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CAST

Final report on ^{14}C behaviour in Zr fuel clad wastes under disposal conditions
(D3.20)

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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 as dissolved and gaseous species.

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

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

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

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Final report on ^{14}C behaviour in Zr fuel clad wastes under disposal conditions (D3.20)

Executive Summary

The presented study focuses on Zircaloys for which C-14 is found either in the alloying part of Zircaloy cladding due to the neutron activation of ^{14}N impurities by $^{14}N(n,p)^{14}C$ reaction, or in the oxide layer (ZrO_2) formed at the metal surface by the neutron activation of ^{17}O from UO_2 or $(U\text{-}Pu)O_2$ fuel and water from the primary circuit in the reactor by $^{17}O(n,\alpha)^{14}C$ reaction.

A literature review was initially carried out to establish the State of the Art. The corrosion behaviour of zirconium alloys was reported in the review highlighting the high resistance to uniform corrosion at low or moderate temperatures. Various studies have shown that the uniform corrosion rates of zirconium alloys are very low in anaerobic neutral or alkaline waters at low temperature with an envelope value of 20 nm.y^{-1}. The zirconia solubility remains very low for carbonate concentrations lower than 10^{-2} M. The susceptibility to localised corrosion (pitting, crevice corrosion and stress corrosion cracking) is negligible in anaerobic groundwaters. 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.

In the CAST project, various irradiated and unirradiated Zircaloys (Zr, Zr-2, Zr-4 and M5^{TM}) have been studied. Particular attention was brought to characterise the materials in terms of microstructure, composition and oxide layer by means of optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). The characterisations were carried out before and after running the experiments. The total C-14 inventory has been determined both experimentally and by calculations. The results seem to be in good agreement. The vast majority of C-14 inventory (90%) is released as gaseous organic compounds during dissolution of Zircaloy into the gas phase.

Leaching experiments were conducted in alkaline media (NaOH and $Ca(OH)_2$) under anoxic conditions at room temperature for several time durations ranging from 14 days to 6.5 years.

Considerable effort was put to develop analytical techniques able to measure C-14 in low concentrations, such as those expected in deep geological repository conditions. The liquid scintillation counting (LSC) was widely used to determine the total C-14 released in alkaline environment as well as the inorganic / organic partition. The measurements of C-14 in leaching solution were performed after decontamination from other high activity level radionuclides (Cs-137, Co-60, Sb-125, Ru-106/Rh-106) by ion exchange resin. Speciation and quantification of dissolved carbon-14 were performed by using separation technique (collection of fractions by ion chromatography) and analysis by liquid scintillation counting method. In addition, accelerator mass spectroscopy (AMS) was used to quantify organic molecules in very low concentrations. Carboxylic acids such as oxalate, formate and propionate could be determined.

The gas samples were analysed by a gas chromatograph (GC). The results revealed the production of methane, ethene and CO_2.

The results highlight a fast release fraction of C-14 as various experiments showed a relatively constant concentration of C-14 released in static alkaline solution.

Further, corrosion measurements were performed on both, unirradiated and irradiated Zircaloys by using hydrogen measurements and electrochemical measurements such as linear polarisation resistance (LPR). Overall, the results showed that the corrosion rates decreased

with time. Electrochemical measurements enhanced discrepancies of the results while hydrogen measurements seem to be the most reliable technique to measure the corrosion rate.

From a safety assessment point of view, the instant release fraction (IRF) was determined on irradiated Zircaloy-2 based on inventory measurements. The results showed that the C-14 inventory in the oxide was around 7.5%, which is below the 20% commonly used in safety case assessments.

All in all, longer time experiments should be conducted in order to obtain steady state conditions and confirm the current results.

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1 Introduction

The CAST project (CArbon-14 Source Term) aimed 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 CAST project was launched in October 2013 for a total duration of 52 months. The present document focuses on the work carried out within Work Package 3 (WP3) on Zircaloys used as cladding materials in nuclear power plants. The objectives of this WP was to bring a better understanding of the release mechanisms of C-14 from irradiated Zircaloys in alkaline media, relevant to disposal conditions. This WP was divided into four tasks: Task 3.1 relevant to the State of the Art of C-14 in Zircaloy, Task 3.2 on the analytical strategy to measure low concentrations of C-14, Task 3.3 on the leaching experiments and corrosion rate measurements performed on both unirradiated and irradiated Zircaloys; and eventually Task 3.4 to summarize the work conducted in the other Tasks. In total, ten organisations were involved in WP3: ANDRA, AREVA, CEA, EDF, JRC-ITU, KIT, RATEN ICN, RWMC, SCK.CEN and SUBATECH. Table 1 presents the repartition of the work performed in WP3.

Table 1 Repartition of the activities carried out within the CAST project (WP3)

Organisations	ANDRA	CEA /AREVA	RATEN ICN	JRC	KIT	RWMC	SCK-CEN	SUBATECH
Task 3.1 – State of the art	x					x		
Task 3.2 – Development of analytical methods		x	x	x	x	x	x	x
Task 3.3 – Characterisations of ^{14}C released		x	x	x	x	x	x	x
Inventory			x		x	x	x	x
Corrosion rate			x	x		x	x	
Liquid phase		x	x	x	x	x	x	x
Gas phase			x	x	x	x	x	
Task 3.4 – Synthesis / interpretation	x	x	x	x	x	x	x	x
Total person-months per participant	7+2	31	33	15	30	23	21	25

Task 3.1 - The literature review was carried out by Andra with a strong contribution from RWMC who had more experience on the topic;

Task 3.2 - The analytical strategy was developed by most organisations. The liquid scintillation counting (LSC) technique was widely used to measure the inorganic / organic partition. Separation techniques such as ion chromatography (IC) and gas chromatography (GC) allowed the identification of given molecules. In addition, due to the low C-14 released concentrations in alkaline media, accelerator mass spectrometry (AMS) was considered by CEA and SUBATECH to measure and quantify C-14, and more specifically organic molecules.

Task 3.3 - C-14 inventory was modelled and experimentally measured by several organisations: KIT, RATEN-ICN, RWMC and SCK.CEN.

The leaching experiments were conducted for various time durations ranging from 14 days to 6.5 years in NaOH and $Ca(OH)_2$ solutions at room temperature. CEA worked on Zr-4 and M5^{TM} in NaOH solution at 14 days and 6 months, RATEN-ICN conducted experiments for 3 months, 6 months, 10 months, 12 months and 18 months in NaOH solution, RWMC started the experiments before the CAST project, and provided results up to 6.5 years in NaOH solution, $Ca(OH)_2$ solution and pure water. SCK.CEN worked in $Ca(OH)_2$ for 6 months.

RATEN ICN, RWMC and SCK.CEN measured the corrosion rate of various unirradiated and irradiated Zircaloys by the use of different techniques including electrochemical measurements and hydrogen measurements.

EDF worked on modelling C-14 mechanisms of transport through the metal and external oxide.

Task 3.4 - The synthesis of the work performed in the previous tasks involved all the WP3 participants. It has taken into consideration the influence of the materials (type, history…), leaching solution, time exposure of the samples, radiation and the techniques involved to carry out the measurements.

The following sections report the studies conducted throughout the duration of the CAST project in terms of literature review, materials, analytical strategy developed in WP3 as well as the leaching experiments and corrosion rate measurements.

2 Task 3.1

In zirconium alloy claddings, the neutron activation of ^{14}N, an 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 actual nitrogen content of zirconium alloys is in the order of 40 ppm, so two times lower than the maximum level of 80 ppm set as specified values.

Inventory

Prior to the CAST project, inventories of ^{14}C in hulls were mainly determined by calculation. For a fuel irradiated at ~ 45 $GWd.tU^{-1}$, the production of ^{14}C in cladding is 30 ± 10 kBq.g-1. According to the Japanese experience, the inventories have often been overestimated, based on higher nitrogen content than the reality.

Japanese workers have worked on the distribution of ^{14}C between the metal cladding and zirconia oxide layer. RWMC worked on Zircaloy-2 and Zircaloy-4 in WP3.

The literature survey carried out by [GRA, 2014] pointed out a lack of reliable data on the chemical state of ^{14}C in the metal and in zirconium oxide layer. A modelling approach at the atomic scale was carried out by EDF to complete the current knowledge.

Release mechanisms

The mechanisms and rate of ^{14}C release from hulls were assumed to be controlled in large part by the uniform corrosion rate of Zircaloy, the diffusion rate of ^{14}C from zirconia oxide layers and/or the dissolution rate of zirconia oxide layers, at the time of the contact between hulls and the infiltrated water under repository conditions. Nevertheless, various questions have arisen regarding the physical conditions of these hulls, i.e., their state of division and fragmentation. Indeed, 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.

Zirconium alloys are highly resistant to uniform corrosion at low or moderate temperatures, and their susceptibility to localised corrosion appears unlikely in anaerobic groundwaters. However, uncertainties have remained regarding the possibility of hydrogen-induced cracking of press compacted hulls under repository conditions. The leaching experiments have been carried out to validate a congruent release between the corrosion rate and ^{14}C release rate. In addition, the 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 was also been considered. According to [YAM, 1999 ; YAM, 2013], the 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. Prior to the CAST project, the envelope value of 20 nm.y^{-1} was adopted in some assessment models and seemed excessively conservative.

Before the CAST project, the corrosion resistance of zirconium alloys was investigated at low temperature for the very beginning of the corrosion regime. Study of the corrosion behaviour of Zircaloy in high temperature water showed 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 in the corrosion regime: the corrosion kinetics first follow a power law (a priori a cubic law) and after the break-away, point pseudo-linear kinetics apply. It is not possible, 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. Therefore, in the CAST project, corrosion tests on pre-oxidized samples (oxide thickness > 2.5 µm) were conducted by RATEN ICN to complete the range of tests already performed.

The hydrogen pick-up ratio for Zircaloy reaches values of about 90 % in alkaline media as well as in pure water between 30 and 50°C. So the non-corroded metal of hulls will be gradually transformed into brittle zirconium hydride, as it corrodes. This will generate on the external surface of hulls a high-density region of hydrides. The influence of hydrides on the corrosion behaviour was also discussed within WP3.

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 in 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, except in $CaCl_2$ solutions of concentration higher than 0.05 M at $pH > 10$ due to the formation of a highly soluble complex with calcium.

A lack of knowledge of whether the release of radionuclides can be considered as congruent with the dissolution of zirconia led to the conservative assumption in performance assessment studies that the oxide layer provides no delay to the release of radionuclides. Nevertheless the instant release fraction (IRF) considered in safety assessment was too conservative with an envelope value of 20%. In the CAST project, RWMC investigated the IRF and believe that a lower value below 10% should be applied in safety assessment instead of the 20% commonly used.

Speciation

Previous studies revealed that both organic and inorganic carbons were identified in leaching experiments with irradiated hulls or non-activated Zr-based materials (Zr and ZrC powders), although a higher proportion was clearly released as small organic molecules. In the CAST project, considerable effort was put to identify the speciation of the released molecules containing ^{14}C.

3 Materials

In WP3, various unirradiated and irradiated materials were investigated: Zircaloy, Zircaloy-2, Zircaloy-4, M5^{TM}; their history was also different (e.g. burn-up, time exposure, cleaning process). Consequently, there was a wide range of available materials and conditions for WP3. These materials were studied for the leaching and corrosion experiments in alkaline media. Analyses were conducted on liquid and / or gas samples taken from the leaching solution. C-14 inventory and speciation were determined subsequently. When it was possible, the nitrogen content was determined as accurately as possible. Metallography was carried out to identify the microstructure of the metal and zirconia layers. It was decided to clean the samples with ethanol for unirradiated materials and HNO_3 for spent fuel (which contains other radioelements), followed by rinsing with water and air drying. For irradiated materials other than spent fuel, simple rinsing with water and air drying was performed. Table 2 gives a summary of the unirradiated materials investigated within WP3. In addition, Figure 1, Figure 2 and Figure 3 present some of the characterisations carried out on unirradiated Zircaloy. Figure 1 highlights the oxide layer naturally formed on Zircaloy. Figure 2 shows the microstructure as well as the precipitates. Figure 3 presents the oxide formed on a pre-oxidised Zircaloy as well as the hydrides.

Table 2 Unirradiated materials

Participants	Zr alloys types	Chemical composition (real N)	Metallography	Pre-treatment of the surface specimen	Oxide thickness (µm)
ITU/JRC[1]	Zr-4	< 45 ppm	OM	As-received	~ 30
RATEN ICN	Zr-4	30 ppm	OM, SEM	Pre-oxidation	2.2 – 2.7
RWMC	Zr-4 (plate), Zr-2, Zr	28 ppm 32ppm 10ppm	OM, SEM	Cold-rolling, and vacuum annealing Surface condition: alumina powder polishing (0.02 mm)	0.005 – 0.02
	Zr-4 (tube)	30ppm	OM, SEM *Mean Diameter of intermetallic compound: 0.16µm (outer side)*	As-received	~ 0.005 (naturally formed under in air)
SCK.CEN	Zr-4	17 – 25 ppm	OM, SEM, TEM	As-received	naturally formed in air

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[1] JRC/ITU conducted only material preparation during the CAST project (see D3.14)

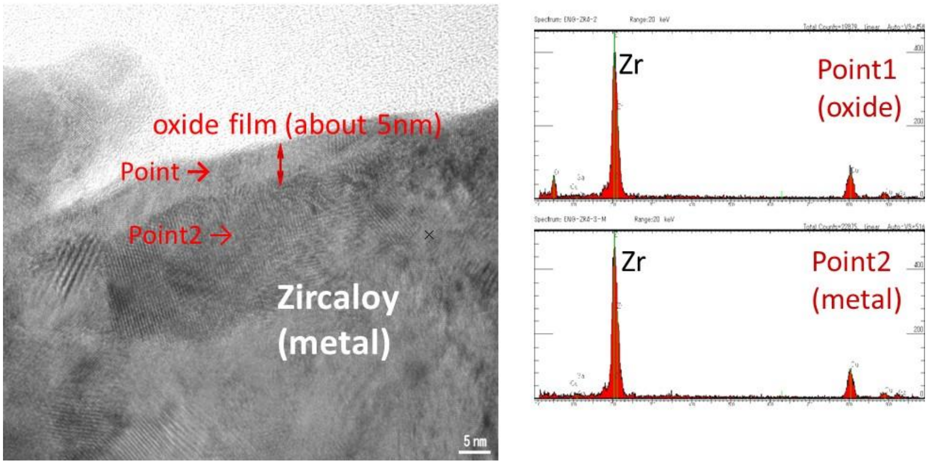


Figure 1 SEM of an unirradiated Zr-4 before testing (RWMC)

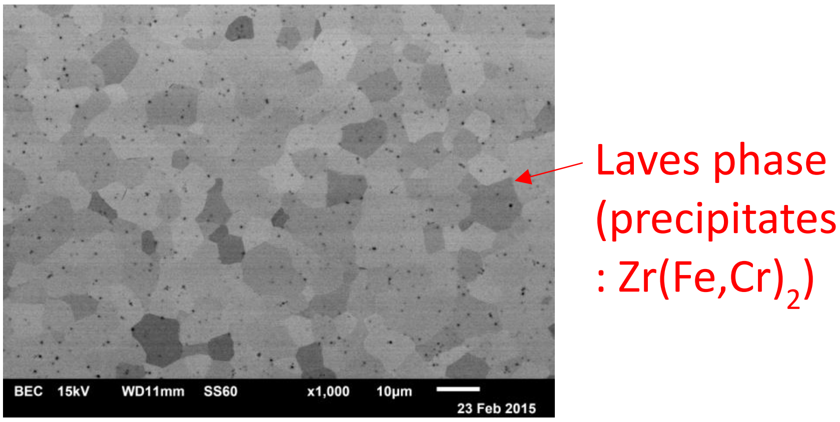


Figure 2 Scanning electron microscopy (BSE mode) of an unirradiated Zr-4 (dislocation density: $4.1\times10^{13}/m^2$ (SCK.CEN)

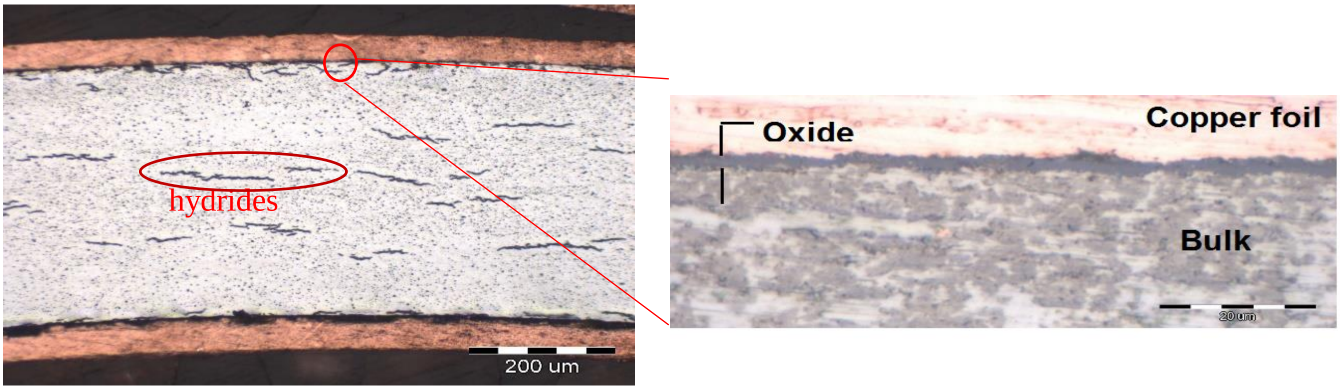


Figure 3 Pre-oxidised unirradiated Zr-4 (Oxide thickness = 2.7 μm) (RATEN ICN)

Table 3 gives a summary of the irradiated materials investigated in WP3. Figure 4, Figure 5 and Figure 6 show some examples of characterisations carried out on irradiated Zircaloys. Figure 4 shows the oxide layer along a Zr-4 cladding as well as the hydrides. Figure 5 presents the ring samples taken from a Zr-2 cladding as well as a cross section revealing the oxide thickness. Figure 6 presents micrographs of radiation induced defects on an irradiated Zr-4.

Table 3 Irradiated materials

Participants	**Zr alloys types**	**Chemical composition (N in ppm)**	**Microstructure**	**Activation history (GWd/tHM)**	**^{14}C Inventory (Bq/g)**	**Pre-treatment of specimen, i.e. surface condition etc.**
AREVA	AREVA supplied the materials to CEA					
CEA	M5^{TM} / Zr4(inner layer)Zr-0.8%Sn (outer layer) Tube shape	27 34	OM	46.570 54.500	$3.03\ 10^4$ $1.78\ 10^4$	Industrial treatment (shearing, fuel dissolution in boiling HNO_3, rinsing)
ITU/JRC	Zr-4 with Zr-2.5Nb (external cladding) Ring shape	-	-	Max 100.5	-	Acid cleaning with HNO_3 and /or 15%H_2SO_4 (depending on their original location) + water and drying in air
KIT	Zr-4 + Zr-0.8%Sn (outer layer) Ring shape	Nominal	OM	50.4	Calculated: $3.2(\pm0.3)\times10^4$ Experimental: $3.7(\pm0.4)\times10^4$	wash cycle with ultrapure water / ultrasonic bath
RATEN ICN	Zr-4 Tube shape	30	OM	7.5	To be done	spent fuel dissolution using HNO_3; rinsing with pure water
RWMC	Zr-2 STEP3	Not available	OM	39.7 3 cycles	Metal ; $1.74\ \text{x}10^4$	Polishing and rinsing with pure water, (removal of the oxide layer)
	Zr-2 STEP1	Not available	OM	41.6 5 cycles	Metal ; $2.48\ \text{x}10^4$	Polishing and rinsing with pure water, (removal of the oxide layer)
	Zr-2 STEP 1	Not available	OM	40.4 34.2 41.6	Metal + outer oxide film; $3.57\text{x}10^4$, $1.53\ \text{x}10^4$ $3.42\ \text{x}10^4$	Polishing inner surface and rinsing with pure water. (samples with oxide of outer surface)
	Zr-2 STEP 1	Not available	OM	34.2 41.6 37.4	Oxide (outer film) $4.04\ \text{x}10^4$ $5.69\ \text{x}10^4$ $5.82\ \text{x}10^4$ (Bq/g)* *Bq/g is in terms of Zr metal weight, not the weight of ZrO_2 (gr-ZrO_2 corrected to gr-Zr using each density)	Removed from Zr-2 tube
SCK.CEN	Zr-4	17-25 (measured)	OM + TEM	49	Calculated: $1.33\ \text{x}10^4$ $1.95\ \text{x}10^4$	Rinsing with water + drying in air
SUBATECH	Zr-4 (Identical to CEA)					

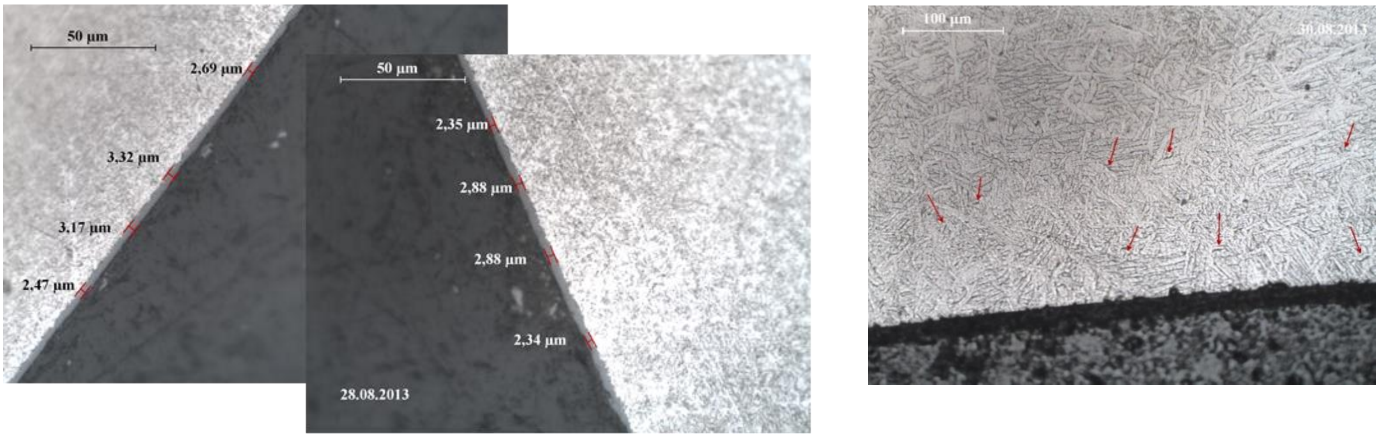


Figure 4 Transmission electron microscopy of an irradiated Zr-4: Outside oxide layer along the spent fuel cladding (left); hydrides (right) (RATEN ICN)

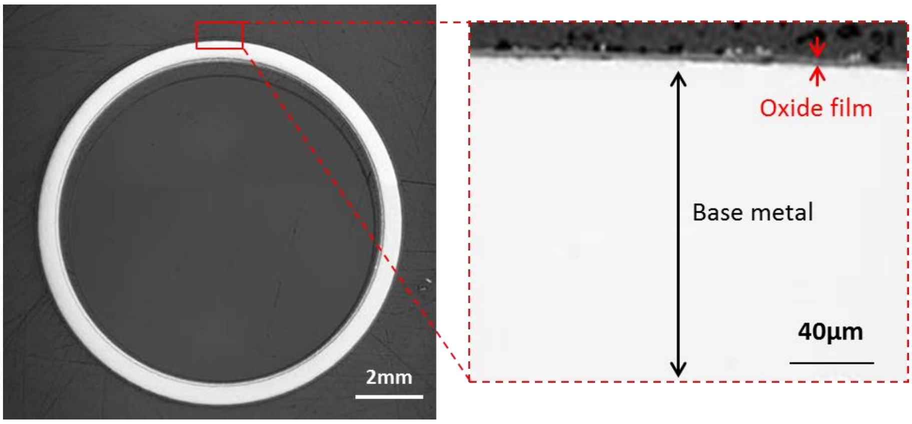


Figure 5 Scanning electron microscopy of an irradiated Zr-2 (BWR STEP III) before testing, oxide thickness = 2.7 µm (RWMC)

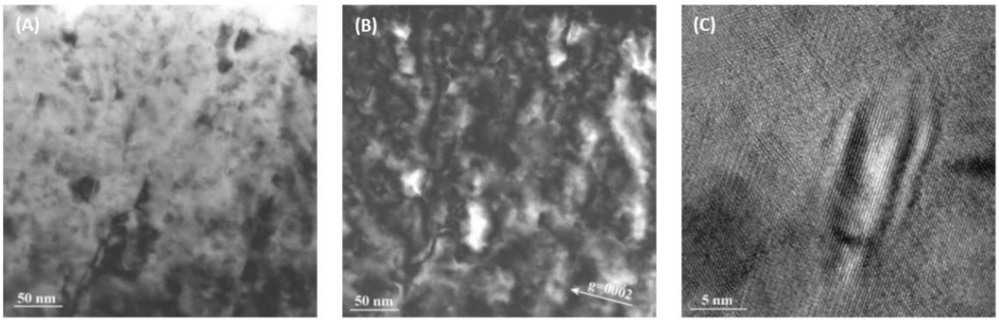


Figure 6 Micrographs of the radiation induced defects in the cladding of Zr-4: (A) Bright field, (B) dark field, (C) High resolution micrograph of a radiation induced dislocation loop (SCK.CEN)

4.1 *Task 3.2*

Task 3.2 was devoted to the analytical development based on the outstanding issues raised in Task 3.1. All the participants contributed to this task, which took significantly more time than initially planned. In 2015, a workshop was held at PSI on the analytical strategy developed in WP2 and WP3. Overall, three deliverables [HER, 2014; CAR, 2015; BAH, 2017] focused on the analytical strategy developed within WP3.

Table 4 gives an overview of the techniques used to analyse ^{14}C in terms of inventory, speciation and quantification for the liquid and gas phases.

Inventory:

KIT, RWMC and SCK.CEN measured inventory by using the LSC technique.

Inorganic / organic partition:

The LSC technique was used to determine the ^{14}C inorganic / organic partition.

Speciation:

IC, GC and ICP-MS were used to determine ^{14}C speciation.

Activity:

α-γ-spectrometry was used to determine the activity of the Zircaloy samples.

Table 4 Analytical development

Participants	Sampling (gas/liquid)	Techniques	Aims
CEA	Liquid	TC analyser (TIC + TOC) LSC and AMS IC GC-MS	Total Carbon Inorganic / organic partition Speciation (organic molecules)
ITU/JRC	Gas and liquid	LSC ICP-MS GC-MS	Inorganic / organic partition
KIT	Gas and liquid	LSC ICP-MS GC-MS α-γ-spectrometry	TIC-14/TOC-14 Inventory Activity
RATEN ICN	Liquid	LSC	Inorganic / organic partition
RWMC	Gas and liquid	LSC γ-spectrometry IC-MS	Inventory Inorganic / organic partition Activity Speciation
SCK-CEN	Gas and liquid	γ-spectrometry LSC GC IC	Activity Inventory Inorganic / organic partition Speciation
Subatech / Armines	Liquid	LSC AMS IC	Inorganic / organic partition Speciation

5 Task 3.3

5.1 *Deliverables*

This task involved fifteen deliverables [CAR, 2014; JOB, 2014; NEC, 2014; BOT, 2015; HER, 2015; BAH, 2016; JOB, 2015; NEC, 2014; DRU, 2012; NEC, 2016; HER, 2017; BUC, 2017; CAE, 2017; CAR, 2017; SAK, 2018] and focused on the experimental and modelling work carried out to determine the C-14 release in geological disposal conditions in terms of inventory, speciation and quantification.

5.2 *Leaching experiments:*

Considerable efforts were put on the experimental concepts including the purchase, design of equipment, preliminary tests, and determination of the reference leaching solution, time duration and temperature. Considering the timeframe of the CAST project, a reference time of 6 months minimum as well as an alkaline reference solution of NaOH (pH 12) were chosen to perform the experiments. In addition, some experiments were conducted for shorter times such as 14 days (CEA) and longer times: 10-18 months (RATEN ICN) and up to 6.5 years (RWMC). To diversify the environmental conditions, SCK.CEN chose to perform the leaching experiments in $Ca(OH)_2$ solution. To enhance pitting corrosion, SCK.CEN added chloride to the leaching solution. To be relevant to the long terms disposal conditions, all the leaching experiments were conducted at room temperature under nitrogen atmosphere.

Solutions	**T**	**pH**	**Durations**	**Organisations**
NaOH (deaerated)	Room T 50°C 80°C	12 – 12.5	14 days 3 months 6 months 10 months 12 months 18 months 2 years 5.5 years 6.5 years	CEA RATEN ICN CEA, RATEN ICN RATEN ICN RATEN ICN RATEN ICN RWMC RWMC RWMC
$Ca(OH)_2$ (deaerated)	Room T	12.5	6 months	SCK.CEN

5.3 *C-14 measurements:*

5.3.1 Inventory

C-14 inventory was measured experimentally as well as by modelling. KIT measured the inventory on irradiated Zr-4 from irradiated UO_2 fuel rod segment. The inventory of ^{14}C and other radionuclides present in irradiated Zircaloy-4 (burn up of 50.4 GWd/tHM) was experimentally determined independently in five specimens using acid digestion in a flask or an autoclave. The results obtained by LSC measurements revealed an average C-14 inventory of 3.7 $\pm 0.4\times10^4$ Bq/g Zr-4 with sufficient reproducibility. The vast majority of ^{14}C inventory (88 ± 10)% is released as gaseous organic compounds during dissolution of Zircaloy into the gas phase. Moreover, about (11 ± 10) % remains as dissolved organic ^{14}C-bearing compounds in the acidic digestion liquor.

The activation of the fuel rod segment was calculated using two independent approaches: (i) The neutron flux of the subassembly was simulated using the Monte Carlo N-particle code (MCNP) and finally the CINDER program calculated the activation of the material [WIL, 2008; PEL, 2011]. (ii) The SCALE/TRITON package was used to develop cladding macro-cross-section libraries, which were used in the ORIGEN-S program to calculate the radioactive inventory of the cladding [GAU, 2009; ORN, 2011]. The former gave a C-14 inventory of 3.5 $\pm 0.4\times10^4$ Bq/g Zr-4 and the latter showed an equivalent C-14 inventory of 3.6 $\pm 0.4\times10^4$ Bq/g Zr-4. Overall, the results obtained by modelling and experimentally showed similar C-14 inventory for the irradiated Zr-4 studied by KIT.

RWMC determined the C-14 inventory on irradiated Zr-2 (BWR-STEP I and STEPIII). The results revealed a specific concentration of C-14 in the order of 1.5 -3.5×10^4 Bq/g Zr for burnups ranging from 34 to 41 GWd/tU. Work was also carried out to determine the specific activity of C-14 in the metal and outer oxide specifically. The results showed a concentration twice higher in the oxide than in the metal: about 5×10^4 Bq/g Zr against 2.5×10^4 Bq/g Zr.

RATEN ICN determined experimentally the C-14 inventory on irradiated CANDU Zr (burn-up 7.5 GWd/tHM). The results revealed an average of 2.12 $\pm 0.3\times10^4$ Bq/g of Zr-4. The accumulation of the C-14 in the CANDU Zy-4 tube was evaluated by using the ORIGEN code. The calculations gave a C-14 inventory in the order of 1.78×10^4 Bq/g of Zr-4. Organic carbon was essentially determined (99%).

SCK.CEN determined the nitrogen content of irradiated Zr-4. Then, to determine the C-14 inventory, a simple single cell model was therefore developed in the SCALE-6.1 code using the 'Triton' depletion sequence. For a burn-up of 60 GWd/th$_U$, the inventory was estimated at 1.3-1.9 $\times10^4$ Bq/g Zr.

NAGRA carried out calculations for CEA, who worked on M5^{TM} and Zr-4 hulls. The burn-ups were respectively 46.57 GWd/tHM and 54.50 GWd/tHM. The calculations showed an inventory of 1.78×10^4 Bq/g of Zr-4 and 3.03×10^4 Bq/g of M5^{TM}.

Overall the experimental results are in good agreement with the calculations. In addition they confirm the data reviewed in the D3.1 report [GRA, 2014] with a C-14 specific activity in the order of 1-3 $\times10^4$ Bq/g of Zr. The results do not show a clear relationship between the burn-up and C-14 specific activity. Indeed, the irradiated Zircaloys investigated in the CAST project were subjected to a burn-up varying from 7 to 60 Gwd/tU and the determined specific activity seems to remain similar bearing in mind that the Zircaloy type is not the same (Zr-2, Zr-4, M5^{TM}…). In most cases, the inventory was determined as the total specific activity in the metal and oxide. Besides, RWMC worked more specifically on the repartition between the metal and oxide. Table 5 summarises the results discussed above.

Table 5 Summary of the inventory measurements performed in WP3

Organisations	Zircaloy Type	N content (ppm)	Burnups GWd/ThU	Inventory Modelling (Bq/g)	Inventory Experiments (Bq/g)	Gas/Liquid
KIT	Zr-4	50	50.4	3.5 $\pm0.4\times10^4$	3.7 $\pm0.4\times10^4$	90/10
RATEN ICN	Zr-4 (CANDU)	30	7.5	1.78×10^4	2.12 $\pm0.3\times10^4$	99/1
SCK.CEN	Zr-4	17-25	60	1.3-1.9 $\times10^4$		-
RWMC	Zr-2 Zr-2 metal Zr-2 outer oxide	NA	34 - 41		1.5 -3.5×10^4 2.5×10^4 5×10^4	-
CEA*	Zr-4 M5^{TM}	34 27	54.50 46.57	1.78 $\times10^4$ 3.03 $\times10^4$		-

**NAGRA's calculations*

5.3.2 Inorganic / organic partition

As mentioned in §4, the inorganic / organic partition was determined by using the LSC technique. Most analyses were carried out on liquid samples. In many cases, C-14 was released as organic compounds. Table 6 gives a summary of the results obtained by the different organisations for various time exposures. The results show that for Zircaloys containing both, the metal and oxide, the ratio of inorganic/organic molecules is about 40/60 except for the Zr-4 samples studied by CEA. The material composition seems to influence the C-14 release. Indeed, CEA carried out the leaching experiments in similar conditions and the results are significantly different. For Zr-4, C-14 is mainly released as inorganic molecules while M5^{TM} is released as both inorganic and organic molecules.

RWMC conducted leaching experiments on hulls free from oxides (see Figure 7). The results revealed that up to one year, C-14 was essentially released as gas (55% of released C-14). The liquid phase contained both inorganic (30%) and organic (70%) species. Overtime, the gas fraction decreased and the organic fraction in the liquid phase increased. Indeed, after 5.5 years, the gas fraction represented only 7% of the total C-14 released, against 75% for the organic compounds in the liquid phase and about 18% for the inorganics. Further, hulls subjected to similar burn-ups (40 GWd/tu) with different external oxide layer thicknesses (2.7 and 19.9 µm) were exposed to NaOH solution for 5.5 years after removal of their oxide. The measurements of the C-14 released as gas and dissolved species showed similar results: about 27% for the dissolved inorganic compounds, 66% for the organic compounds and the remaining as gas. These results suggest that the release mechanism from the oxide does not depend on its thickness.

Table 6: Summary on the inorganic/organic partition determined in the liquid phase (NaOH solution pH 12) and gas

Organisations	Inorganic (%)	Organic (%)	Gas	Leaching time	Zircaloy type
CEA	55 80	45 20	ND	14 days and 6 months	M5^{TM} Zr-4
RATEN ICN	40	60	ND	18 days, 6 months, 8 months, 10 months, 12 months and 18 months	CANDU-Zr-4
RWMC	20.6	63.3	16.2	6.5 years	Zr-2

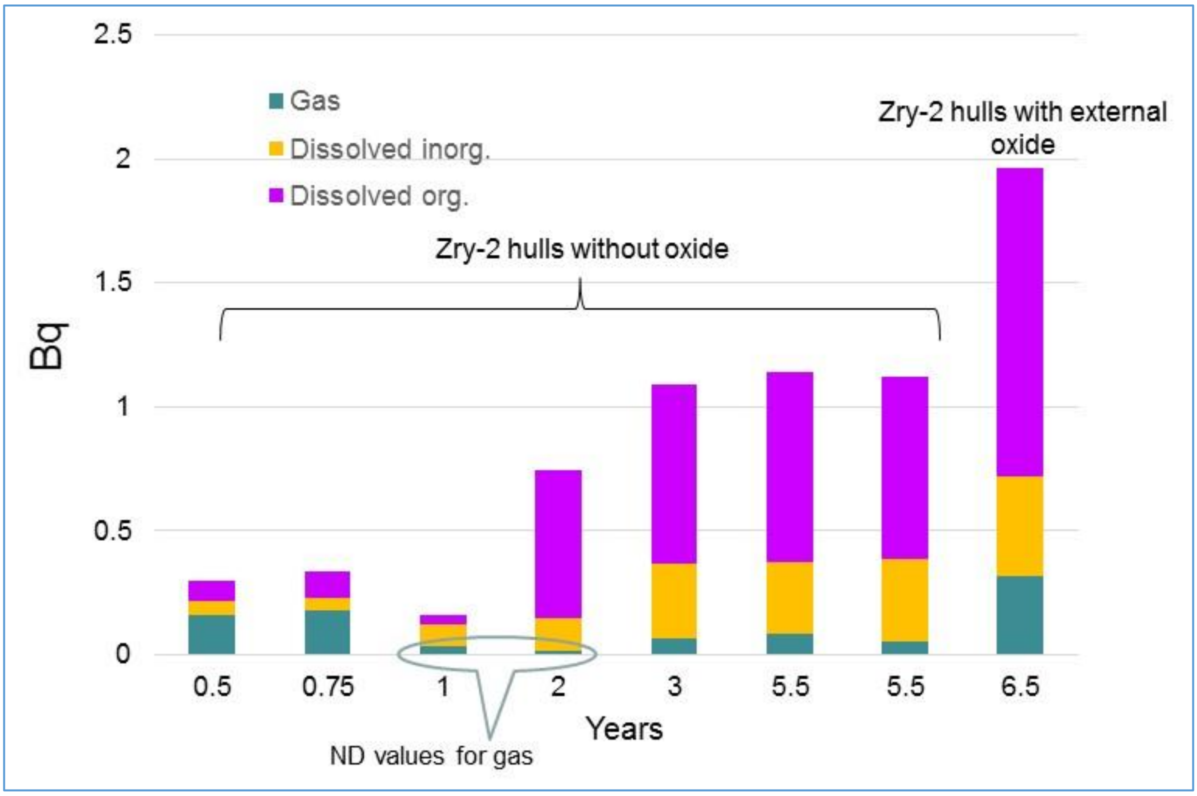


Figure 7 C-14 measured on irradiated Zircaloy-2 (metal + oxide) and Zircaloy-2 (metal only)

5.3.3 Speciation

C-14 speciation was determined for compounds released in NaOH and $Ca(OH)_2$ solutions (see

Table 7).

In NaOH solution:

CEA used anionic chromatography to detect various inorganic anions such as fluoride, chloride, nitrite, nitrate and sulfate. Carbonate was the only one with inorganic carbon. In addition, several organic anions could be detected such as glycolate, acetate, formate and oxalate. As acetate and formate were also detected in blank solutions, a potential contamination may have occurred. These compounds could be identified on both hulls' types: M5^{TM} and Zr-4 and for both time exposures, 14 days and 6 months.

SUBATECH carried out analyses by using ion chromatography on the same leachates. Formate, acetate and propionate were collected by ion exclusion column, specific to low molecular weight organic acid, while oxalate was collected by anion column.

These results confirm the difficulty of conducting speciation analyses. For identical leachates, two different laboratories did not find the same results. On the one hand the analytical procedure was not the same and on the other hand the laboratories were different, which influenced the samples' history. Nevertheless the results confirm the presence of carboxylic acids released in solution; glycolate and oxalate were identified by all the techniques and laboratories.

In $Ca(OH)_2$ solution:

SCK.CEN carried out ion chromatography analyses on liquid samples. Both blank samples and leachates were analysed. Formate and acetate were identified in both samples types, suggesting a contamination, likewise CEA. SCK.CEN used also gas chromatography to identify the speciation of C-14 released as gas. For the static corrosion tests, methane was the main gas detected. Ethene and CO_2 were also identified.

Table 7 C-14 speciation carried out in WP3

Organisations	**C-14 Speciation**				**Method**
	Solutions	Organics	Inorganics	Gas	
CEA	NaOH	Glycolate Acetate Formate Oxalate	Carbonate		Anionic Chromatography
	Blank	Acetate Formate	Carbonate		Anionic Chromatography
SCK.CEN	$Ca(OH)_2$	Acetate Formate		Methane Ethene CO_2	Ion Chromatography Gas Chromatography
SUBATECH	NaOH	Formate Acetate Propionate Oxalate			Ion Chromatography

5.3.4 Quantification

The quantification of C-14 released in solution was carried out by the LSC technique and AMS (see Table 8). For the former, the inorganic / organic partition concentrations were determined and for the latter, the concentration of given organic molecule was measured.

The various time exposures show that between 14 days and 18 months, the C-14 concentrations released in solution does not evolve, suggesting a fast released fraction.

For CEA, this concentration is estimated around 101 ± 10 Bq/g for organic compounds and 110 ± 10 Bq/g for inorganic compounds released from M5^{TM} hulls. For Zr-4 hulls, the measurements remained below the detection limit.

SUBATECH focused on the organic fraction. Their results revealed that 83% of the total released organic carbon was identified as carboxylic acids. More specifically, LSC measurements revealed a very low contribution of C-14 in the total carbon and organic carbon concentrations: 0.002% of the total organic carbon (TOC) and 0.0002% of the total carbon (TC).

Analyses were also conducted on the oxalate molecule in order to determine the specific activity of C-14 by using the LSC technique as well as the AMS. The results for the M5^{TM} hull leached for 6 months in NaOH solution, showed a specific activity of 19 Bq/g hulls and 9 Bq/g hulls respectively.

The results obtained on the M5^{TM} hull leached for 6 months in NaOH solution highlight the discrepancy between CEA and SUBATECH. Indeed, the samples were taken from the same leachate. However the analytical techniques involved were different. CEA determined a total organic concentration of 110 Bq/g against 334 Bq/g for the four organic molecules identified by SUBATECH.

For RATEN ICN, the concentration of organic compounds was estimated at 7.32 ±1.0 Bq/g while that for the inorganic compounds was around 4.0 ± 0.6 Bq/g.

RWMC measured a total C-14 concentration of 0.49 Bq/g Zr in the case of Zr-2 (metal + oxide) and 0.14 Bq/g Zr in the case of Zr-2 (free from oxide).

Table 8 C-14 quantification carried out in WP3

Organisations	Durations	Materials	Organic (Bq/g)	Inorganic (Bq/g)	Method
CEA	14 days and 6 months	M5^{TM}	101 ± 10	110 ± 10	LSC
RATEN ICN	From 18 d to 18 mths	Zr-4 (CANDU)	7 ± 1.0	4.0 ± 1.0	LSC
RWMC	5.5 yrs	Zr-2 (Metal + Oxide) Metal	0.49 0.14		LSC

SUBATECH	6 months	M5^{TM}	179 (Formate) 71 (Acetate) 65 (Propionate) 19 (Oxalate)	-	LSC
	6 months	M5^{TM}	9 (Oxalate)		AMS

5.4 *Corrosion rate measurements*

RWMC used hydrogen measurements for unirradiated Zircaloys based on Equation 1.The corrosion rate for unirradiated Zr alloys can be obtained from the total amount of generated hydrogen (gas and absorbed).

$$\mathrm{Zr} + 2\mathrm{H_2O} \rightarrow \mathrm{ZrO_2} + 2\mathrm{H_2} \qquad (1)$$

The corrosion rate for irradiated Zircaloy-2 was obtained from the released ^{14}C fraction, using boiling water reactor (BWR) cladding without oxide film immersed in a dilute NaOH solution of pH 12.5 and nitrogen atmosphere at room temperature around 293 K. Detailed experiments are described in [SAK, 2018]. ^{14}C in gas and aqueous phase was measured by LSC. Assuming that the activated ^{14}C is distributed homogeneously in the cladding, the equivalent corrosion rate, R_{eq}, can be obtained from Equation 2.

$$R_{eq} = \frac{aL}{2At} \qquad (2)$$

where, a is the leached amount of ^{14}C (Bq), A is the inventory in the cladding (Bq), L is the thickness of the cladding (nm), and t is the test time (years).

Figure 8 shows the results of the corrosion rate for unirradiated Zircaloys and the equivalent corrosion rate for irradiated Zircaloys. The solid lines represent the corrosion rate obtained from the high temperature corrosion equation [HIL, 1977].

The corrosion rate decreases with time and increases with the temperature. There is no difference of corrosion rate between Zr, Zircaloy-2 and Zircaloy-4. Other factors are not significant at temperatures above 323 K. **Erreur ! Source du renvoi introuvable.** shows the data obtained at 303 K at higher magnification. The corrosion rates in the ampoule tests show slightly larger corrosion rates than that obtained by the gas flow system. The experiments were also conducted in pure water and cementitious water. The results follow a similar trend. However, the CR was decreasing more slowly in cementitious water than in pure water. This suggests that species such as chloride ion may influence the corrosion rate. The results show higher corrosion rates for unirradiated materials. However, the tested temperatures were lower for irradiated materials, which could explain the data.

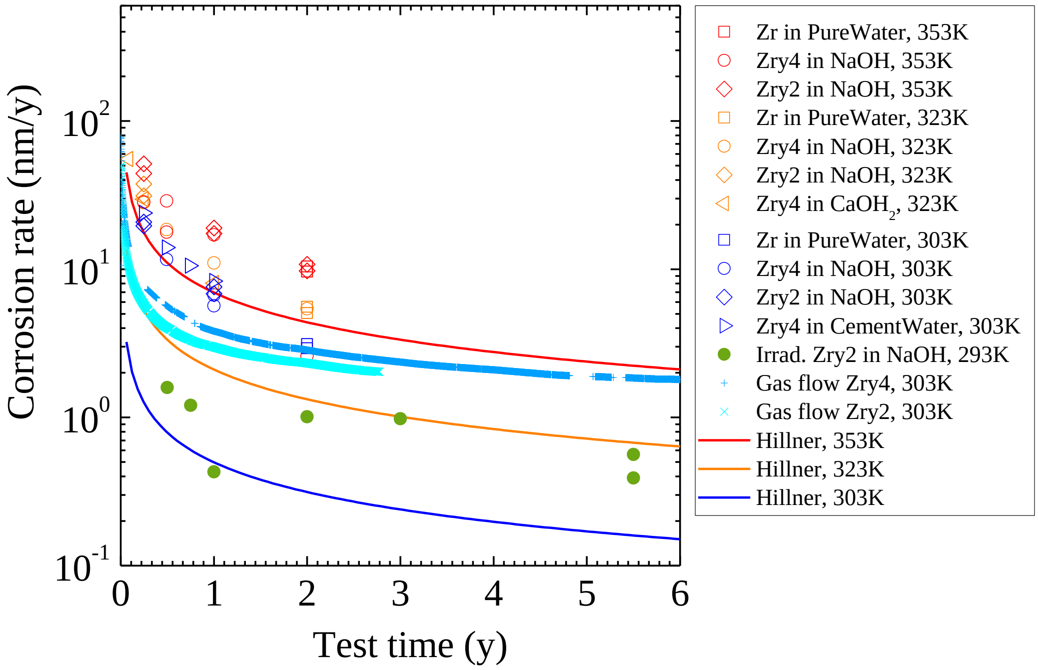


Figure 8 Corrosion rate for the unirradiated Zr alloys by the glass ampoule method under various conditions. As well as by using the gas flow system [SAK, 2013], the equivalent corrosion rate for irradiated Zircaloy-2 (BWR cladding without oxide) obtained from leached ^{14}C, and the corrosion rate obtained from the Hillner equation [HIL, 1977] at any temperatures.

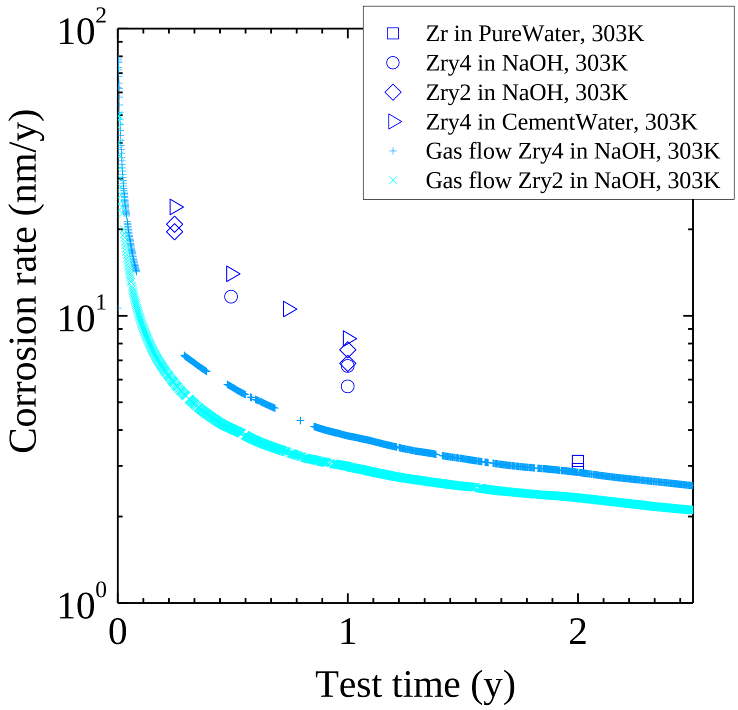


Figure 9 Corrosion rate of unirradiated Zr alloys versus time at 303 K

By contrast, RATEN ICN and SCK.CEN found lower corrosion rates for unirradiated Zircaloys by using electrochemical measurements. In addition, RATEN ICN found that the oxide layer plays a key role on the corrosion rate. Indeed, three types of samples were investigated: as-received (free from oxide), pre-oxidised (oxide thickness of about 2.7 µm) and cut at one end (to represent hulls). The results revealed a lower corrosion rate for the oxidised sample (0.31 nm/yr), and the highest corrosion rate for the as-received one (111 nm/yr). The sample cut at one end revealed an intermediate corrosion rate of 63 nm/yr. Overall, all the samples showed a decrease of the corrosion rate over time, likewise RWMC.

For irradiated samples, the corrosion rate decreased with time from about 110 nm/yr after 6 months to 50 nm/yr after 18 months. Additional characterisations were conducted on the oxide and the results showed the presence of microcracks when the samples were irradiated. These observations did not apply to unirradiated oxidised samples. This suggests that the cracks could be potential pathways for the transport of dissolved species.

SCK.CEN calculated the corrosion rate assuming it is congruent with the release rate of C-14. The total C-14 released as gas was used and the mean corrosion rate was estimated as 84 nm/yr for irradiated Zr-2 exposed to $Ca(OH)_2$ for 6 months. However, this assumption does not take into consideration the C-14 release in solution and the background in terms of C-14. According to RWMC, the releases of C-14 and dissolved Zr^{2+} do not seem to be congruent in NaOH solution at room temperature (Figure 10). Table 9 gives a summary of the corrosion rate measured experimentally for unirradiated and irradiated Zircaloy in WP3.

Organisations		**Corrosion rate (nm/yr)**					
	Materials	Durations	Unirradiated		Durations	Irradiated	
Methods			H_2 meas.	Electrochemistry		C-14 leaching fraction	Electrochemistry
RATEN ICN	Zr-4 (CANDU)	12mths			6 mths 18 mths		110 50
	Pre-oxidised (2.7 µm)			0.3			
	As-received			110			
	Cut at one end			60			
RWMC	Zr-2	2 yrs	~5		6.5 yrs	~ 1	
SCK.CEN	Zr-4				6 mths	84	

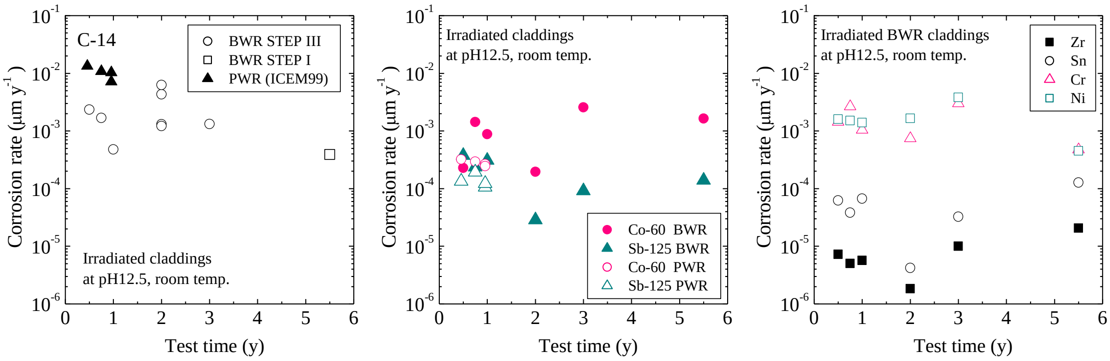


Figure 10 Equivalent corrosion rate of irradiated claddings: (left): Corrosion rate versus time with regards to the C-14 release rate; (middle): Corrosion rate versus time with regards to Co and Sn release rate; (right): Corrosion rate versus time with regards to Zr, Sn, Cr and Ni release rate [YAM, 2014].

Table 9 Summary of the corrosion rate measured experimentally on irradiated and unirradiated Zircaloys in WP3

5.5 *Material characterisation carried out after the leaching and corrosion experiments*

Surface characterisation was conducted further to the leaching and/or corrosion experiments in order to investigate the potential influence on the material (metal + oxide). CEA conducted Raman spectroscopy on Zr-4 and M5^{TM}. **Erreur ! Source du renvoi introuvable.** presents the Raman analyses for Zr-4 and M5^{TM} hulls before and after leaching in NaOH solution. Monoclinic zirconia was confirmed. In addition, several spectra show a band defects around 710 cm^{-1}. From the literature, this band forms on irradiated zirconia either in reactor or under a heavy ions beam. The intensity of these defects band may vary along with the irradiation damage, but also with the orientation of the zirconia grains. This defect band was attributed to oxygen vacancies. Time exposure did not influence the oxide layer according to the Raman observations.

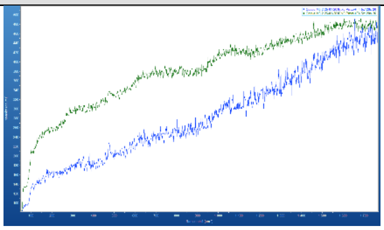
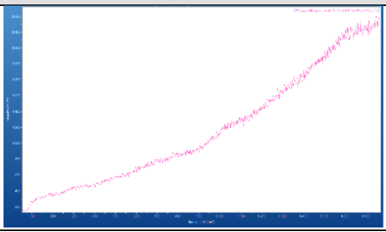
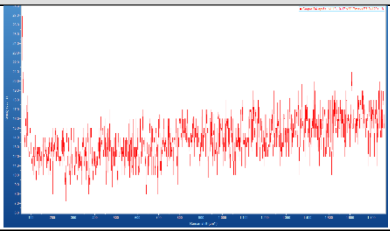
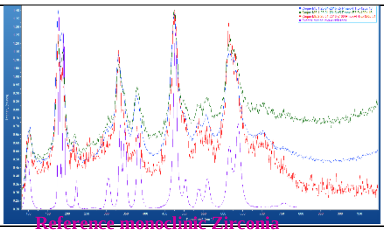
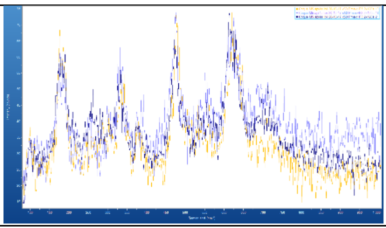
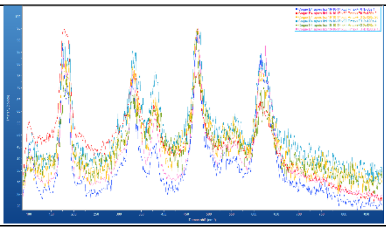
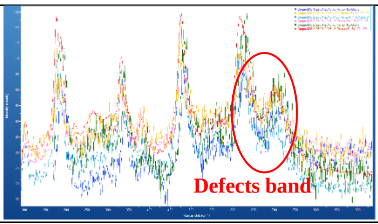
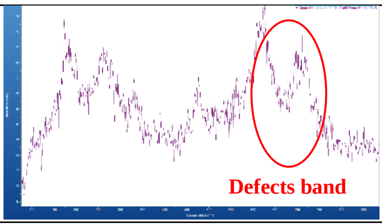
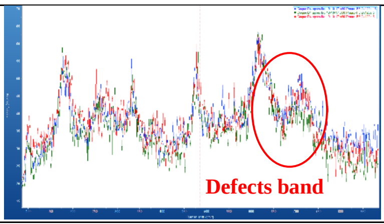
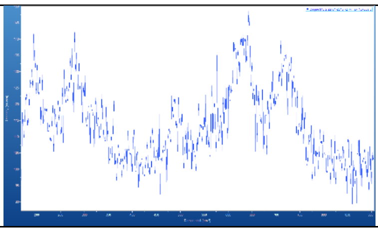
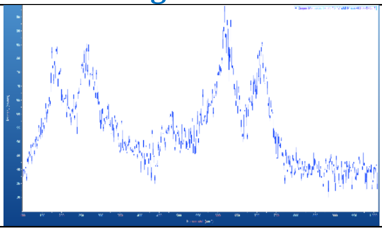
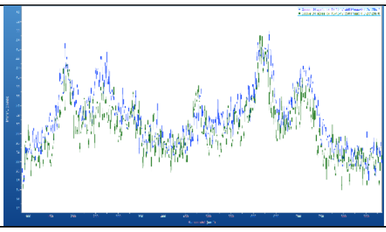
M5^{TM} hull before leaching	**M5^{TM} hull after leaching (6 months)**	**Zr-4 hull after leaching (6 months)**
		
Metallic areas		
		
Monoclinic Zirconia		
		
Damaged Zirconia		
		
Totally damaged Zirconia		

Figure 11 Raman spectra obtained on Zr-4 and M5^{TM} hulls (CEA)

5.6 *Instant release fraction (IRF)*

The oxide film formed on the Zircaloy cladding surface is regarded as a source of IRF. In the preliminary Japanese safety case, 20% of C-14 in cladding was assumed as an IRF and the remaining 80% was assumed to be in the form of a corrosion-related congruent release from the base Zircaloy metal [FPE, 2007]. From a safety assessment point of view, the C-14 inventory in the oxide, as well as its release, are of great importance. In order to investigate the IRF, RWMC measured the C-14 inventory in the oxide using irradiated cladding with a

25.3 µm thick external oxide film (Zr-2, average rod burnup of 41.6 GWd/t_U). The specific activity (Bq/g) between oxide and base Zircaloy differs by a factor of 2.8. However, the C-14 activity in the oxide and the base Zircaloy, which is obtained from the cladding geometry, can be estimated at 7.5% and 92.5%, respectively. This suggests that the 20% used in safety assessment is too conservative. However, previous studies carried out on PWR cladding (Zr-4) revealed 17% for the total C-14 measured in the oxide [YAM, 1999], knowing that the oxide was significantly thicker (80µm).

Recent studies were carried out for 6.5 years on the Zr-2 samples (free from internal oxide) in NaOH solution. The leached C-14 was measured.

The leaching ratio, which represents the leached amount (gaseous + dissolved) divided by the initial inventory, is very low (0.0038%). RWMC tried to determine the released fraction from the oxide. According to Equation 3, the C-14 released from the oxide layer can be expressed from the total release of C-14 (r_{total}) obtained by the experiment.

$$r_{out-oxide} = r_{total} - r_{in-Zry} - r_{out-Zry} \qquad (3)$$

Where:

($r_{in\text{-}Zry}$) *is the* interior bare Zircaloy;
($r_{out\text{-}Zry}$) *is* the external Zircaloy and oxide interface; and
($r_{out\text{-}oxide}$) is the external oxide layer.

Considering the corrosion kinetics laws as well as the oxide thickness (25.3 µm), the C-14 release could be calculated for both, the internal and external parts of the cladding. Thus the C-14 release from the external oxide was calculated by subtracting the C-14 release from the metal to the total measured C-14. So, with the assumption of a congruent C-14 release with the corrosion rate, the main source of C-14 release is from the oxide.

6 Discussion

In the literature review carried out by [GRA, 2014], some outstanding issues were highlighted with regards to the inventory, C-14 speciation and quantification, corrosion rate of Zircaloy at low temperature and C-14 release mechanisms. In WP3, the work carried out reduced several uncertainties, discussed as follows.

Prior to the CAST project, the determination of the amount of C-14 produced in the spent fuel claddings was carried out by calculation, using codes like ORIGEN or CESAR, and experimentally. The work conducted by SCK.CEN revealed that the N content was significantly below the specified value (~ 20 ppm vs. 80 ppm), which directly impacted the C-14 inventory in cladding material. In WP3, both modelling and experimental work were conducted to determine the inventory. Whatever the code used, the results were in good agreement, which brought confidence in the C-14 inventory determination.

The measurements of C-14 were very challenging and required the development of very highly sensitive techniques well adapted to measure very low C-14 concentrations.

The LSC technique was widely used to determine the inorganic/organic partition. However this technique presented some limits when it came to quantify a given collected fraction. SUBATECH used an AMS and confirmed the presence of organic molecules such as oxalate, identified by ion chromatography IC. The quantification obtained by the AMS and LSC techniques was very different by several orders of magnitude. The AMS was more accurate due to its low detection limit. An inconvenience of the methods is their high risk of contamination and memory effect from previous analyses. Despite the blank test to measure the background, it was difficult to get rid of contamination. Complementary investigations are needed to reduce the uncertainties. In parallel, CEA developed AMS measurements with PSI. The analyses were carried out on the total organic fraction and the results revealed relatively lower concentrations than those obtained by SUBATECH for a single molecule. Although the quantification of organic species was one of the objectives of the CAST project and some progress has been made in the project, further work is needed to provide a more thorough understanding. From the literature [GRA, 2014; WIE, 2010], the aqueous C-H-O system in complete thermodynamic redox equilibrium would be dominated by carbonate and methane. In WP3, the analyses were essentially carried out for liquid samples. The various results highlighted the presence of organic molecules (mainly carboxylic acids). Inorganics were also detected at lower concentrations according to the

LSC measurements. The results obtained from the leaching experiments, conducted up to 6.5 years, revealed an evolution of the speciation with time, therefore long term predictions relevant to repository conditions cannot be given based on the work performed in WP3. A fast release was confirmed in the early stage, followed by an extremely low rate afterwards. The release mechanisms pointed out by [GRA, 2014] involved the corrosion processes of the metal, the dissolution of the oxide, and potentially migration or diffusion through the metal and oxide. These mechanisms are discussed below.

- <u>The corrosion processes (mainly general corrosion for Zircaloy)</u>

Significant work was carried out prior to the CAST project in high temperature conditions. In pure water, the zirconium alloys exhibit excellent corrosion resistance at temperatures up to 350°C, thanks to the formation of the protective oxide film of ZrO_2. The existence of various models developed to account for the kinetics of uniform corrosion of Zircaloy-2 and -4 in high temperature water between 250 and 400°C was mentioned in the literature [GAR, 1980; COX, 1985; GRA, 1988; IAE, 1998; TAN, 2013]. The models are semi-empirical models with a cubic rate law for the pre-transition period and a linear post-transition kinetic regime. At low temperature, it was more complicated to determine experimentally the corrosion kinetics considering the excellent corrosion resistance of Zircaloy and consequently the time required to conduct experimental measurements. However, before CAST, high temperature laws were extrapolated at low temperature based on the assumption that mechanisms do not change with temperature [ROT, 1984]. The extrapolation of all the models at low temperature led to uniform corrosion rates being extremely low, having no physical meaning and no possibility to measure them with the existing techniques. In WP3, RWMC confirmed the low corrosion rate at low temperature (30, 50 and 80°C) in NaOH solution for Zr-2 and Zr-4 by using hydrogen measurements on unirradiated materials. The results confirmed that the Zircaloy type did not influence the corrosion rate. The corrosion rate decreased with time and increased with temperature. The results were consistent with previous work performed by [KAT, 2013]. By applying the high temperature model to a low temperature, the data did not match the results obtained experimentally, suggesting different corrosion processes between high and low temperatures [SAK, 2018]. The pH, temperature and time had already been pointed at as key parameters influencing the corrosion rates. The work conducted by RWMC in pure water and cementitious solution highlighted the potential influence of chloride, as higher corrosion rates were measured in the latter solution. This assumption seems to be confirmed by SCK.CEN, who found a higher corrosion rate with the addition of chloride in a solution of $Ca(OH)_2$ [CAE, 2017]. Prior to the CAST project, the experiments were conducted on as-received Zircaloy, which means that the available results concerned the pre-transition regime (cubic law) only with an oxide thickness << 2.5µm. In WP3, unirradiated Zr-4 samples were pre-oxidized to complete the knowledge on the post-transition regime as well [BUC, 2017]. Linear polarization measurements were conducted on as-received and pre-oxidised Zr-4 (oxide thickness ~ 2.7 µm) in NaOH solution, pH 12.5.

After 12 months, the corrosion rate was higher by three orders of magnitude for the as-received sample. The results support the change of kinetics as the oxide grows. Further data would help determine more accurately the applied law for the post-transition regime at low temperature.

In WP3, the corrosion rates were determined for both unirradiated and irradiated Zircaloys. Despite the discrepancy of the values, the work conducted in the CAST project confirmed the low corrosion rate of Zircaloy in an alkaline environment. According to RWMC, the irradiated samples had a lower corrosion rate. By contrast, RATEN ICN and SCK.CEN found lower corrosion rates for unirradiated materials. However, for RWMC, the tested temperature was higher for the unirradiated samples. In addition, different techniques were applied: hydrogen measurements for unirradiated materials and the released fraction of C-14 for irradiated Zircaloy. The latter assumed a congruent release of C-14 with the metal corrosion rate. Currently this assumption is not verified. Regarding RATEN ICN and SCK.CEN, electrochemistry was applied. This technique is not sufficiently sensitive to measure very low corrosion rates and the results obtained are likely within the range of experimental error of irradiated samples, optical observations confirmed radiation-induced defects as potential pathways for C-14 release, which could explain the higher corrosion rates measured for irradiated Zr-4 against pre-oxidised Zr-4.

- Oxide dissolution and migration, diffusion through the bulk and oxide,

From the literature, oxide dissolution is very unlikely at alkaline pH such as expected in repository conditions. Nevertheless, the influence of chloride should be investigated further.

Recently, EDF has launched several studies regarding the diffusivity of carbon in Zircaloy. At ambient temperature, the very low diffusivity of carbon is difficult to measure; ab-initio calculations have been used to determine the diffusivity. These are extremely powerful but require modelling of the system in a simple way. It was confirmed that carbon diffusion is very slow either in bulk zirconium or in bulk monoclinic zirconia.

In terms of C-14 release mechanisms, corrosion is the main work in progress by EDF to estimate how carbon atoms leave the surface of monoclinic zirconia as well as carbon speciation in the presence of water using ab-initio techniques. It is known that corrosion of zirconium is highly textured, probably because of the stress generated by the oxidation swelling. The grains organize themselves so that stress is minimised. Therefore, the surfaces are mainly the (-111) crystallographic planes, which is the most stable surface index and allows to define the system of interest.

From a safety assessment point of view, the IRF is very important. Prior to the CAST project, the IRF concerned the C-14 concentrated in the external oxide layer estimated at 20% of the total C-14 concentration. The work conducted within CAST (WP3 and WP6), confirmed lower C-14 inventories than expected. In addition, RWMC estimated an IRF below 10% based on a congruent release rate with corrosion. However, regarding C-14 in the oxide as an IRF would be overly conservative, because the total leached C-14 from the hull with oxide is 0.0038% after 6.5 years of immersion as mentioned before [SAK, 2018]. Both the low amount of C-14 in the oxide and the low leaching rate indicate that C-14 in the oxide does not have a major impact on the instant release fraction; this understanding should be reflected in the safety case. Other mechanisms need to be taken into consideration to explain the C-14 release from the oxide and metal.

7 Conclusions

In the CAST project, WP3 focused on Zircaloy cladding materials. A wide range of materials and history were investigated. The key objectives in WP3 were successfully achieved with some remaining issues. Task 3.1 (literature review) was conducted during the first semester of the CAST project. Task 3.2 (analytical development) was conducted up to the end of the project, especially for the use of AMS. This task was time-consuming and needed more time than initially planned. Measuring low C-14 concentrations needed highly sensitive techniques and particular precaution to handle the samples. Various techniques could be used and compared by the different laboratories involved in WP3. Task 3.3 was carried out by selecting reference testing conditions to optimise the understanding of the mechanisms. The leaching experiments were conducted in NaOH and $Ca(OH)_2$ solutions up to 80°C. The C-14 inventory was determined experimentally and by modelling; there was good consistency between the respective results. N content was determined experimentally (SCK.CEN) and the results revealed a concentration in the order of 20-30 ppm. C-14 activity was confirmed to be higher in the oxide than in the metal (RWMC). The corrosion rates of unirradiated and irradiated Zircaloys were estimated by using several methods (hydrogen measurements, electrochemistry, fraction of released C-14). For irradiated Zircaloys, the corrosion rates seem to be around 1-2 nm/yr on the longer term (experimental time was 6.5 years), but initially higher over the first year (up to 100 nm/yr). For unirradiated Zircaloys, most investigations show lower corrosion rates. The oxide layer seems to lower the corrosion kinetics (RWMC, RATEN ICN). The temperature tends to increase the corrosion kinetics (RWMC). The Zircaloy type does not seem to influence the corrosion rate (RWMC). The Zircaloy type influences C-14 inventory and speciation (CEA results on Zr-4 and M5^{TM}). The C-14 release is mainly dominated by the oxide (RWMC). The IRF is relatively low (<<20%). A fast release of C-14 was observed (CEA + RATEN ICN).

In terms of C-14 speciation: the organic fraction is more important than the inorganic fraction; speciation seems to evolve with time; carboxylic acids were identified (CEA, SUBATECH and SCK.CEN); and oxalate was quantified by AMS.

Finally, the release mechanisms of C-14 are not very well understood. Indeed, the congruent release of C-14 with the metal corrosion rate has not been confirmed. Dissolution of zirconia is extremely low at alkaline pH relevant to repository conditions. In addition, diffusion of C-14 through the metal and oxide is being investigated (EDF).

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Glossary

AMS: Accelerated Mass Spectrometer

BWR: Boiling Water Reactor

GC: Gas Chromatography

GMS: Gas Mass spectrometer

HLPC: High Performance Liquid Chromatography

IR: Infra-Red Spectroscopy

LPR: Linear Polarisation Resistance

LSC: Liquid Scintillation Counting

OM: Optical Microscopy

PWR: Pressurised Water Reactor

SEM: Scanning Electron Microscopy

Zr-2: Zircaloy-2

Zr-4: Zircaloy-4