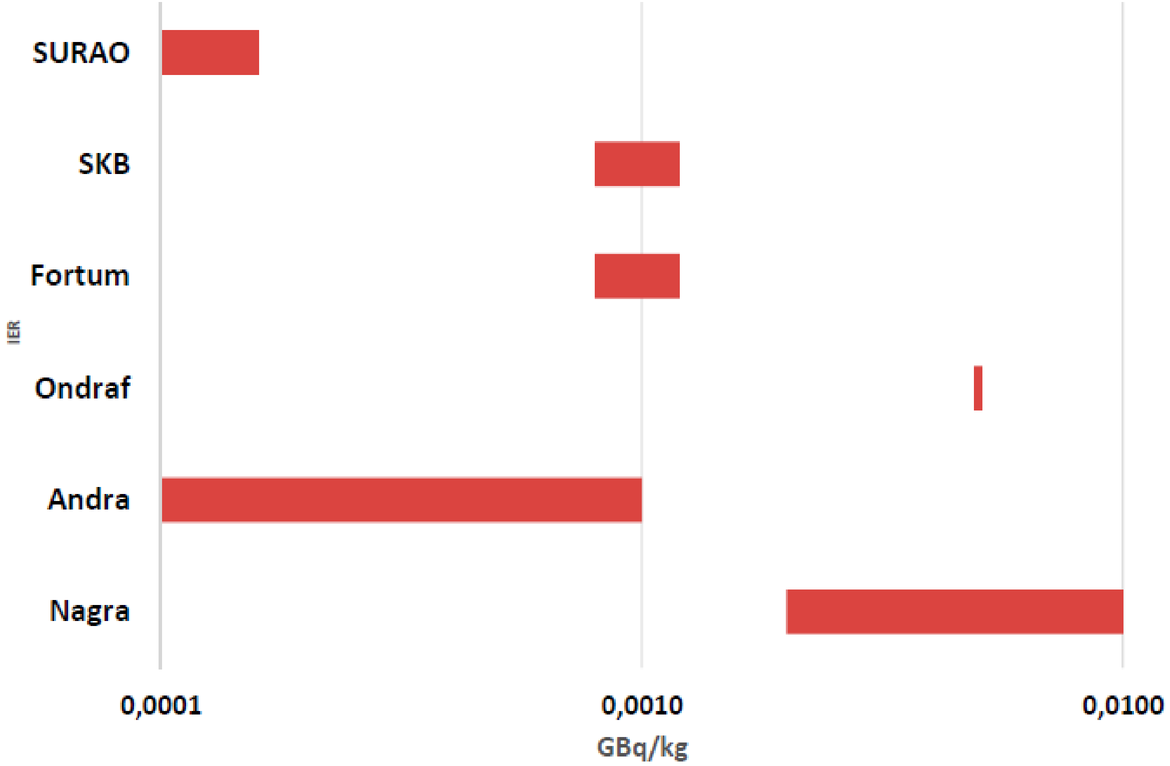

Figure 3: ^{14}C inventory in Spent Ion Exchange Resins

Release rate from SIER is dependent on the matrix and concrete package degradation, IRF of 10% to 100% is assumed. As regards speciation, the dominant distribution in SA is assumed to be in organic form (usually at least 75%).

6.2 *Safety Concepts*

The speciation, relevant transport processes and sensitivity to radiotoxicity depend on the host rock. Three formations are analysed in SA: clay, crystalline rocks and salt.

In clay, migration limited to diffusion regime combined with radioactive decay effectively reduces the radiological impact. Because of its relatively rapid decay (with respect to transport), the effective dose rate of ^{14}C is extremely sensitive to the diffusion rate. Indeed a reduction of a factor 2 of the diffusion rate of ^{14}C can have an impact on the dose of one order of magnitude (diffusion in 40 m clay). It follows that in reference scenarios in clay where carbon is assumed to be in inorganic form, the typical transport time can range from tens of thousands years to virtually infinite if isotopic exchanges between calcite and carbonates take place in the clay formation.

In safety assessment scenarios in clay, carbon might also migrate as organic gas (conservatively assumed to be methane) dissolved in pore water or as free gas (mixed with an active carrier gas) without retention. In the latter case, the advective transport occurs through two-phase flow or pathway dilation in function of the characteristics of the porous media. Past calculations have indicated a limited impact of ^{14}C due to the strong influence of the back diffusion into the host rock. Consequently, ^{14}C might not be a primary determinant of safety, however the large uncertainty regarding its transport mode through the disposal system might reduce confidence in a safety case. Resolving this conceptual uncertainty is recognized as an important point for future investigation.

In crystalline rocks, transport occurs along the fracture network in the host rock. Consequently, the transport time through the host rock is small compared to the half-life of ^{14}C and the retention capacity of the crystalline host rock has limited influence. It follows that ^{14}C is among the most important contributors to dose and its impact is governed by the performance of the containment. Retention of organics in concrete is not accounted for, or only in a marginal way, in safety assessment. However reducing the uncertainties of the speciation, even by identifying chemical families might allow to set retention to a non-zero Kd. Because of the short transport times, IRF are usually more visible in dose rate of crystalline rock than in clay formation where diffusion brings a smoothing effect. Therefore, measures to reduce the uncertainty related to IRF might also have a positive impact in term of long-term safety.

The specific of the salt formation is that unsaturated conditions will remain until the end of the assessment period. The convergence of salt will reduce the permeability of the formation to very low (as low as 1E-20 m^2). The reference scenario considered is based on very conservative hypothesis: A lifetime of a few hundred years is assumed for the waste containers, with the exception of a number of initial defects at the time of emplacement. The flow of ^{14}C released from the initially defect spent fuel containers is caused by the convergence of the salt host rock and the decreasing porosity in the salt grit. Gas is released under the form of CO_2 and IRF is the most, if not the only contributor to the radiological impact. Should dissolved ^{14}C be released through the drifts and the shaft, characteristic diffusive transport times exceed 100 000 years.

6.3 *Key messages*

At this stage of the project, the following key messages (different importance for the different disposal concepts) from WP6 can be drawn:

- CAST findings might not be translated (only) into dose curve but also in additional lines of qualitative argumentation demonstrating the conservatisms of hypothesis pertaining to ^{14}C source term.

- Elements of ^{14}C speciation such as functional groups or molecular structure might provide basis for rough estimation of retention capacities of ^{14}C.

- IRF plays a non-negligible role in terms of safety impact in disposal concepts. Do the experimental results of CAST confirm or challenge the conservatism adopted for the IRF in safety assessment?

- Consistency exercise of ^{14}C inventories for the most relevant waste families is an element strengthening reliability of the data provided in a safety case. Consistency check of the inventory will be carried on in WP6 although not the focus of the project.

- There is a need to consider the representativeness of experimental results with respect to real geological disposal conditions: How should the laboratory results be extrapolated? For which scenarios are these results representative (e.g. unsaturated conditions)? Can an interim storage/the conditioning process have impact on the source term? These questions will be addressed in the next phase of WP6 touching to the integration of the preliminary experimental results produced in CAST.

7 Conclusions

The CAST project aims to develop understanding of the potential release mechanisms of ^{14}C from radioactive waste materials: irradiated steels, irradiated Zircaloy and Zr alloys, spent ion exchange resins and irradiated graphite. A lot of work has already been done: literature surveys have been completed; analytical development is in progress; and some initial experimental work has been completed with the majority of the experiments and measurements about to start. It is expected that the outcomes from the CAST will give a better understanding of ^{14}C inventory in the waste under consideration, its release rate, speciation, partition between gas and liquid phases and effect of selected waste treatment options and provide a reasonable background to support assumptions and models related to ^{14}C while developing the disposal concept and evaluating the safety of disposal facilities.

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