CArbon-14 Source Term

CAST

2nd Annual WP3 progress report (D3.11)

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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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2^{nd} Annual WP3 Progress Report

Executive Summary

Work Package 3 (WP3) is related to Zircaloy in the CAST project. It aims to better understand C-14 behaviour in waste Zr fuel claddings under disposal conditions with regard to C-14 inventory (and origins), release from waste packages and speciation of released C-14. In order to achieve these objectives, WP3 has been divided into four tasks (from 3.1 to 3.4) and 20 deliverables (from D3.1 to D3.20).

Task 3.1 is completed and was devoted to the State of the Art review, Task 3.2 focuses on analytical development, Task 3.3 aims to characterise the C-14 inventory and C-14 release from leaching experiments and corrosion experiments in alkaline media representative of disposal conditions. Finally, Task 3.4 will summarise and synthesise the work performed during the previous Tasks.

During the second year of the CAST project, WP3 participants have worked on Tasks 3.2 and 3.3. In total 5 deliverables, including this one, have been issued during the year and are available on the CAST website. For Task 3.2, deliverable D3.7 presents the analytical strategy. Completion of D3.9, which also forms part of Task 3.2, has been delayed until January 2016. The analytical strategy has highlighted the possible analytical techniques to measure C-14 inventory and speciation. The main techniques foreseen to determine carbon mass balance are LSC (Liquid Scintillation Counting) and accelerator mass spectrometry (AMS).

Regarding the speciation of organic molecules, spectroscopic methods such as Infra-red will be used to identify the main families of chemical functions (carboxylic acids, aromatic compounds, ketones, alcohols etc...). Chromatographic techniques will be used to detect and quantify families of molecules with low mass molecules. Electrospray – mass spectrometry analysis (ESI-MS) will be used to detect the molecules with higher molecular weight.

For Task 3.3, WP3 participants have started to run leaching tests in an acidic medium (for C-14 inventory purposes) as well as in alkaline medium (repository pH conditions). Deliverable D3.6 describes the leaching experiment of Zircaloy in an autoclave filled with a solution of NaOH (pH 12) as well as the analysis to quantify C-14 content.

Deliverable D3.8 presents the digestion experiments performed by KIT, in acidic media (H_2SO_4/HF) to measure total C-14 inventory on irradiated Zr4. Deliverable D3.10 gives an update on the corrosion studies carried out within WP3. Most teams will work with a reference leaching solution of NaOH, pH=12 at room temperature between 6 months and one year. However, a few laboratories will conduct their leaching test for shorter durations (15 days and 3 months) and/or in different leaching solution such as $Ca(OH)_2$, pH 12.

Corrosion experiments will be performed on both, non-irradiated and irradiated Zr, in the reference solution or in $Ca(OH)_2$. Electrochemical measurements (Linear Polarisation Resistance (LPR) and hydrogen measurement techniques will be carried out to measure the low corrosion rates expected (<10nm/yr). A technique involving Co-60 gamma counting of the leaching solution will also be experimented with to measure the corrosion rate of Zircaloy. The measurements of the released fractions of C-14 and Zr have been performed by RWMC on irradiated Zr to investigate the relationship between the corrosion rate of Zr and the release of C-14.

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1 Introduction

Work Package 3 (WP3) is related to Zircaloy in the CAST project. It aims to obtain a better understanding of C-14 behaviour in waste Zr fuel claddings under disposal conditions with regard to C-14 inventory (and origins), release from waste packages and speciation of released C-14. In order to achieve these objectives, WP3 has been divided into four tasks (from 3.1 to 3.4) and 20 deliverables (from D3.1 to D3.20).

Task 3.1 has been completed and was devoted to establishing the State of the Art on the C-14 release from zirconium alloy fuel claddings. Task 3.2 is devoted to developing analytical methods for the characterisation of C-14 organic and inorganic molecules. Task 3.3 is devoted to characterising the C-14 inventory and C-14 release from irradiated zirconium alloy fuel claddings sampled from different BWRs and PWRs. This will be determined from corrosion of activated materials (Zr2, Zr4 and M5) in experiments under conditions relevant to deep geological disposal (cementitious/argillaceous media, aerobic/anaerobic). Acid dissolution of irradiated hulls has been used to measure total amounts of C-14. Finally, Task 3.4 will synthetise the work undertaken in the other tasks in a final report, to develop an interpretation of C-14 behaviour in zirconium alloy fuel claddings (C-14 inventories, release rates and speciation of released C-14) under disposal conditions.

This annual report summarises the work undertaken during the 2nd year of the CAST Project by all the organisations involved in WP3; Andra, Areva, Armines/Subatech, CEA, ITU, KIT, RATEN ICN (ex INR), RWMC and SCK/CEN. It focuses mainly on Tasks 3.2 and 3.3, for which there were a total of 5 deliverables approved and issued in 2015. These are all available on the CAST website.

2 Progress

This section describes the contributions of the participants in WP3.

2.1 Andra

Andra is in charge of coordinating WP3, which also involves the edition of five deliverables over a period of four years (2014-2017) (D3.1 (submitted in 2014), D3.5 (submitted in 2014), D3.11, D3.13 (due in 2016) and D3.20 (due in 2017). Two progress meetings were organised in 2015. One, in October 2014, and the other one in May 2015. In addition, a joint workshop dedicated to the analytical strategy, took place at PSI in May 2015.. In April 2015 (20 months), WP3 reached the MS5 milestone entitled “Experimental set-up for Zircaloy corrosion tests in hot cell completed”. Overall, the second year was dedicated to discuss and clarify the following points:

- The reference solution for the leaching and corrosion tests
- The reference time
- The reference temperature
- The reference pH
- The analytical techniques to determine the C-14 inventory and speciation in gas and liquid
- The techniques to measure the corrosion rate (CR) of Zr
- The characterisations to conduct on Zr before and after the leaching / corrosion tests

2.2 Armines/ Subatech contribution in WP3

During the 2nd year of the CAST project, Armines / Subatech was in charge of D3.9 in Task 3.2 entitled “Quantification of C-14 in liquid and gas phases”. Completion of this deliverable has been delayed until January 2016 as preliminary tests took more time than expected. It will consist of a description of the analytical method used to analyse the organic carbon compounds released from irradiated materials containing ^{14}C.

2.2.1 Analytical strategy

The objective of this work is to propose an analytical method for the detection and the quantification of carbon-14 species released from irradiated Zircaloys in repository conditions (alkaline solution pH 12 and 12.4). The strategy proposes a suitable method taking into account the leaching conditions, the history of the irradiated materials leached and the radiochemical analysis (see Figure 1).

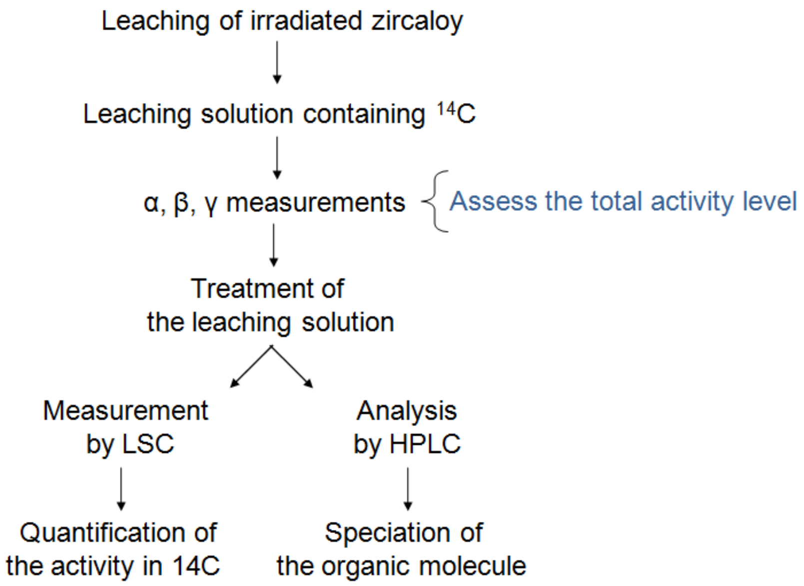


Figure 1 analytical strategy for the speciation of carbon-14 in solution

The treatment of the leaching solution for analysis purposes is a key point of the analytical strategy. Some options are available:

- Acidification for the separation of inorganic and organic compounds
- Extraction (Fe, Ni, Co, Cs,…) by ion exchange resin to reduce the activity level and interfering species for beta-detection by liquid scintillation counting. This section will be developed in more detail in the deliverable D 3.9.

For the period of the second year of the CAST project, the effect of acidification for the separation of inorganic and organic compounds has been evaluated / assessed.

2.2.2 Definition of the leaching solution composition

The definition of the leaching conditions needs to reflect those expected to be found in repository conditions. They could be defined as follows (Figure 2):

- dissolution of alkali hydroxides, pH ~13.5
- dissolution controlled by the Portlandite $Ca(OH)_2$ phase, pH ~12.5
- dissolution of hydrated calcium silicate phases C-S-H, pH from 12.5 to 9
- dissolution of silica

To represent the long term repository of the wastes, the leaching conditions in Portlandite water at pH ~12.5 were selected and analytical tests were performed.

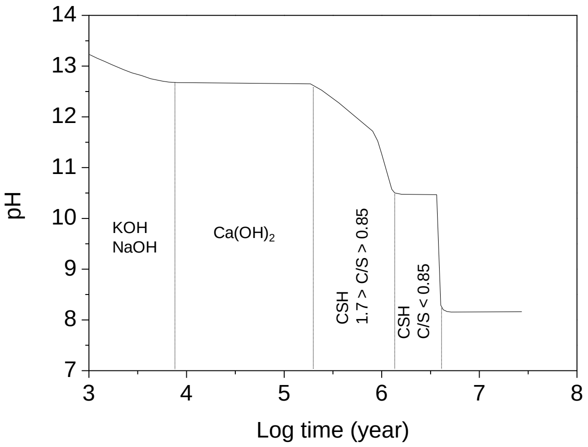


Figure 2 Evolution of the pH as a function of time in the reference case repository (Atkinson, Goult et al. 1985)

Stability tests of the 4 sets of organic molecules (acetate, formate, propionate and oxalate) were prepared in a solution of $Ca(OH)_2$ (pH 12.5) and compared to a solution of NaOH (pH 12) in order to assess the effects of the pH and matrix solution. All experiments were prepared in a glove box under controlled atmosphere (Ar gas). The results showed that:

- The measured concentration of oxalate is not affected by the concentration and the matrix composition. Indeed, it does not precipitate or degrade.

- The presence of acetate and formate depends on their concentrations but is not influenced by the matrix composition.
    - ○Absence of detection for concentration in acetate below 300 ppb.
    - ○Absence of detection for concentration in formate below 100 ppb.
- The availability to detect propionate depends on its concentration and the matrix composition.
- The absence of detection of a given species for concentration below 300 ppb in $Ca(OH)_2$ and below 100 ppb in NaOH.

Complementary analyses were performed on the stability of these molecules over time. The same set of organic molecules were analysed after 1 min, 6 hours and 24 hours in $Ca(OH)_2$ solution. The results indicate that only for the case of oxalate, the concentration in solution decreases by a factor of 2 indicating a precipitation with calcium in solution. This result highlights the necessity to work with a solution of NaOH instead of $Ca(OH)_2$ in order to determine the C-14 speciation with accuracy and avoid the possibility pf precipitation.

2.2.3 Speciation of organic compounds

The speciation of the organic compounds in NaOH pH 12 solution was studied by ionic chromatography (IC). The procedure was optimised in the laboratory to separate and quantify small carboxylic acid in alkaline solution:

- separation with a DIONEX Thermo electron AS11-HC,
- 4 mm-column specifically designed for the separation of inorganic anions and small carboxylic acids anions.
- gradient (1 – 30 mM in 29 min) of KOH eluent to increase the separation of molecules, in particular for formate and propionate which co-elute.

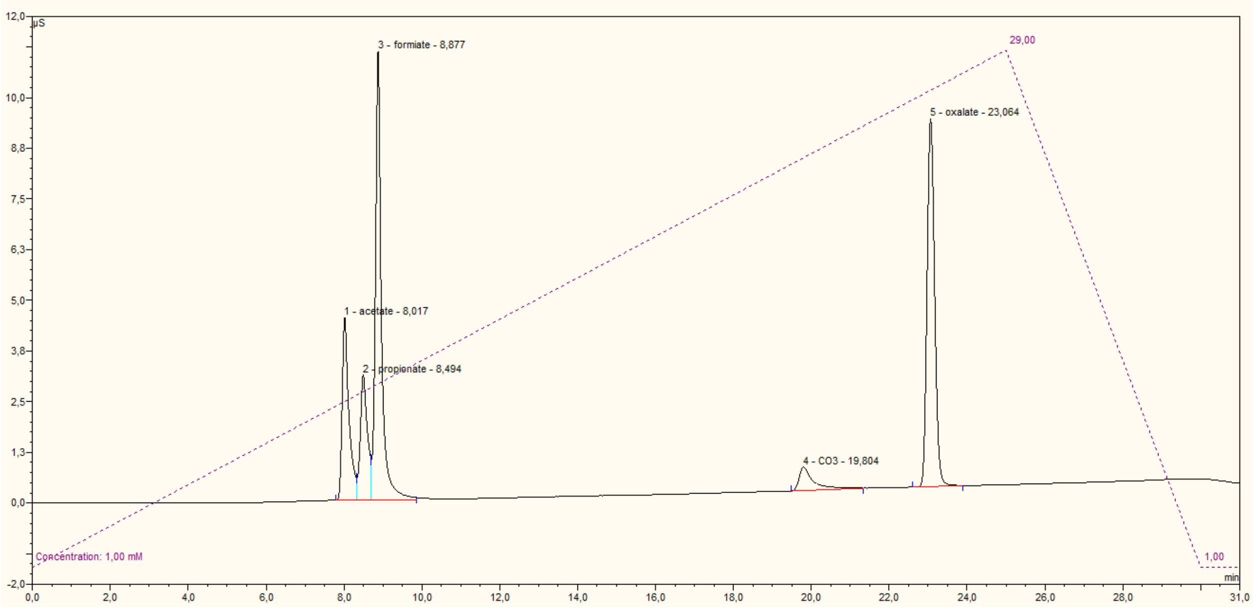


Figure 3 chromatogram for the separation of small carboxylic acid (DIONEX Thermo electron AS11-HC)

2.2.4 Treatment of solution by acidification

Acidification by HCl 0.01M was carried out to treat the solution before analysing by ionic chromatography. Organic molecules at 5 ppm (acetate, formiate, propionate, pentaoate and oxalate) were prepared in NaOH (pH 12) and $Ca(OH)_2$ solutions. After acidification, the final pH was 4. The measurements were performed with TOC-meter (TOC-VCSH, Shimadzu). The device uses a combustion catalytic oxidation method at 680°C to decompose organic compounds in ultra-pure water and even in highly charged water. The results indicate that the acidification of an alkaline solution has not modified the speciation of organic compounds. However, the method of acidification should be adapted to the speciation methods. Here, the acidification was tested with HCl and the presence of Cl^- anion may interfere with organic compounds during the analyses by ionic chromatography. Indeed, the retention time of Cl^- is close to those of small carboxylic acids such as acetate, formate, propionate and butyrate. Acidification by nitric acid or sulfuric acid will present the same drawback. Phosphoric acid may be a suitable candidate since the retention time of phosphate is longer than the retention time of oxalate. The same phosphoric acid is used in the TOC-meter method to acidify the solution and remove carbonate in solution prior to the analysis of the solution for the residual organic carbon. Anionic species (F^-, Cl^-, CO_3^{2-}, SO_4^{2-}, Br^-, NO_3^-, PO_4^{3-}) were tested in similar conditions as the organic compounds with ionic chromatography. The results clearly show that chloride, sulfuric and nitric acid may not be suitable candidates for acidification (**Figure 5**) as they elute in the same region.

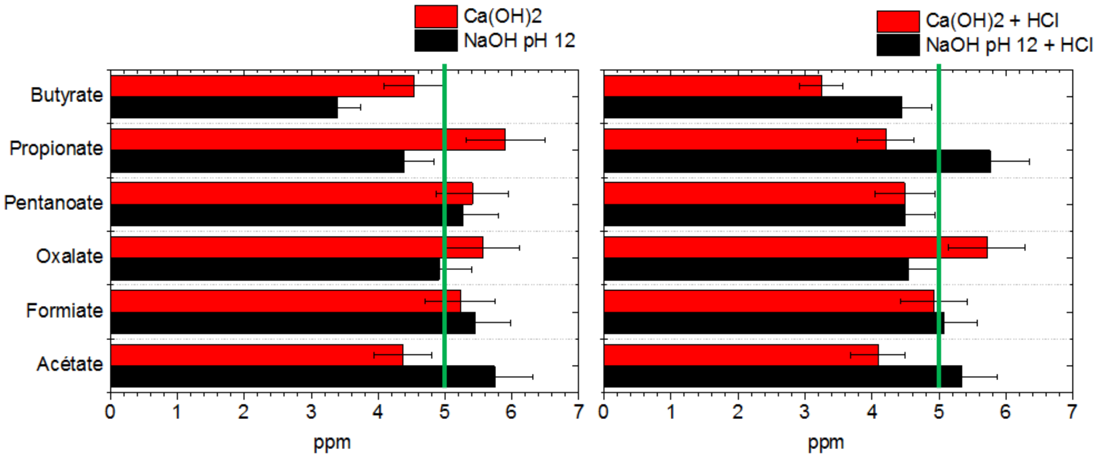


Figure 4 concentrations (ppm) of acetate, formiate, propionate, pentanoate and oxalate prepared in NaOH or $Ca(OH)_2$ solutions, in the presence and absence of HCl 0.01M. Initial theoretical concentration: 5 ppm.

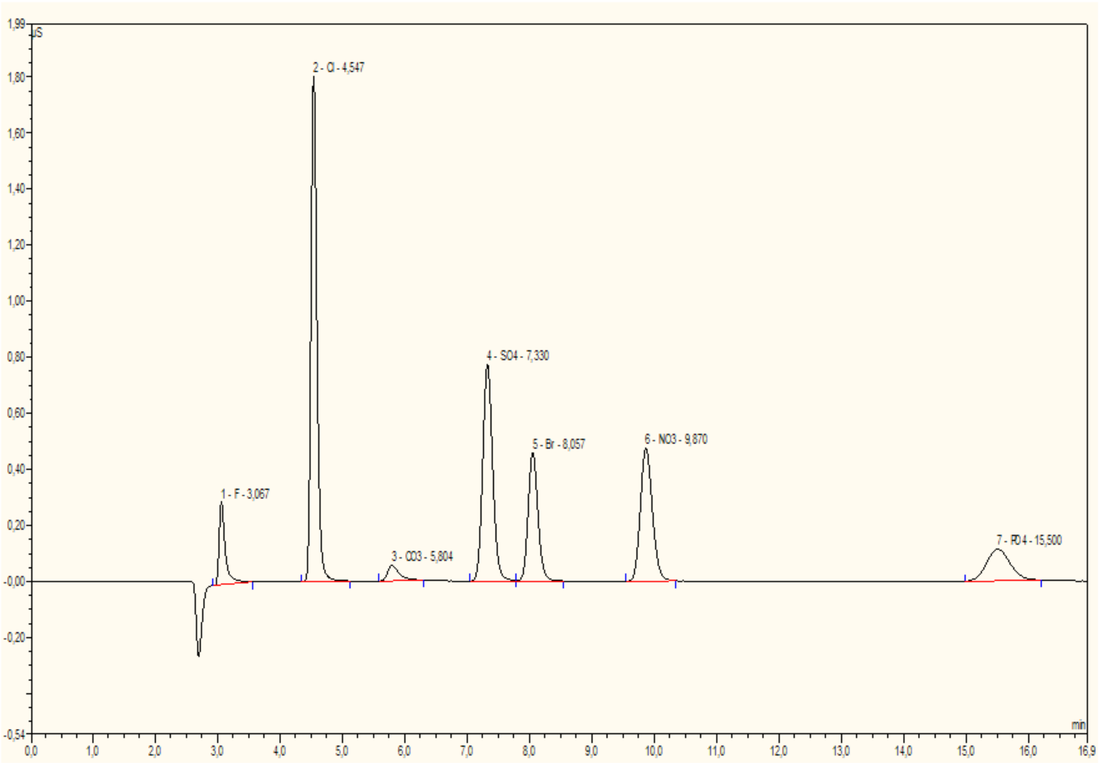


Figure 5: Separation of 1 ppm F$^-$, Cl$^-$, CO_3^{2-}, SO_4^{2-}, Br$^-$, NO_3^-, PO_4^{3-} by ionic chromatography (DIONEX Thermo electron AS11-HC)

2.2.5 Acknowledgements

The authors acknowledge V. Baty for ionic chromatography analyses, and B. Zitouni for the experimental tests.

2.3 *CEA contribution in WP3*

During the 2^{nd} year of the CAST project, CEA was in charge of the D3.7 report in Task 3.2 entitled “Definition of the analytical strategy for C-14 measurements”. It consists of describing the leaching experiment as well as the analytical method foreseen to analyse released C-14 from irradiated Zircaloy. The analyses will focus on the speciation and determination of small organic molecules, under deaerated conditions in a solution of

NaOH, at pH 12 and room temperature. Concerning WP3, CEA is in charge of three deliverables; D3.2 (issued in 2014), D3.7 (issued in May 2015) and D3.18 (due in January 2017).

2.3.1 Leaching experiment

2.3.1.1 Facilities

Initially, the leaching tests were planned to be realised in the LECI hot laboratory (Saclay research center, France). As the leaching experiments were a new technique at the LECI hot laboratory, a nuclear safety report was prepared. In October 2014, due to nuclear safety reasons, it was decided to carry out the leaching experiment in the LMPA (Laboratory of radioactive materials and vitrification processes) hot laboratory (ATALANTE facility) located in Marcoule. This laboratory conducts studies on the leaching behaviour of radioactive materials such as glass and spent fuels. The leaching tests are carried out in the hot cells and the chemical and radiochemical analyses of the leachate solutions are realised in a glove box laboratory connected by a pneumatic transfer system to the hot cell. The leaching reactor was transferred to the ATALANTE facility at the end of 2014 and the sealing tests are in progress.

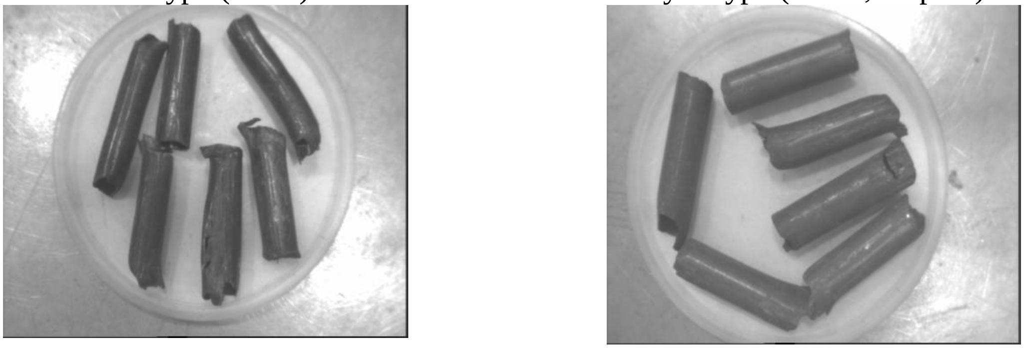
2.3.1.2 Materials

Zircaloy-based alloy hulls, M5-type (UOX) and Zy-4-type (Duplex, MOX), supplied by AREVA, will be studied. These samples come from the reprocessing of irradiated spent fuel in PWR reactors. They were subjected to an industrial treatment in AREVA – La Hague (fuel dissolution in boiling nitric acid for reprocessing as explained in D3.2).The irradiation conditions of these spent fuels are presented in Table 1.

Table 1 Hulls irradiation characteristics.

Hulls reference	**M5**	**MOX D4**
Cladding material	M5	Inner layer = Zircaloy 4 Outer layer= Zr-0,8% Sn
Fuel type	UOx (3,88% ^{235}U)	MOX (7,2 % Pu)
Number of cycles	4 cycles	4 cycles
Mean burn-up	46570 MWd/t_{HM}	54500 MWd/t_{HM}
Reactor	EDF PWR 1300 (Nogent 2)	PWR Gösgen (Switzerland)
Discharged from reactor	June 2004	2002
Output of the hull rinser (La Hague)	October 2009	September 2008

Two batches of 6 hulls (M5 and MOX D4) were transferred by internal transfer from the hot cells, where the hulls were stored, to the leaching dedicated hot cells on 1st July 2015 (Figure 6).



M5-type (UOX)

Zy-4-type (MOX, Duplex)

Figure 6 Image of the two batches of 6 Zircaloy based alloy hulls : M5-type (UOX) (left) and Zy-4-type (Duplex, MOX) (right)

The selected samples have a defined geometry with a cylindrical shape in order to have approximatively the same surface in contact with the leachate solution. The kinetics of the ^{14}C release in the leaching solution can thus be compared. The general characteristics of the selected hulls are presented in Table 2.

Table 2 General characteristics of the selected hulls.

Parameters	**Values**
Length	~ 35 mm
External Diameter	9.5 mm
Thickness of the clad	0.57 mm

2.3.1.3 Description of the leaching tests

Preliminary test:

Before starting the leaching tests, a blank test in aerated and alkaline (NaOH) conditions at pH 12 was carried out with one M5-type hull during 14 days. This blank test was conducted in July 2015 and radiochemical analyses of the solution sample are currently in progress. The feasibility of radiochemical analysis in NaOH conditions will thus be approved. Moreover, the radiochemical analyses of the leachates will help determine the experimental parameters of the leaching tests such as the time duration and volume of leachates.

Experimental setup:

Argon will be injected in the reactor for at least 3 h before initiating the leaching tests. The sampling time as well as the volume of each solution sample will depend on the blank test results. The solution sample will be collected in plastic vials. Depending on the activity of the solution sample, dilution step may be performed. The solution sample having an acceptable radiochemical activity will be sent to the radiochemical laboratory, outside the ATALANTE facility for ^{14}C chemical analysis purposes.

The experimental setup is presented in Figure 7 and also described in deliverable D3.2.

In the reactor, two hulls will be inserted in reactor containing the alkaline solution for leaching tests (Figure 7). The three valves in the head of the reactor will be used to sample the solution, purge gas and adjust the pressure with argon gas during the experiment. The valves and the closing system are designed for remote handling equipment. The argon atmosphere within the reactor (3.5 bar) will ensure the anoxic conditions. The leachate solution will not be refilled during this static leaching phase. It will be stirred via argon bubbling.

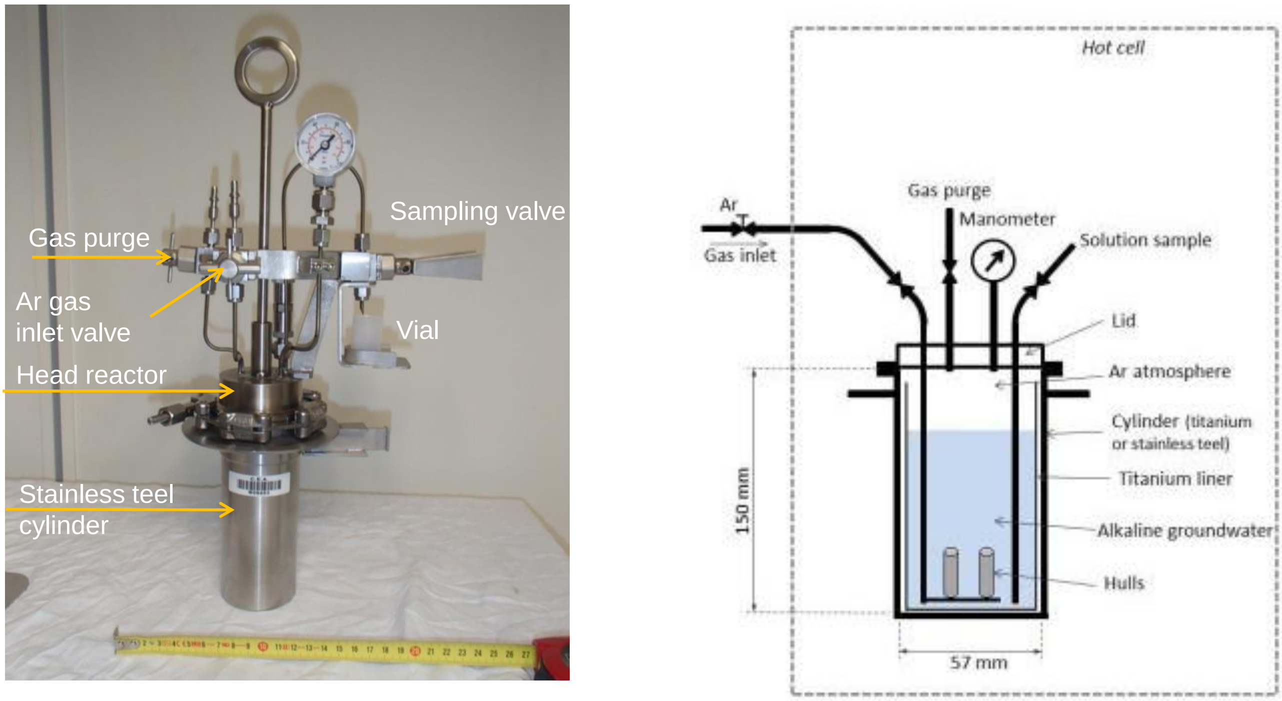


Figure 7 Experimental setup for static leaching tests : photograph (left) ; schematic diagram (right)

2.3.2 Analytical strategy

In 2014, an analytical strategy was developed (see Table 3). The different objectives of this study and the analytical techniques are also detailed in deliverable D3.7.

Table 3 Analytical techniques and associated goals

	Aim	Analytical techniques
CARBON MASS BALANCE	Organic and inorganic total carbon	Total carbon analyser
	Total ^{14}C	Pyrolysis followed by LSC or AMS measurement
	Organic and inorganic ^{14}C partition	Reaction with H_3PO_2 under N_2 / LSC or AMS measurement for inorganic ^{14}C/ Pyrolysis followed by LSC or AMS measurement for organic ^{14}C
SAMPLE PREPARATION	Desalination	Ion exchange
ORGANIC SPECIATION	Qualitative analysis for determination of chemical families	Fourier transform infrared (FTIR)
	Quantification of low mass carboxylic acids (C1-C5)	Ion chromatography (IC)
	Detection of low mass molecule	Gas chromatography coupled with mass spectrometry (GC-MS)
	Detection of molecules with higher molecular weight	Electrospray-mass spectrometry analysis (ESI-MS)

2.3.2.1 Carbon mass balance

Total, organic and inorganic carbon

The analysis of total organic and inorganic carbon (TOC and TIC respectively) will be conducted by using a TC analyser located in a glove box.

Currently, the calibration curve allows to determine a detection limit (in TOC and TIC (without sample dilution)) and quantification limit of 4 and 14 mgC/L respectively (see Figure 8).

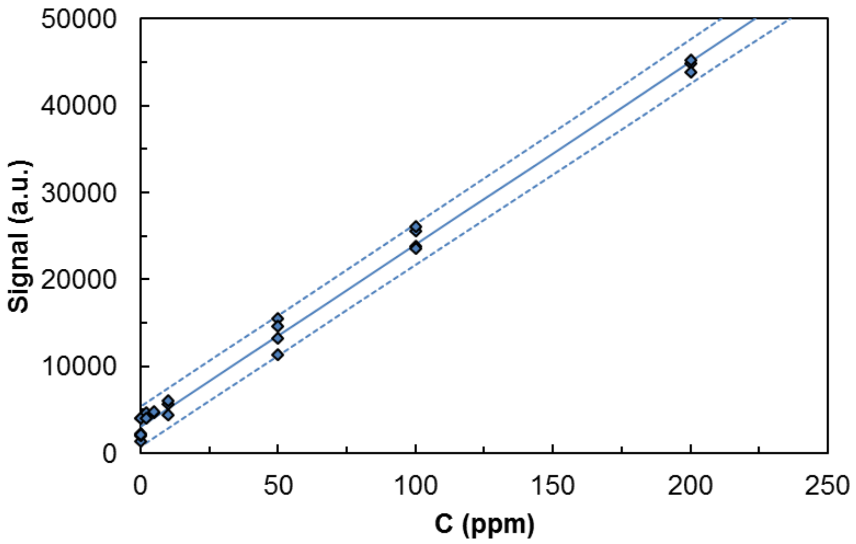


Figure 8 Calibration for detection limit and quantification of TOC and TIC

Total 14C determination

A triple-tube pyrolysis furnace manufactured by ERALY will be used to extract total ^{14}C from the leachate sample.

^{14}C trapped in the NaOH solution can be measured by Liquid Scintillation Counting on a Tricarb 2910TR apparatus or by AMS (Accelerator Mass Spectrometry) at the CEA/LMC14 laboratory on Saclay.

Organic and inorganic 14C partition

The LASE laboratory has no previous experience on the analysis of ^{14}C partitioning. Based on the reaction used to make organic/inorganic partition in commercial apparatus, a mixture of two labelled organic and inorganic molecules (glucose $^{14}C_6H_{12}O_6$ and $Na_2{}^{14}CO_3$), with a solution of H_3PO_4 25 % under N_2 bubbling, will be considered. Released CO_2 will be retained in a trap solution (NaOH). An aliquot of the trap solution will be analysed by LSC to determine the inorganic ^{14}C. The remaining solution in the reaction vessel will be pyrolysed to measure the organic ^{14}C. If the result from LSC is below the detection limit, it is foreseen to use AMS.

This procedure will be attempted from July to October 2015. If it is not successful, only the total ^{14}C content in the leachate solution will be available.

2.3.2.2 Organic carbon speciation

Sample preparation

To help the detection of organic molecules, a step of sample preparation is required. Desalination of the sample using ion exchange resin to replace Na^+ ions with H^+ will be used.

A solution of organic molecules (mixture of acids and diacids) in an alkaline buffer (0.16 mol/L KOH and 0.07 mol/L NaOH) was analysed by Total Organic Carbon method (TOC) and Inductively Coupled Plasma / Atomic Emission Spectroscopy (ICP/AES) before and after treatment with ion exchange resin (CHROMAFIX PS-H+ (S) brand Macherey Nagel). TOC is used to confirm that no organic matter is released from the resin, and ICP/AES is used for potassium and sodium quantification to control the efficiency of the sample purification.

The initial concentration of total organic carbon was 414 mgC/L. The results presented in Table 4 shows:

1. an efficient removal of salts present in solution
2. a slight decrease in TOC , knowing that the uncertainties of the measurements is in the order of 2%
3. a high concentration in TIC observed before ion exchange

Table 4 First results of desalination.

IEX treatment	TIC (mgC/L)	TOC (mgC/L)	K (mol/L)	Na (mol/L)
Without	555	451	0.148	0.063
With	7	419	0,0004	0.0018

A high concentration in TIC was measured before filtration probably due to the carbonation of solution. The first results highlight the removal of salts but complementary tests will demonstrate if this decrease in TOC is significant.

2.3.2.3 Fourier transform infrared

The aim is to identify functional groups of organic compounds present in solution (carboxylic acids, aromatic compounds, ketones, etc…).

The use of 'OmniCell' universal cell" was considered to analyse radioactive liquid samples. This removable system waterproof and equipped with sealed CaF_2 windows suitable to analyse liquid. However, two major difficulties must be overcome:

- Sample activity has to be compatible with laboratory bench manipulation,
- Manipulation and cleaning of CaF_2 sealed windows must be possible without contamination.

2.3.2.4 Ion chromatography

Iron chromatography will be used to determine the carboxylic molecules. This technique was developed in the LRMO laboratory for the detection of carboxylic acids from C_1 to C_5 in high NaOH concentrations (0.2 mol/L). This device is equipped with a conductimetric detector, to detect carboxylic acids (containing or not ^{14}C).

The first results showed a detection limit around 1 mg/L according to the interference sample and matrix.

The identification of molecules (by using a scintillator counter coupled with IC) will not be possible. This option was studied by the LRMO laboratory but there is not enough room for the installation of the equipment in the glove box.

2.3.2.5 Electrospray-mass spectrometry analysis

Electrospray-mass spectrometry will be used to analyse molecules with molecular weight higher than 100 g/mol. This technique is a soft ionisation technique to detect intact polar molecules in complex mixtures. For molecular weights lower than 1000 g/mol, the resolution of mass spectrum may be sufficient to determine $^{12}C/^{13}C/^{14}C$ ratio. The detection of molecules labelled with ^{14}C can be conducted if the concentration of ^{14}C is sufficient. To determine the detection limit of this technique, tests will be performed by using standard ^{14}C-labelled molecules.

Palmitic acid with different ^{14}C-labelled, was used to run the tests:

- Palmitic acid without ^{14}C
- [1-14C]- palmitic acid with one ^{14}C on the carboxylic group
- [14C(U)] palmitic acid with all carbon labelled with ^{14}C.

The purchase of standards is ongoing and their analyses will be carried out this year. Analytical parameters need to be optimised to obtain the best isotopic resolution as well as a good detection limit.

2.3.3 Conclusions

Following the definition of the analytical strategy, first development was conducted to optimise the analytical techniques before working on the leaching solutions (NaOH).

Table 5 synthetises the principal results.

Table 5 Analytical Strategy - Implementation at the end of July 2015.

	Technique	**Advance**
CARBON MASS BALANCE	TIC/TOC	Detection limit around 1 mgC/L
	Total ^{14}C	Detection limit by LSC:~ 0.5 Bq/mL by AMS: ~ 0.5 mBq/mL Recovery of ^{14}C by pyrolysis above 90% for liquid samples
	TIC/TOC ^{14}C	On-going tests with a mixture of two labelled molecules with LSC and AMS measurement
SAMPLE PREPARATION	Ion exchange	Efficient salts removal needs to be confirmed
ORGANIC SPECIATION	FTIR	Under consideration with a priority to GC-MS
	IC	Carboxylic acids (C1-C5) analyses without ^{14}C detection Detection limit around 1mg/L
	GC-MS	Depending on sample activities for experiments in fume hood
	ESI-MS	^{14}C labelled molecules have been ordered

2.4 *ITU/JRC contribution in WP3*

During the 2nd year of the CAST project, ITU/JRC was in charge of D3.6 entitled "Intermediate report on the analysis of Zircaloy C-14 content". The report presents the materials (irradiated Zr) as well as the setup of the autoclave for leaching test and C-14 analyses from the leachates. ITU/JRC also contributed to D3.10 entitled "Annual progress report on corrosion test". Concerning WP3, ITU/JRC is in charge of two deliverables; D3.6 (submitted in May 2015) and D3.14 (due in January 2017).

2.4.1 Materials

2.4.1.1 Zircaloy cladding composition and Burn-Up

The PWR cladding test material is documented as a duplex Zircaloy cladding: Zircaloy -4 cladding with a thin external Zr-2.5Nb cladding. The cladding comes from a high burn-up fuel with a mean burn-up of 100.5 GW/tU. Cutting plans were prepared and the upper plenum (no fuel) were cut; the mid-height positions will be cut by the end of 2015. The mid-height position will present higher burn-up and C-14 content. Non-destructive and destructive examinations were performed, and permission is pending to be able to use these results. Non-irradiated samples are not available for this specific cladding, therefore either a value measured elsewhere may be used or a sample of in-house Zircaloy-4 could be analysed (by ICP-MS) to obtain a typical value.

2.4.1.2 Sample preparation

Samples were cut as 3-5mm long rings or half-rings (1-0.5g) at mid-height (max. power) and at the upper plenum. The fuel is yet to be removed for the mid-height position in the next month. These will have fuel mechanically removed (pressed out) but will require fuel dissolution by 7M HNO_3 (or 15% H_2SO_4) followed by cleaning in water and then drying in air.

Further samples were cut from above fuel height (lower burn-up and C-14 content) but will have fission product deposits, particularly Cs. These samples will require acid cleaning with 7M HNO_3 (possibly 1M HNO_3) or 15%H_2SO_4 acid for dissolution of the fission products before washing in water and drying in air.

One plenum sample will be mounted for metallography (determination of the oxide thickness); the fuel sample has already undergone optical microscopy, another sample from fuel and plenum position will be used for total C content determination. SEM-EDS may be available to examine the cladding condition, especially the oxide thickness (using either the mounted or a fracture surface sample). The remaining samples will be for leach testing in the autoclave. Excess samples will be kept in case repeat testing is necessary.

2.4.2 Autoclave for leach tests

The ITU autoclave (able to go to 250°C and 150 bar pressure) now has a PEEK lining constructed to replace the Teflon lining that is considered unstable under strong irradiation fields. The autoclave testing parameters will be 30°C and 1-2 bar pressure (slight excess pressure for gas sample extraction). The autoclave and the PEEK lining are seen in Figure 9.

If there is enough time, tests will be carried out at elevated temperature (80°C) by using an existing heating mantle in the Hot Cell 4. Adaptations for the hot cell connections to the glove box will be performed when the glove–box is in position; alternatively a gas capsule system has been purchased as an alternative means of transferring the gas samples into the C-14 analysis glove box. The cladding corrosion rates will be assessed by Co-60 gamma counting of the solution (following discussions at the last WP2 & 3 meeting on 27-28 May 2015).

The first autoclave tests will be expected to start in the final quarter 2015/early 2016 as the glove box commissioning is nearing completion.

The leaching solution will be NaOH at pH 12 at 30°C and 80°C (if there is enough time). Separate gas and liquid samples will be taken at the end of the 3 month leaching experiments, with no intermediate samples.

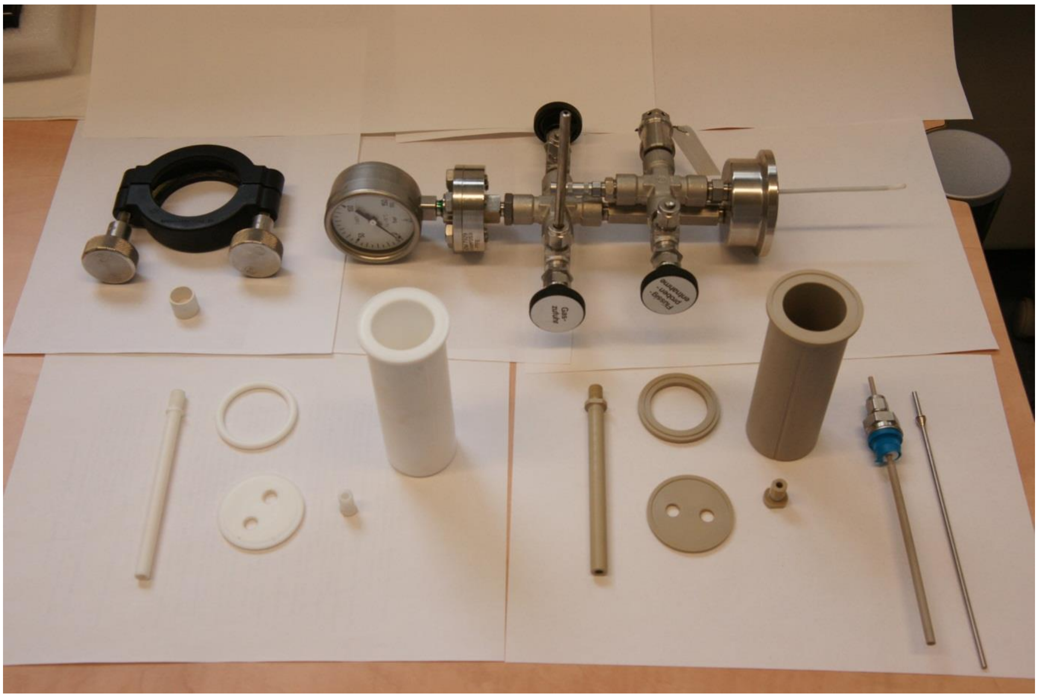


Figure 9 Autoclave with old Teflon (left) and new PEEK (right) linings. The autoclave will be used with the more stable PEEK lining in small PEEK crucibles with holes to allow the water to drain from the sample.

2.4.3 Analysis

2.4.3.1 Glove box preparation

A glove box is under construction at ITU main Workshop for collection and analysis of the carbon-containing gases and liquids from the autoclave. The glassware has been ordered as well as 2 ovens, a balance and vessel heating plate. The catalysts and chemicals have also been ordered. The construction of the wash bottles and gas lines in the glove box started during summer 2015. The connection between the autoclave in the hot cell and the glove box will be made during installation of the glove box (this may involve use of gas capsules for gas transfer).

The analytical technique will be as close as possible to that used by KIT-INE. It is intended that ITU and INE will collaborate on the technical construction of the analytical glove box, to optimise the analytical technique and make the best comparison possible (given INE's experience in this field).

A schematic diagram of the analytical glove box layout is shown in Figure 10.

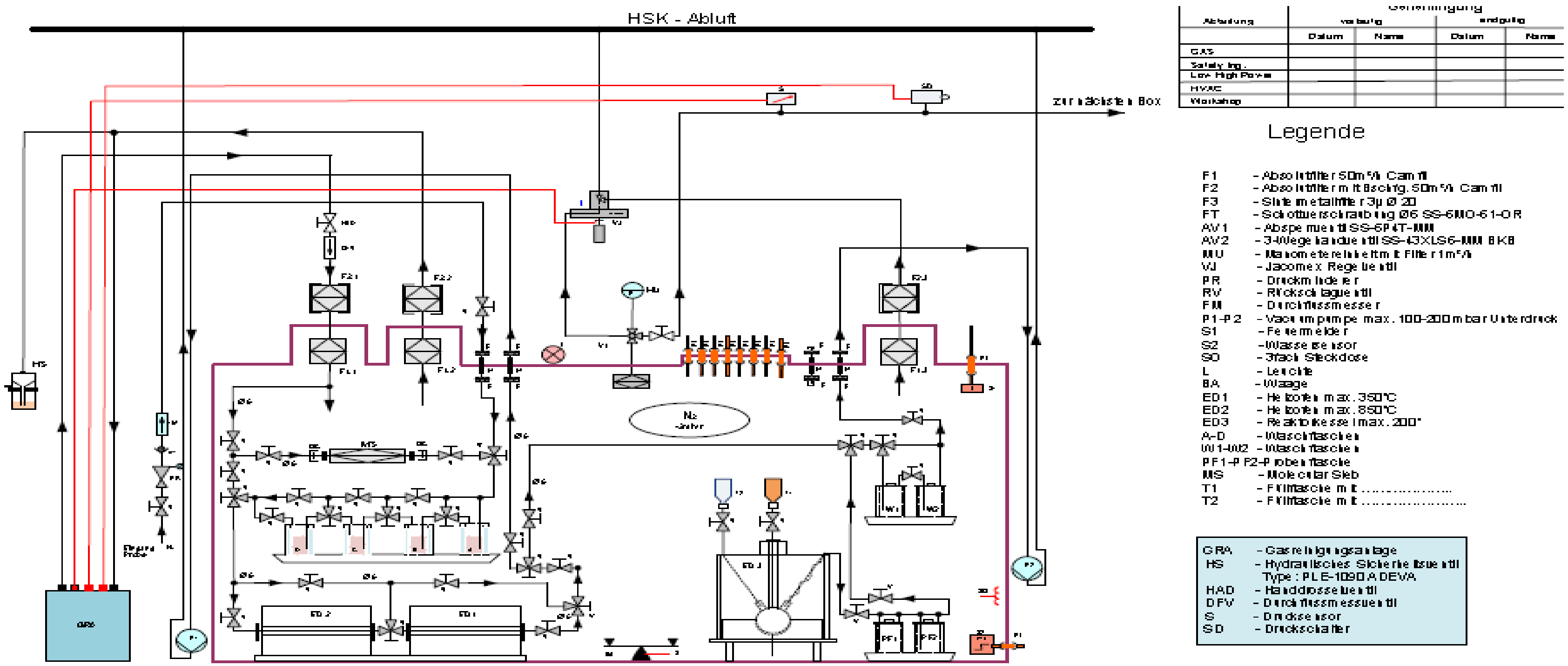


Figure 10 Technical drawing of the ITU C-14 aliquot testing glove box based on the KIT-INE glove box design.

2.4.3.2 Device for total C content determination

An ICARUS H4 total inorganic C determination device is currently under construction for installation in the hot cell. This is for determination of total C in irradiated cladding samples (C is converted to CO_2 by burning in O_2 and then measured by IR absorption). A molecular sieve filter in the off-gas line will also be used for collection of the CO_2 gas. This filter can then be transferred to the analytical glove box for analysis and C-14 determination by beta-counting. The total C device is under construction at the manufacturers (Bruker Elemental, Karlsruhe) and it is expected that it will be completed by the end of September 2015 for testing. Then, installation in the hot cell and cold testing can begin along with the addition of a small glove box to exchange the molecular sieve in the return gas line. The first tests could be launched for early 2016, with initial samples in the following months (2^{nd} Qtr 2016).

2.5 *KIT contribution in WP3*

During the 2^{nd} year of the CAST project, KIT was in charge of the D3.8 in Task 3.3 entitled “Description of Zircaloy-4 dissolution experiment in a shielded box”. This deliverable consists of presenting the digestion experiment of irradiated Zry in order to measure the amount and chemical form of C-14 as well as the inventories of Sb-125 and Cs-137 by means of radiochemical methods. Within WP3, KIT is in charge of three deliverables; D3.3 (submitted in 2014), D3.8 (submitted in May 2015) and D3.15 (due in January 2017).

2.5.1 Introduction

In 2015, KIT finished the development of the separation, quantification and speciation methods of C-14 in aqueous and gaseous samples derived from dissolution experiments with irradiated Zircaloy-4 cladding of the plenum of a PWR fuel rod segment. Furthermore Monte Carlo N-particle (MCNP-X) calculations were performed for the cladding taking into account nominal chemical composition data and the irradiation characteristics of the fuel rod. The sample preparation, acid digestion experiments in a glass reactor or autoclave, as well as preliminary results obtained in the second project year are summarised in the following sections.

2.5.2 Preparation of irradiated Zircaloy-4 specimen

In total, six Zircaloy-4 specimens were dry cut in the KIT-INE shielded box-line from the plenum of the irradiated fuel rod segment using a low speed saw (Isomet 11-1180, Buehler Ltd.) equipped with a diamond saw blade. Sample characteristics are given in Table 6 and Figure 11. The inner and outer surface of the samples were analysed by means of an optical microscope (DigiMicro 2.0, Drahtlose Nachrichtentechnik, dnt) inside the shielded box. In accordance with the German Radiation Protection Ordinance (BGBL 2005) and the technical advisory board of KIT-INE, the samples were removed from the shielded box-line and dissolution experiments with the irradiated Zircaloy-4 specimens were conducted in a specifically manufactured glove box.

Table 6 Characteristic data of the irradiated Zircaloy-4 samples.

Sample	**#1**	**#2**	**#3**	**#4**	**#5**	**#6**
mass [mg]	184.4	130.1	119.7	177.5	189.0	183.3
dose rate [µSv/h]	≤ 270	≤ 150	≤ 170	≤ 260	≤ 280	≤ 220

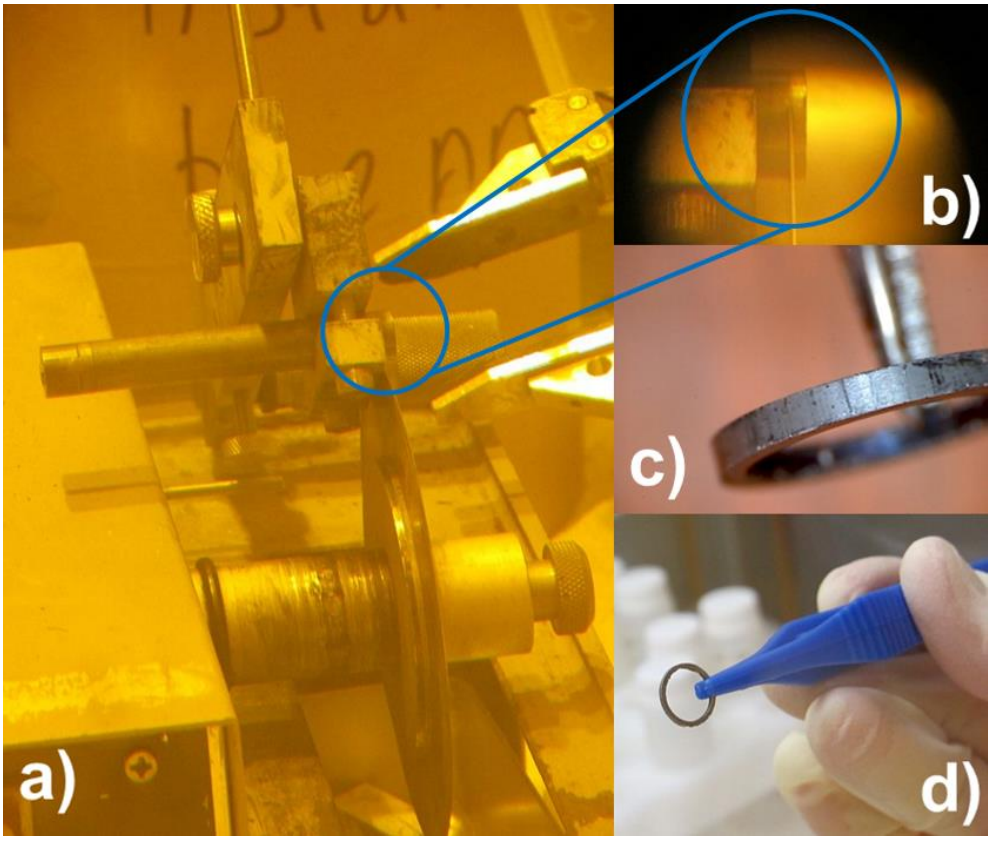


Figure 11 a) shows the low speed saw and the Zircaloy-4 plenum cutting half through a sample b). The photo in c) was made using the optical microscope available inside the shielded box and d) shows the preparation of the sample for the dissolution experiments inside a specifically manufactured glove box.

2.6 *Dissolution experiments with irradiated Zircaloy-4 cladding*

2.6.1 Experimental setup

Three cladding samples (#1 to #3) were digested in dilute H_2SO_4/HF in a flask of the C-14 extraction apparatus, whereas the cladding specimens #4 and #6 were digested using an autoclave equipped with a glass liner and a gas collecting cylinder with two valves. The sample #5 was digested and analysed by α-, γ-spectrometry, ICP-MS and liquid scintillation counting (LSC) to demonstrate that the radioactive inventory of the samples is within the regulatory limits for working in a glove box.

In experiments conducted with the samples #1 to #3, the cladding specimen was placed in the flask connected to a CO_2 gas absorption system (see Figure 12). Sulphuric acid was added immediately to the sample container through a dropping funnel. Then, hydrofluoric acid was added dropwise. The Zircaloy-4 cladding specimen was digested within 30 min at room temperature. Gases evolving during the digestion process were absorbed in alkaline washing bottles directly or after oxidation to CO_2 in a catalytic furnace. Samples were collected from all containers and analysed by α-, γ-spectrometry, ICP-MS and LSC.

Samples #4 and #6 were placed in an autoclave equipped with a glass liner, respectively (see Figure 13). The autoclave was sealed air tight and an evacuated gas collecting cylinder with two valves was mounted on top. The autoclave was flushed with nitrogen or argon and 20 mL of a dilute H_2SO_4/HF mixture was added trough one of the two valves in the lid of the autoclave. All valves in the lid of the autoclave were closed immediately after the addition of the chemicals. The autoclave developed a pressure of about 1.4 bar during the digestion. After five hours and ensuring constant pressure, the gas phase was sampled. The gaseous sample was analysed by gas-MS. The aqueous solution, as well as, the remaining gas phase in the gas collecting cylinder were also analysed for C-14.

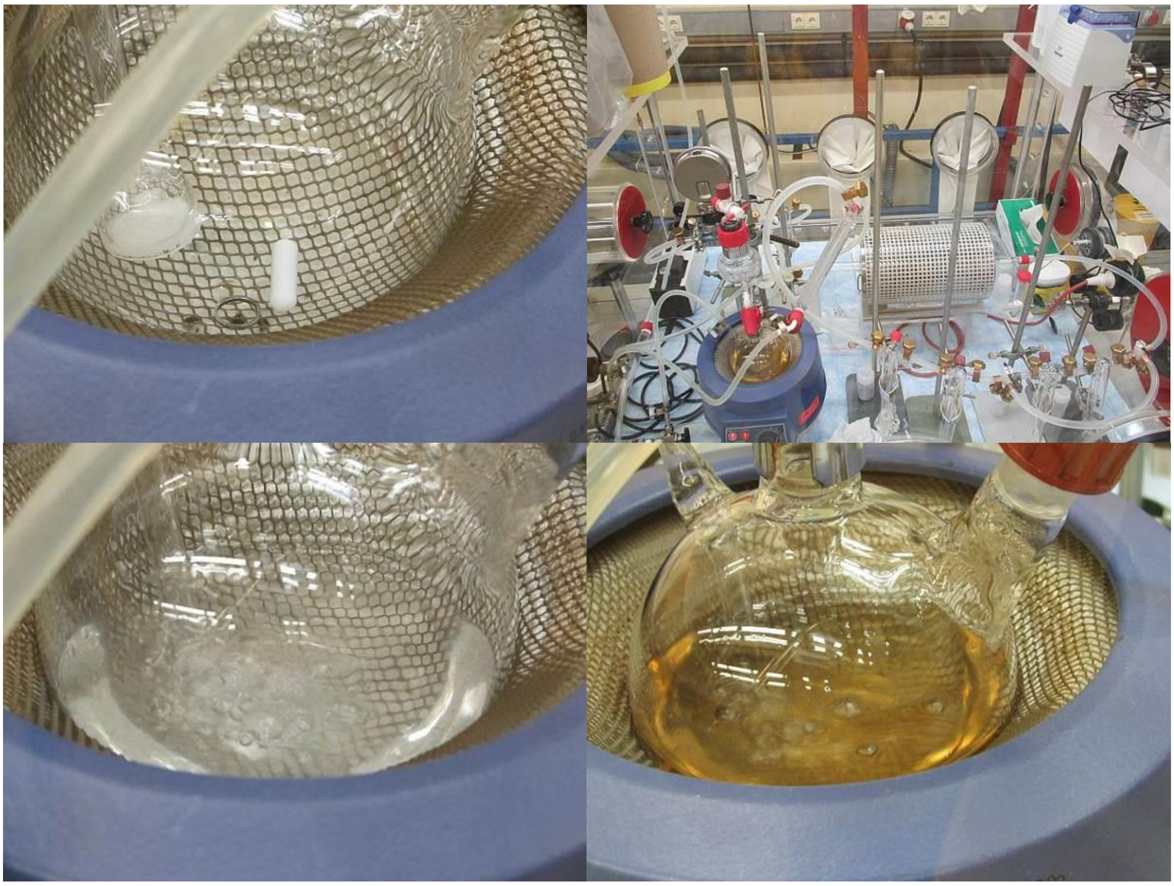


Figure 12: The upper pictures show the Zircaloy-4 sample inside the flask (left) and the whole CO2 absorption apparatus including the catalytic furnace (right). The lower left pictures shows the digestion of the sample at room temperature and the lower right picture shows the wet oxidation process during which the solution turns gold/brownish before decolouring again.

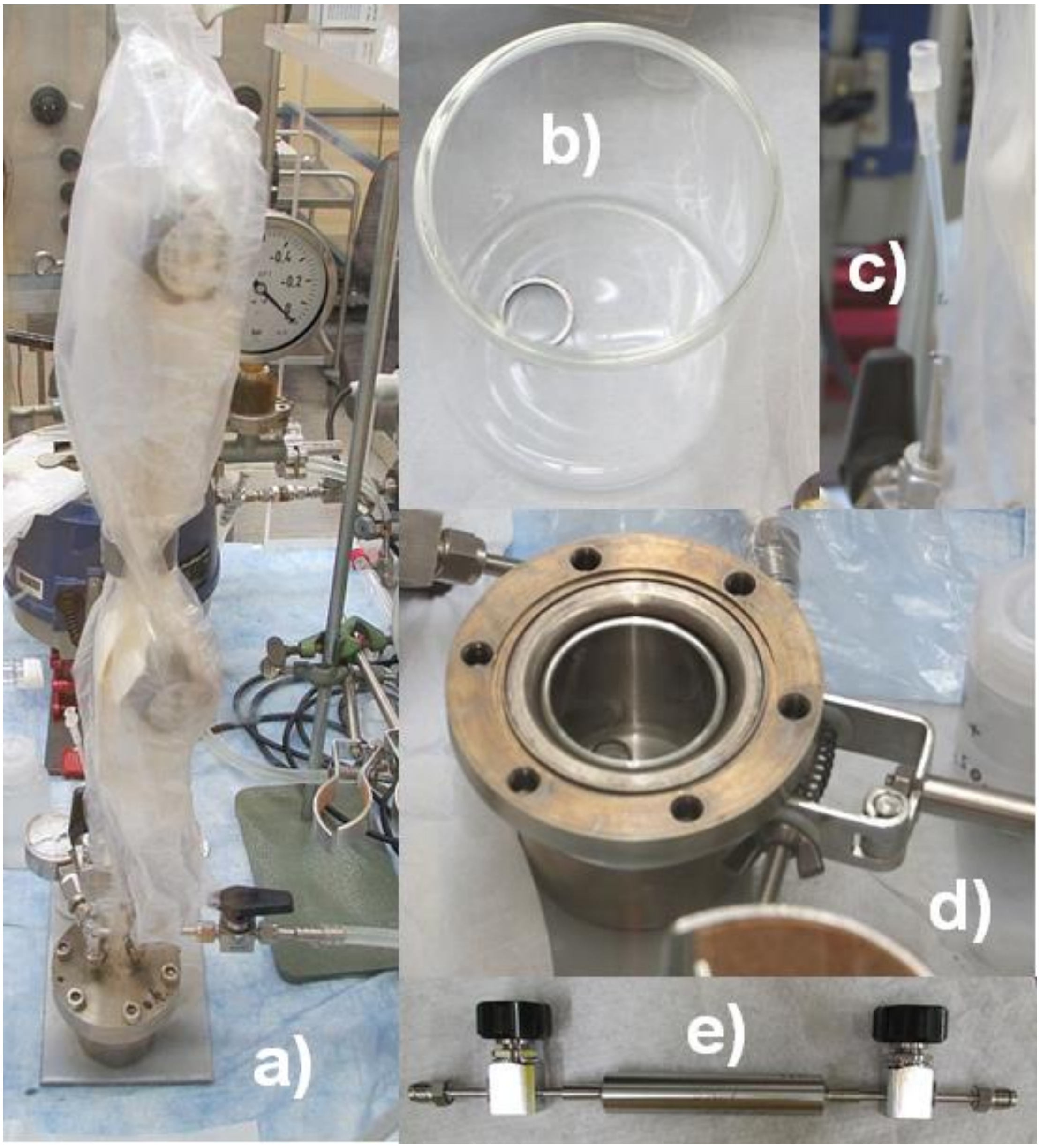


Figure 13: a) shows the sealed autoclave with gas collecting cylinder mounted on top. The glass liner with the Zircaloy-4 sample is seen in b); c) shows the tube used for the addition of the acid. The glass liner with sample in the open autoclave is shown in d). The gas collecting cylinder with two valves is seen in e).

2.6.2 Preliminary results of the dissolution experiments

In the digestion experiment with sample #5, it was observed, that the oxide layer of the Zircaloy-4 has remained physically intact after the complete digestion of the alloy at room temperature without stirring, purging or heating the solution (see Figure 14). However, it is assumed that radionuclides present in the oxide layer are released during the digestion of the Zircaloy sample. Therefore, a sample of the oxide remnant was taken and analysed by scanning electron microscopy – energy dispersive X-ray spectroscopy (SEM-EDS) (see Figure 15). The oxide layer gradually dissolved during the C-14 extraction process as the solution in the flask was stirred, purged with nitrogen and heated during the wet oxidation step.

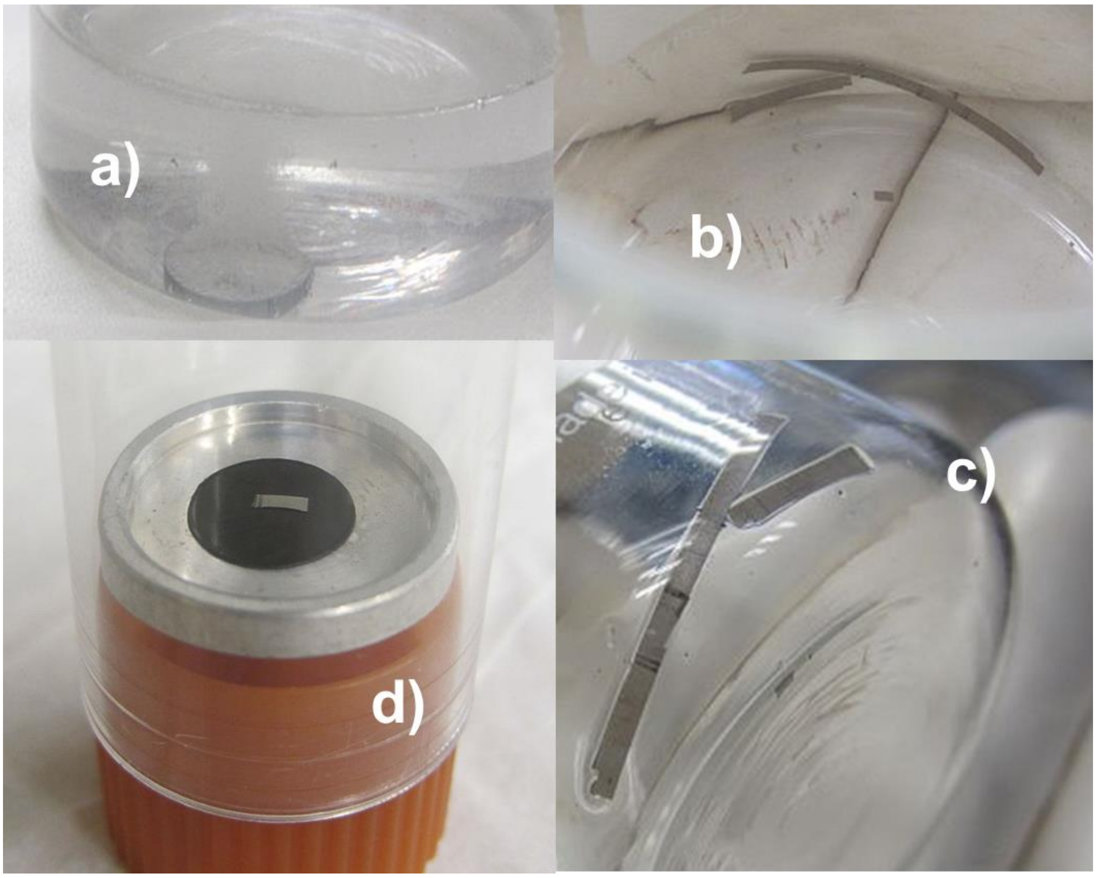


Figure 14: **a) shows the Zircaloy-4 sample 5 during digestion whereas b) and c) show the remaining oxide layer after the digestion and in d) the oxide layer prepared for the SEM-EDS measurements is shown.**

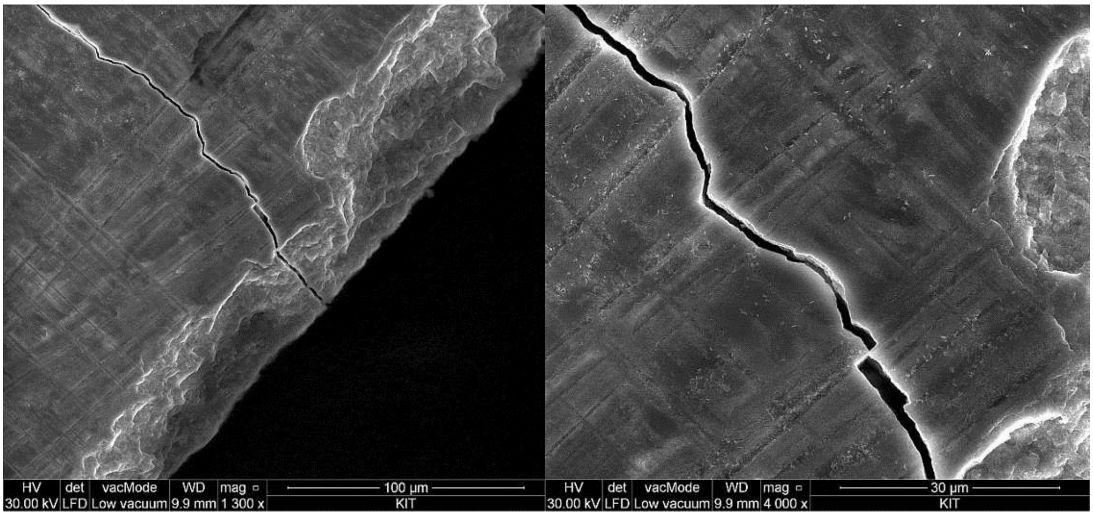


Figure 15: SEM images of the irradiated Zircaloy-4 oxide layer.

During the optical examination of the Zircaloy-4 samples, using the microscope available in the shielded box-line, black/blueish precipitates were observed on the inner surface of the cladding (see Figure 16). According to previous studies on similar precipitates on the inner surface of plenum claddings, these precipitates consist of cesium. To determine the characteristics of these precipitates XAS investigations at the INE Beamline for Actinide and Radionuclide Science at ANKA are foreseen with the irradiated and a non-irradiated Zircaloy-4 cladding.

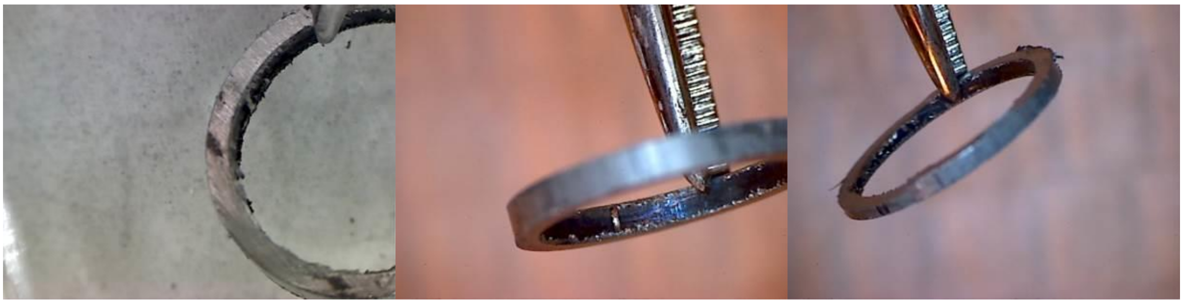


Figure 16: Black/blueish precipitates seen on the inner surface of the irradiated Zircaloy-4 cladding.

Table 7 summarises the experimentally determined inventories of C-14, Fe-55, Cs-137 and Sb-125. These were further compared to our MCNP-X calculations. A Japanese team (T.Yamaguchi, S.Tanuma et al. 1999) studied a hull specimen of a spent PWR fuel rod with a burn-up of 47.9 GWd/t_{HM} which, is similar to the burn-up of the PWR fuel rod segment used in this study (50.4 GWd/t_{HM}). The experimental results obtained in this study for C-14, Fe-55 and Sb-125 are in good agreement with the calculations and in the case of C-14, also with the literature data (T.Yamaguchi, S.Tanuma et al. 1999). The experimental Cs-137 inventory exceeds, by a factor of 117, the calculated value. The excess of Cs-137 is related to the precipitation on the inner Zircaloy-4 surface. The volatile cesium is released during reactor operation from subjacent UO_2 pellets and precipitates in the cooler plenum part of the fuel rod segment. The additional Cs-137 inventory is not taken into account in the MCNP-X calculations.

From the autoclave experiments, additional information about the partitioning between solution and gas phase of C-14 compounds released during the acid digestion was obtained. About 90% of C-14 was released as gaseous hydrocarbons/CO during the dissolution of the irradiated Zircaloy-4 and only about 9% remains as liquid hydrocarbons in the acidic solution and is released during the wet oxidation. In all experiments (glass reactor and autoclave) almost no inorganic C-14 compounds were found (< 1%).

Table 7: Results of the inventory analyses.

radionuclide	**C-14 [Bq/g]**	**Fe-55 [Bq/g]**	**Cs-137 [Bq/g]**	**Sb-125 [Bq/g]**
measured contents in Zyr-4 of segment SBS1108–N0204 (50.4 GWd/t_{HM}) [p.w.]	$3.7(\pm0.4)\times10^4$	$1.5(\pm0.2)\times10^5$	$3.4(\pm0.3)\times10^6$	$2.4(\pm0.2)\times10^5$
calculated contents in Zyr-4 of segment SBS1108–N0204 (50.4 GWd/t_{HM}) [p.w.]	3.2×10^4	1.3×10^5	2.9×10^4	2.6×10^5
measured contents in Zyr-4 of spent PWR fuel rod hull specimen (47.9 GWd/t_{HM}) (Yamaguchi, Tanuma et al. 1999)	3.0×10^4			

2.7 RATEN ICN contribution in WP3

During the 2nd year of the CAST project, RATEN ICN contributed to D3.10 in Task 3.3 entitled “Annual progress report on corrosion test”. Their activities were focused on corrosion tests on un-irradiated Zy-4 samples as well as testing the experimental set-up to measure the inventory and speciation of C-14 in the irradiated Zy-4 from CANDU spent fuel.

Concerning WP3, RATEN ICN is in charge of the deliverable D3.16 (due in January 2017).

2.7.1 Electrochemical tests on un-irradiated Zircaloy-4 in NaOH solution

2.7.1.1 Sample preparation

To define the experimental conditions for corrosion/leaching tests to be performed on the irradiated Zy-4, electrochemical tests were carried out on un-irradiated Zy-4 samples. The samples used in these tests were cut from an as-received Zy-4 tube with an outer diameter (OD) of 13 mm and a wall thickness of 0.4 mm. To get an oxide layer similar to that measured on the irradiated samples, the un-irradiated Zy-4 samples were oxidised in an autoclave (an oxide thickness above 2.5 µm is required for the project).

The tests were conducted in a static isothermal autoclave in similar conditions to those of a CANDU primary circuit (LiOH solution, pH=10.5, T=310 ^{o}C, P=100 atm). After 172 days in the autoclave, the average weight gain of Zr samples was 29.3 mg/dm^2. The weight gain of the corroded specimens can be used as a direct gauge of the oxide film thickness, taking into account that 14.9 mg/dm^2 of Zr oxide represents 1µm thickness. In the case of these samples, the thickness was 1.96 µm corresponding to a weight gain of 29.3 mg/dm^2. The thickness of the oxides after 172 days of exposure in autoclaves was measured by optical microscopy and estimated to be in the range of 1.7-2.2 µm (see Figure 17).

Hydrides present in Zy-4 tubes, were also determined by optical microscopy. The materials were Zy-4 tubes oxidized in simulated conditions of CANDU primary circuit (see Figure 17).

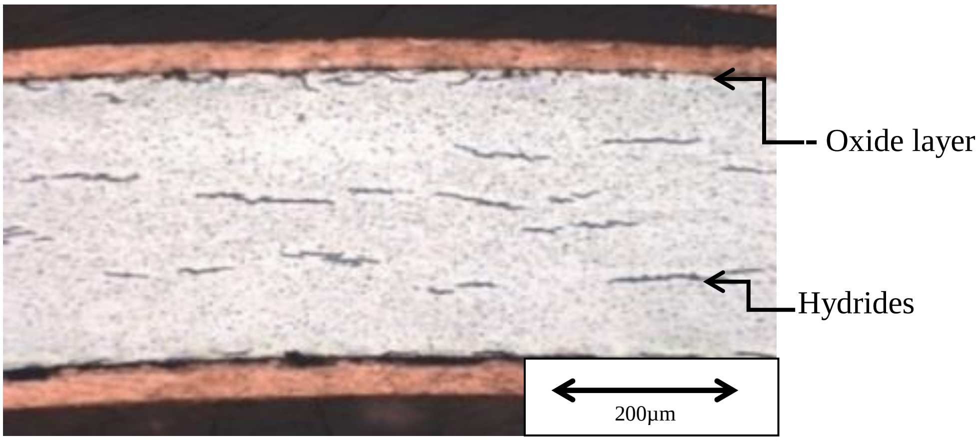


Figure 17 Hydrides into Zy-4 tubes after 172 days of oxidation (optical microscopy x100).

2.7.1.2 Electrochemical set-up

The device used for electrochemical tests was a potentiostat/galvanostat AUTOLAB 302 electrically connected to a corrosion glass cell equipped with a Pt counter electrode and an Ag/AgCl reference electrode. The software used was NOVA 11.1. The electrochemical cell containing three electrodes was filled with a 50 ml solution of NaOH (0.01 M) at pH=12 with a conductivity of 2.1 mS/cm. The working electrode was simply immersed into the electrolyte and electrically connected to the potentiostat. Corrosion tests were only performed at room temperature. Argon was injected for 2 hours before testing as well as throughout the duration of the test. All the electrodes and the gas bubbling tube were introduced through a lid with 5 openings, which were then rendered air tight by sealing them with resin or glue. The electrochemical cell was mounted into a Faraday cage for the duration of the tests in order to protect it from electromagnetic interference from external sources (see Figure 18).

Figure 18 Electrochemical set-up.

The Linear Polarization Resistance measurement were performed by scanning through a potential range very close to the free corrosion potential E_{corr}. At the begining of the test, the sample was kept for 10 minutes in direct contact with the solution (without electrical connection) to stabilise E_{corr}. The applied potential was in the range of ± 25 mV with an error of 2% (± 0.5 mV) around E_{corr} with a scan rate of 0.16 mV/sec. After testing, the NOVA software provided a convenient interface for making Tafel plots, calculating Tafel slopes and corrosion rates. The analysis tool performed a curve fit based on the Buttler-Volmer expression, which allows for more accurate determination of the corrosion current, polarisation resistance (Rp) and corrosion rate.

2.7.1.3 Results from the LPR method

LPR tests have been performed on the following samples:

- – as received Zy-4 tube (aerobic condition);
- – as received Zy-4 tube (anaerobic condition);
- – oxidised Zy-4 tube (aerobic condition);
- – oxidised Zy-4 tube (anaerobic condition);
- – oxidised Zy-4 tube cut at the end (aerobic condition) as in Figure 19.
- – oxidised Zy-4 tube cut and painted (aerobic condition) as in Figure 19.

Figure 19 Oxidised Zy-4 tube cut and painted at the end (left) and oxidised Zy-4 tube cut (right)

The last two samples were tested to take into account the situation of sliced Zy-4 spent cladding when the end of the coupon will be as fresh metal exposed in solution. So, a LPR test was carried out with an oxidised coupon which was cut and exposed in solution with the fresh cut. After that, the fresh cut was painted and another LPR measurement was run. The CR was higher in the case of fresh cut exposed in solution then in the case of the fresh cut covered with paint. The immersed surface of the samples was ~ 2.5cm^2.

An example of the Tafel plots is presented in Figure 20.

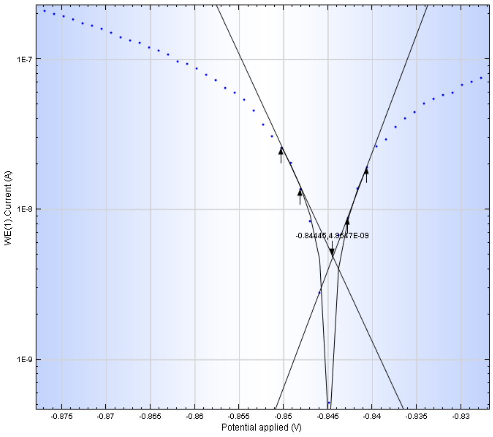


Figure 20 Example of Tafel plots for one tested sample

The conversion of the electrochemical corrosion rates to the mass loss rate was made by using the ASTM G 102-2004 standard (ASTM 2004).

In Table 8, the corrosion rates and mass loss rates are presented for un-irradiated Zy-4 after LPR measurements.

Table 8 Corrosion rates and mass loss rates calculated for un-irradiated Zy-4 samples.

Samples	**Corrosion rate nm/y**	**MR µg/ cm^2 y**
as received Zy-4 aerobic cond	480 ± 10	310 ± 6
as received Zy-4 anaerobic cond	110 ± 2	75 ± 1
Zy-4 oxidised aerobic cond.	9.72 ± 0.1	6.58 ± 0.13
Zy-4 oxidised anaerobic cond	3.16 ± 0.06	2 ± 0.04
Zy-4 oxidised, cut aerobic cond	11.6 ± 0.2	7.5 ± 0.1
Zy-4 oxidised, cut and painted aerobic cond	3.62 ± 0.07	2.31 ± 0.04

The as–received samples presented higher CR (about 40 times higher in given conditions) than the oxidized samples. Aerated conditions seemed to increase the CR by a factor of 4 and 3 for as-received and oxidized samples respectively.

The cut oxidized samples had a slightly higher CR compared to the non-cut aoxidised samples. The addition of paint to the cut oxidized samples lowered the CR to similar values as the non-cut oxidized samples. Painting protects the metal surface by preventing oxygen contact.

2.7.2 Experimental set-up for C-14 measurement in irradiated Zy-4

Measurements will be carried out for the total C-14 on irradiated Zy-4 based on acid stripping of C-14 (using diluted H_2SO_4/HF mixture) followed by oxidation of untrapped C-14 to $^{14}CO_2$ and its subsequent trapping in NaOH 2M, using N_2 as carrier gas (see Figure

21). Four gas washing bottles will be used; one with H_2SO_4 (to retain the gamma emitters present in the irradiated Zy-4) and three with NaOH 2M to ensure the complete absorption of the $^{14}CO_2$.

Figure 21 Experimental set-up for C-14 measurements in irradiated Zy-4.

The C-14 measurement will be made by using the LSC technique. Preliminary tests were carried out un-irradiated Zy-4 marked with C-14 (in form of Na_2CO_3/ $NaHCO_3$) to assess the recovery, reproducibility and memory effect of the method. Also the compatibility of the resulted solution with scintillation cocktail was tested. The experiment will continue with the actual set-up but using a washing solution carbosorb solution to check if a better recovery could be obtained.

The experimental set-up will be completed with a catalytic furnace (to oxidise the gaseous organic C-14) and a second pair of gas washing bottles to be able to measure also the inorganic C-14 species.

2.8 *RWMC contribution in WP3*

During the 2nd year of the CAST project, RWMC contributed to the D3.10 entitled “Annual progress report on corrosion test”. Concerning WP3, RWMC contributed to the D3.1 (issued in 2014) and is in charge of the D3.19 (due in January 2017).

2.8.1 Irradiated Zircaloy cladding

2.8.1.1 Leaching and corrosion test

Irradiated Zircaloy-2 claddings (STEP I and STEP III type) from a BWR were prepared. Here, the STEP I is an older fuel type in Japan (Lattice configuration of 8×8 array, average burnup of 33 GWd/t) and the STEP III is relatively new fuel type in order to respond to the increase in burnup (Lattice configuration of 9×9 array, average burnup of 45 GWd/t). Details of Japanese fuel type are described in literature (Ken’ichi Ito, Katsumasa Haikawa et al. 1998) (Ken'ichi Ito, Katsumasa Haikawa et al. 1998). The claddings were cut to heights of 2 cm for the leaching tests. The bonding fuel elements were removed by mechanical polishing and washed with 4 M boiling nitric acid for 4 hours. The oxide films were also removed by polishing the surfaces. A part of the cladding was used to measure the nuclides inventory. The leaching tests were performed in a dilute NaOH solution of pH 12.5 and nitrogen atmosphere at room temperature using a glass vial with a gastight outer vessel. After corrosion test, C-14 in the gas phase was collected using a plastic bag. Leached radionuclides and Zircaloy additive elements in solution were measured by LSC, gamma spectrometry and ICP-MS. Assuming that the activated radionuclides and additive elements are distributed homogeneously in the cladding, the equivalent corrosion rate, CR_{eq} (μm/y), can be obtained from leachates as described by Equation 1.

Equation 1

$$CR_{eq} = \frac{aL}{2At}$$

Where,

– a is the leached amount of radionuclides or elements (Bq or mol),

– A is the inventory in the cladding (Bq or mol),

–L is the thickness of the cladding (μm),

–t is the test time (years).

Namely, the leaching fraction is represented as a/A. Here, the thickness L is 740 µm based on the cross-section characterised by optical microscopy for the STEP I cladding.

The equivalent corrosion rates for the irradiated claddings are shown in Figure 22. The BWR (Y.Yamashita, H.Tanabe et al. 2014) and PWR data (T.Yamaguchi, S.Tanuma et al. 1999) can be found in the literature. The extremely low values for zirconium are due to the low solubility of zirconia (oxide film). Currently, it is difficult to conclude that the C-14 leaches congruently with metal corrosion as the CR of Zr is 2 orders of magnitude lower than the fraction release rate of C-14.

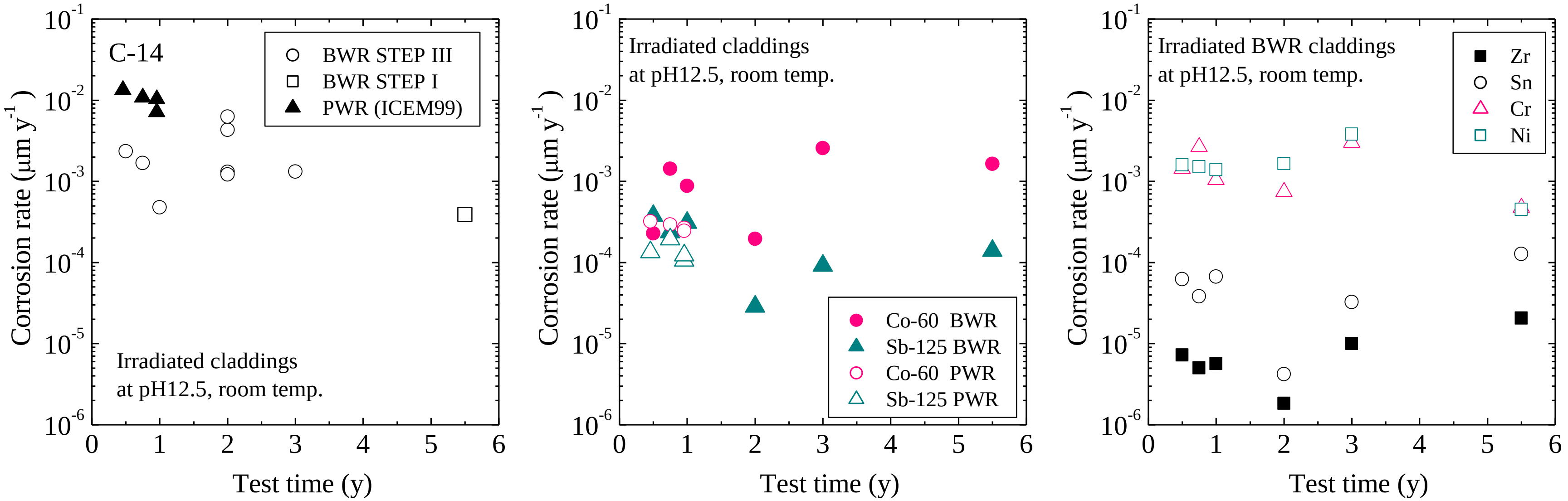


Figure 22 Equivalent corrosion rate of irradiated claddings.

2.8.2 Non-irradiated zirconium materials

2.8.2.1 Corrosion rate measurements

Zircaloy-4 and Zircaloy-2 were obtained from CEZUS Co., Ltd. The final polishing was carried out with a 0.02 mm alumina powder. Two experimental setups, a batch ampoule and the gas flow system, were prepared. Zircaloy foils or strips were immersed in appropriate solutions under anoxic conditions. The evolved hydrogen gas and absorbed hydrogen concentration were measured by using atmospheric pressure ionization mass spectrometry (API-MS) and by gas chromatography (YANACO G-2800 and LECO RH-404). The following corrosion reaction (see Equation 2) was assumed for hydrogen absorption ratio x:

Equation 2 $$(2x+1)\mathrm{Zr}+2\mathrm{H_2O}\rightarrow \mathrm{ZrO_2}+2\mathrm{x}\cdot\mathrm{ZrH_2}+2(1-\mathrm{x})\mathrm{H_2}$$

The corrosion rate, CR (µm/y), is obtained based on the oxidation and hydrogenation reaction under stoichiometry in Equation 2. Details for the gas flow experiment were described (T.Sakuragi, H.Tanabe et al. 2013).It should be noted that the corrosion rates for hydrogen measurements obtained in Equation 1 and Equation 2 take hydriding into account. The corrosion rate at hydrogen pick-up ratio of 100% is 3 times higher than that without hydriding.

The corrosion rates are displayed in Figure 23. The data for gas flow experiments (T.Sakuragi, H.Tanabe et al. 2013) and a part of the ampoule test (O.Kato, H.Tanabe et al. 2014) are obtained from the literature. In hydrogen measurements, the corrosion rate decreased over time. The gas flow data was used to obtain a detailed analysis of the kinetic behaviour that follows a parabolic rate law (Figure 24)(T.Sakuragi, H.Miyakawa et al. 2013). A_{gas} and A_{abs} are the amounts of gaseous and absorbed hydrogen in mol/m^2, respectively. This kinetic result differs from the general out-pile (high temperature) corrosion behaviour of the cubic rate law. The corrosion rate slightly increases with the temperature increase. The difference between Zircaloy-2 and Zircaloy-4 is negligible. In comparison with the case of pure water, the solution components and pH could slightly emphasise the corrosion rate.

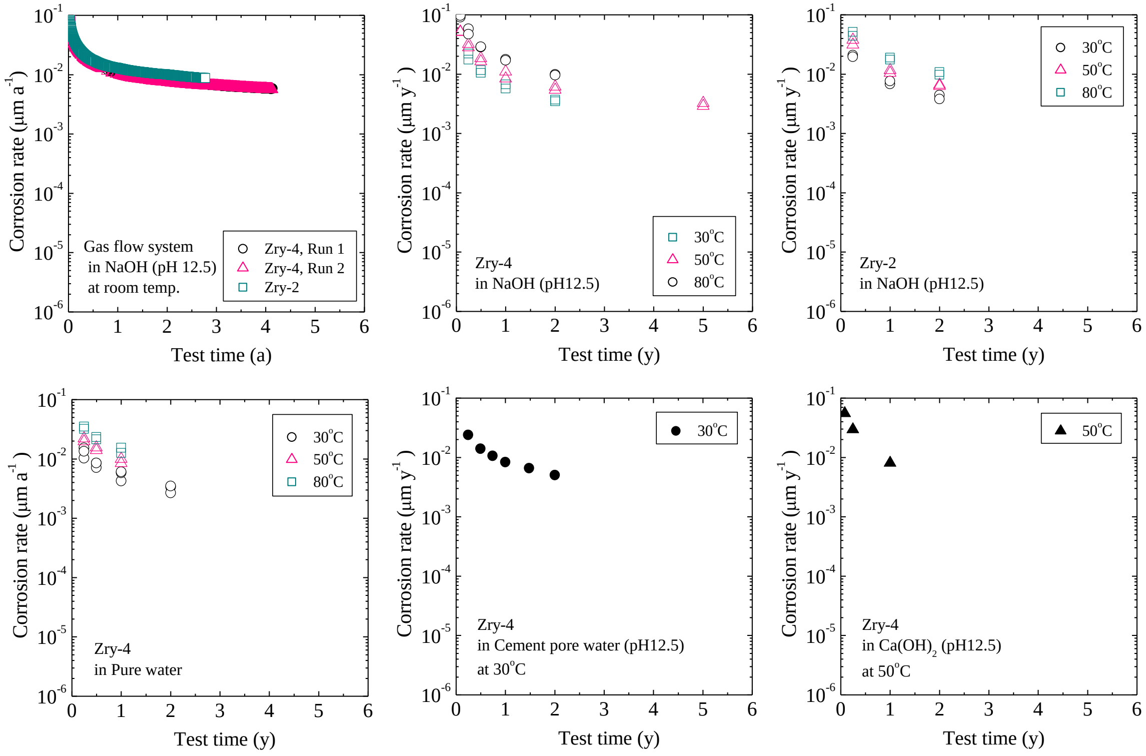


Figure 23 Corrosion rate of zirconium materials.

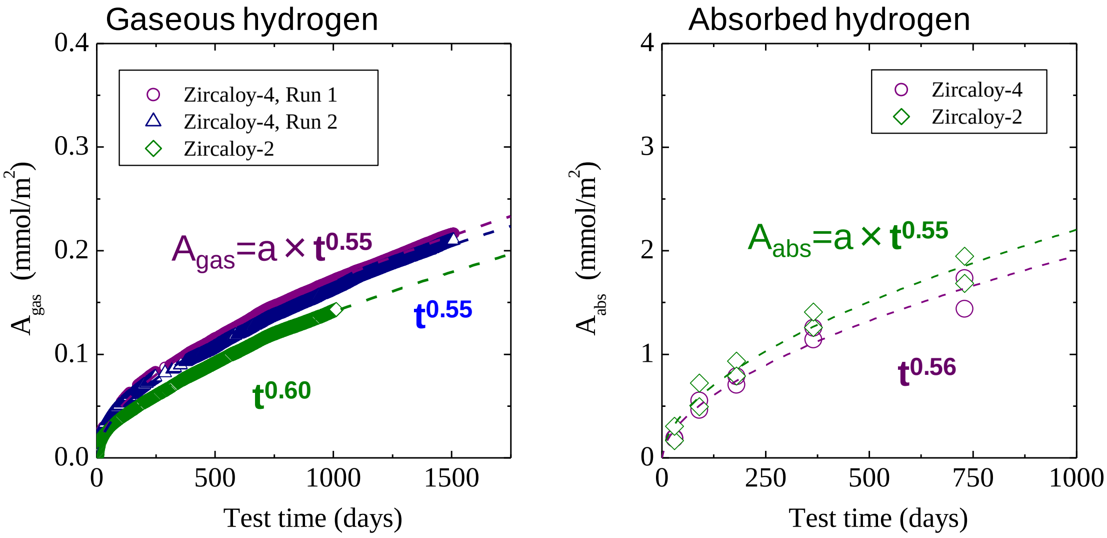


Figure 24 Gaseous hydrogen (left) and absorbed hydrogen (right) generation by the gas flow system. Dashed lines represent the least squares fit under the allometric equation of Agas, abs=a×tb (T.Sakuragi, H.Miyakawa et al. 2013).

2.8.2.2 Characterisation of the oxide film

Figure 25 shows transmission electron microscopy (TEM) analyses of Zircaloy-4 after 12 months of immersion in pure water at different temperatures. The oxide film thickness increases as the temperature increases. Indeed, it was approximately 7 nm at 30°C, 10 nm at 50°C, and 14 nm 80°C. The crystallization of oxide is shown by the electron diffractions. The tetragonal structure is likely to be formed. The XPS analysis also demonstrated the increase of the oxide thickness with temperature.

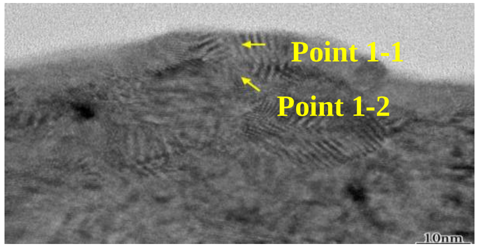
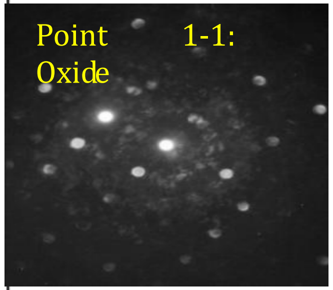
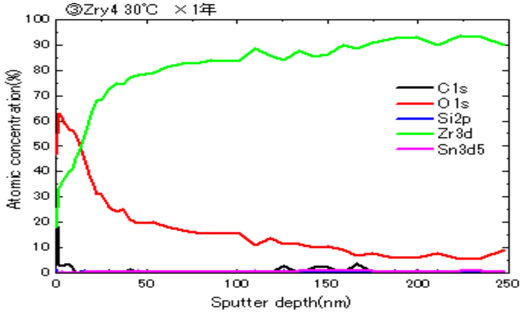
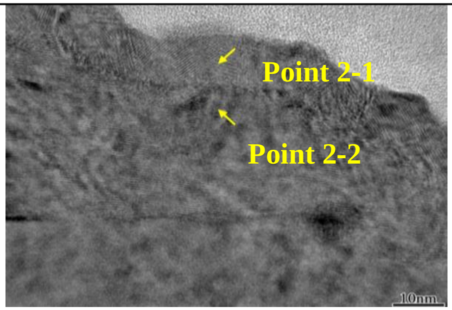
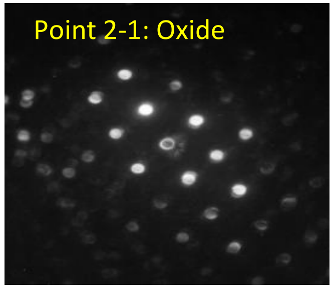
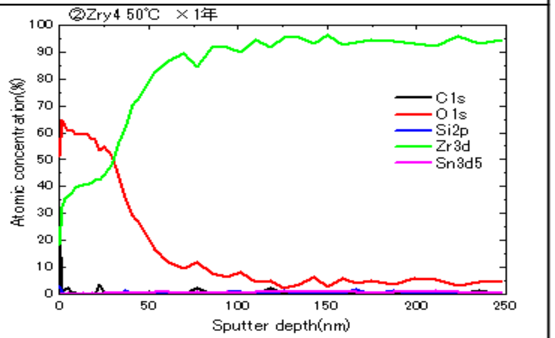
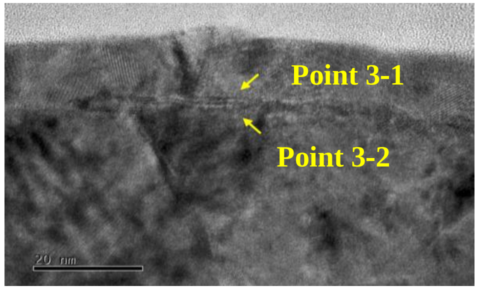
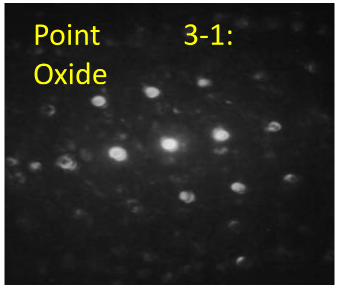
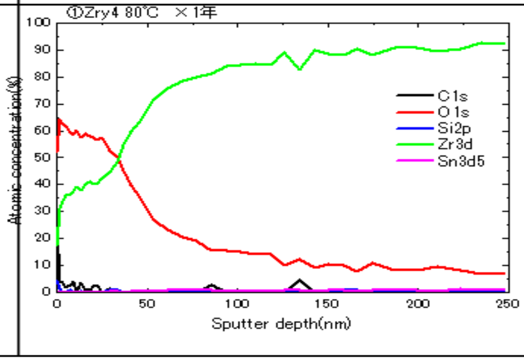
	TEM	Electron diffraction	XPS
30°C			
50°C			
80°C			

Figure 25 Oxide film measurements after 12 months in pure water.

2.8.3 Speciation study

2.8.3.1 Analytical development

The first objectives for our speciation study are the measurements and understandings of generation process of stable carbon species from the corrosion of metal. The targets are gaseous/aqueous and organic/inorganic species. Techniques using sensitive mass spectrometries coupled with chromatography are being developed. Difficulties are the contamination from environment and reagent, especially for the inorganic carbon species. The reproducibility of the measurements must be guaranteed. The developed techniques will be applied for the separation/fractionation process of a C-14 speciation measurement.

The next step is the C14 speciation. The leachates of the irradiated specimen will be analysed. Acceleration mass spectrometry (AMS) is expected to be used to quantify accurately the final C-14. There are over 10 AMS facilities in Japan. However, regulation issue on the AMS measurement must be overcome, knowing that most AMS facilities are not permitted for the use of radionuclides, nuclear fuel materials and their contaminants. If AMS is unavailable in Japan domestically, the analyses of the organic/inorganic ratio will be conducted by using the conventional liquid scintillation counting (LSC) method.

2.8.3.2 Design of the experimental setup

Leaching tests using zirconium materials have been performed by the glass ampoule method. In order to measure the gaseous carbon species in the ampoule, a measurement system, which is a closed collection and measurement system coupled with an ampoule opener and a mass spectrometer, has been developed (Figure 26). The opener was assembled with a pleated flexible tube. A quadrupole mass spectrometer was set at the beginning. The tightness and operating conditions were verified. The next step is to carry out preliminary and blank tests to check the background carbon species prior to running leaching tests and gaseous carbon measurements.

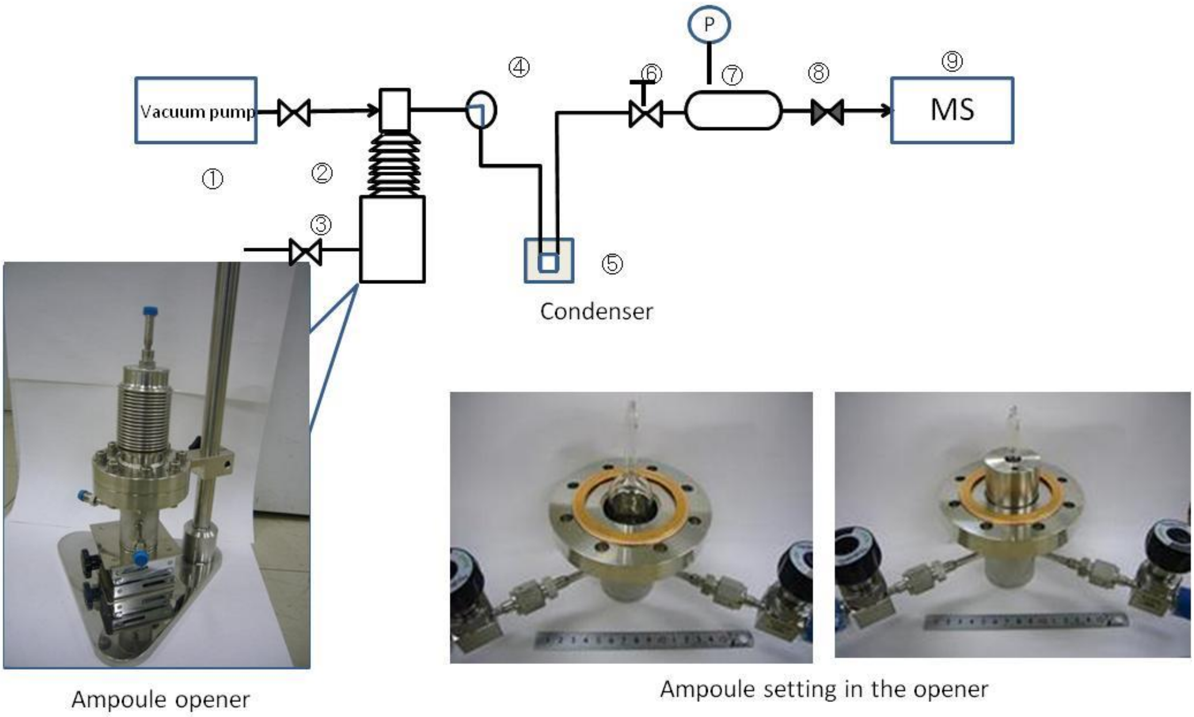


Figure 26 Experimental setup for a closed collection and measurement system of gaseous carbon species coupled with ampoule opener and Q-mass spectrometer.

2.8.4 Acknowledgement

This research is a part of the “Research and development of processing and disposal technique for TRU waste (FY2014)” program funded by Agency for Natural Resources and Energy, Ministry of Economy, Trade and Industry of Japan.

2.9 SCK.CEN contribution in WP3

In 2015, SCK.CEN was in charge of D3.10 in Task 3.3 entitled “2nd year progress report”. This deliverable consists of describing the leaching and corrosion tests including materials characterisation and experimental setup. Within WP3, SCK-CEN is in charge of four deliverables; D3.4 (issued in 2014), D3.10 (issued in 2015), D3.12 (due in 2016), and D3.17 (due in 2017).

2.9.1 Materials

Unirradiated and irradiated Zircaloy samples (Zircaloy-2/4 and M5™ (current reference cladding for AREVA fuel) will be studied. AREVA needs to provide an authorisation to SCK.CEN to work on M5™ material. A request was sent to AREVA in August 2014 but approval is still pending as their official feedback is missing.

2.9.1.1 Metallography

Metallography was carried out on unirradiated metals in the laboratory for high and medium level activity (LHMA) after the appropriate sample treatment (W.Van-Renterghem 2015). The transmission electron microscopy (TEM) investigation was conducted in a JEOL 3010 microscope operating at 300 kV. Bright field, dark field and selected area electron diffraction were used to determine the defect structure and precipitates. Energy dispersive X-ray spectroscopy (EDS) was carried out for the qualitative determination of the composition of the precipitates. The grain size of each material was determined from the backscattered electron images (BEC) of the samples after electrochemical polishing for 10 seconds in a solution of 5% perchloric acid and 95% methanol. To polish Zircaloy, the temperature of the electrolyte was reduced to -30 °C and a voltage of 25 V was applied.The grain size was determined in accordance with the ASTM standard E112-95(ASTM 2013). Figure 27 presents the BEC image of a Zry-4 sample as well as the EDS analyses conducted on a precipitate and the bulk.

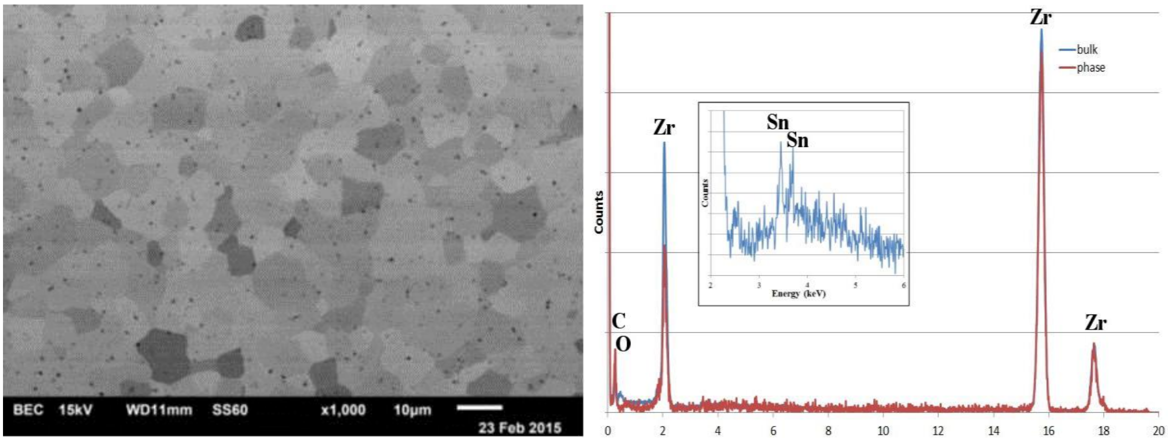


Figure 27: **Backscattered electron images of a Zry-4 sample (left); EDS spectrum (right).**

This Zry-4 material consists of small uniform equiaxed grains. The grain size number determined from the SEM images is 11.8, which corresponds to an average grain surface of 36.4 µm² or a grain diameter of 6 µm. The small black spots can be attributed to the Laves phases.

The EDS spectrum in Figure 27 shows the composition of the precipitate in comparison to the spectrum of the bulk Zry4. According to the spectrum of the precipitate, only Zr and C are detected. In addition, the carbon content is significantly higher than in the spectrum of the bulk material. The EDS results together with the crystal structure analysis confirmed the presence of carbides as ZrC precipitates.

The analysis of the irradiated samples is delayed to the end of 2015 due to staff unavailability.

2.9.1.2 Nitrogen content

Information on the nitrogen content from recent experimental studies and reports were either not available or not presented accurately (i.e. only maximum permitted values). Therefore, the initial nitrogen content within the metals was desirable to realistically estimate the ^{14}C production after irradiation campaigns.

The nitrogen contents of Zircaloy-4 samples were measured by using an inert gas fusion method. The nitrogen content measurements were performed by using a LECO TC436 model analyser. The sample was placed inside a graphite crucible and held between the upper and lower electrodes of impulse furnace. A high current passed through the crucible, enhancing an increase of the inner temperature (> 2500 ºC), and leading eventually to the melting of the sample. Gaseous compounds generated in the furnace were released into a flowing inert gas stream (argon or helium). The gas stream was sent to the appropriate infrared detector. When O as CO_2 was measured, then nitrogen was detected by thermal conductivity detector. The reported lower limit of detection of the method is approximately 1 ppm for N. Results are presented in Table 9.

Table 9 Average nitrogen content (N.avg) of unirradiated Zircaloy samples.

Sample ID	**material**	**N_{avg} (ppm)**
ZR4 19430	Zircaloy-4	17 ± 3.9
ZR4 M92029	Zircaloy-4	25 ± 2.6

The nitrogen content of Zircaloy-4 is lower than the values given in the literature and technical specifications (usually between 40-80 ppm). M5^{TM} sample will be analysed after having the approval from AREVA.

2.9.1.3 Dose rate and gamma ray spectrometry analysis

High purity germanium detector will be used for this analysis to identify the activation products present in the irradiated samples. It is planned to verify the gamma spectrometry results by determining the irradiation history with model calculations.

2.9.2 Leaching experiment

Corrosion test setups are being developed and finalised. The basic design of the setups has slightly evolved with minor modifications. Figure 28 presents a schematic diagram of the experimental setup. More details are given in D3.4 and D3.5.

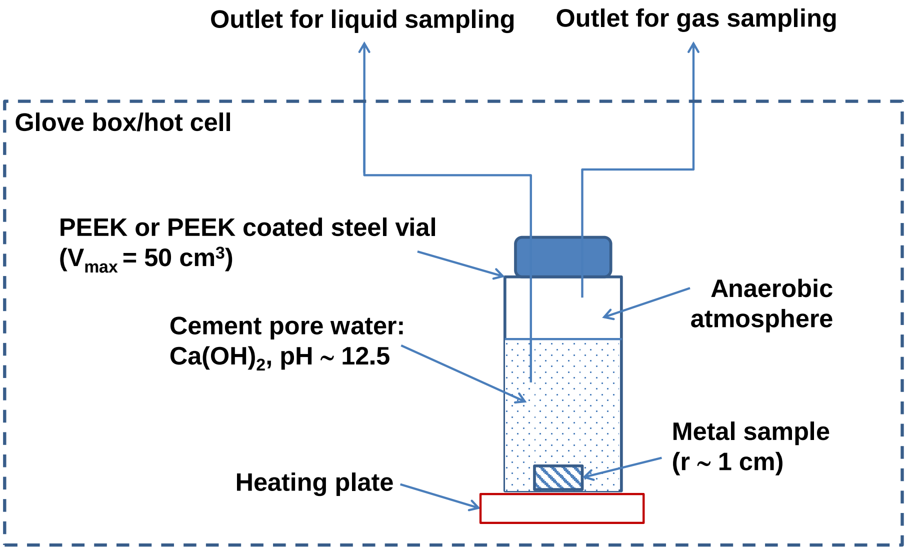


Figure 28 Proposed layout of the static leaching test setup in glove box/hot cell under reducing atmosphere

The test cell volume has been reduced from100 cm^3 to 50 cm^3 in order to reduce the matrix volume (i.e. increasing the concentration of produced carbon species) and to generate less waste volume which can be significant in case of many replicates.

The liquid phase will occupy 70-80 % of the volume and the rest is for the headspace. Sampling is planned through outlets which enable using a gas tight syringe.

2.9.3 Corrosion experiment

Special glass wares and electrodes have been designed for the electrochemical (corrosion) setup using linear polarisation resistance (LPR) technique. The inner part of the glass cell will be covered with a PEEK liner to avoid interference due to glass dissolution at high pH.

Gas tightness of the cells is tested on a cell which is identical to the setup selected for the static leaching experiments. Rubber sealing is used between the cell-lid and bottom. The cell is filled with helium. Both, the operating and ambient air pressure are monitored as well as the ambient temperature. Pressure in the glass cell was set to 1.1 bar, which is 0.1 bar above the atmospheric pressure, in order to prevent air entrance. The glass cell for the electrochemical corrosion experiment is shown in Figure 29. The stability of the gas pressure is demonstrated in Figure 30.

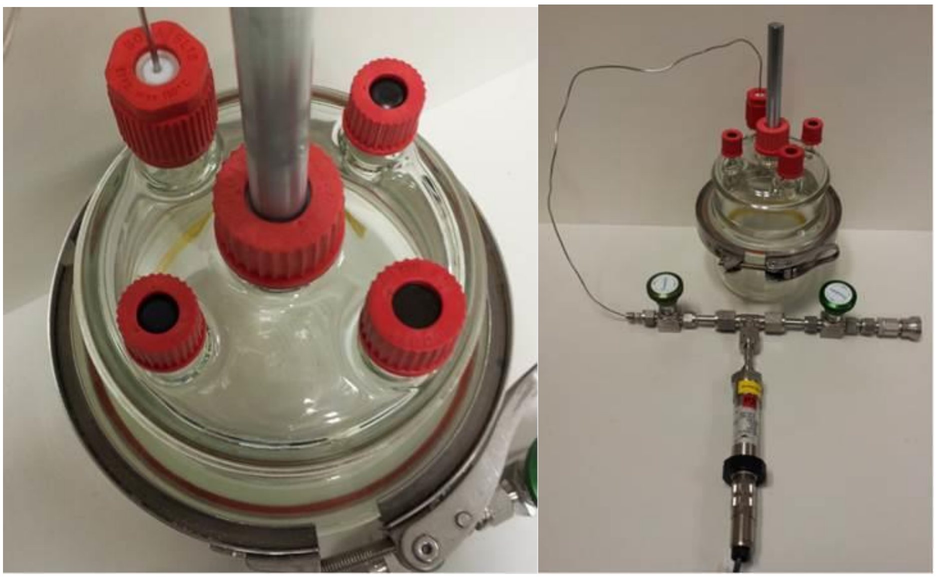


Figure 29 Glass cell for accelerated corrosion test setup.

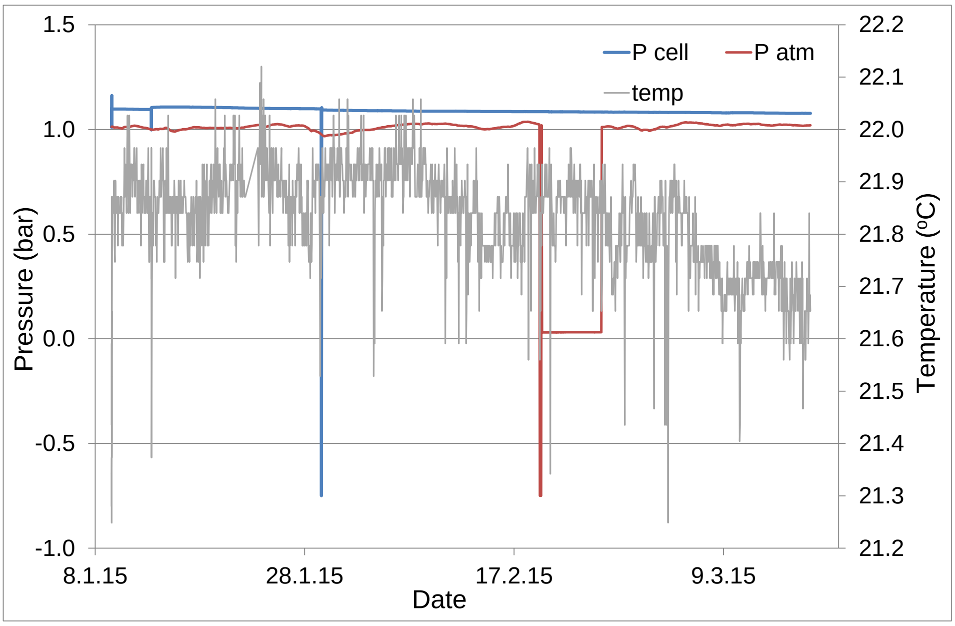


Figure 30 Temperature, internal- and external pressure profile during the gas tightness test.

The sharp decrease in the temperature and pressure indicate the experimental interruptions or sensors replacements.

2.9.4 Carbon -14 estimation

2.9.4.1 Inventory

A simple approach using the ORIGEN-ARP tool, which is part of the SCALE-6.1 package, was applied for ^{14}C production estimation in irradiated metals. This basic tool has pre-built libraries designed for several commercial assembly types for predicting the spent fuel inventory. As input parameters, the experimental nitrogen content of the metals and irradiation properties were introduced with a typical burnup of ~ 50 GWd/t_{HM}. The results from two different calculations methods of the C-14 content in irradiated Zr-4 samples, are summarised in Table 10. The average nitrogen content is in the order of 15-27 ppm.

Table 10 Estimated ^{14}C concentration of the irradiated Zircaloy-4 and their initial nitrogen content.

Sample ID	C_N (ppm)	First calculation C-14 content (Bq/g)	Computer simulation C-14 content (Bq/g)
ZR4 19430	17 ± 3.9	686	13300
ZR4 M92029	25 ± 2.6	1008	19559

The ^{14}C inventory data obtained by the computer simulation will be further refined and compared to the experimental ^{14}C measurements.

2.9.4.2 Speciation experiment

SCK•CEN plans to use the available in-house instrumentations to check if carbon species can be detected and quantified accurately. The following techniques are considered: gas chromatography (GC), high pressure liquid chromatography (HPLC), ion chromatography (IC), total organic analyser (TOC) and for the ^{14}C determination, liquid scintillation counting (LSC). The results from the total organic / inorganic carbon analysis and from the ion chromatographic analysis of the carboxylic acids are presented in Table 11 and Table 12.

Table 11 Results from the total organic and inorganic analysis of the leachates (mg/L).

Sample ID	Electrolyte/Material	TIC	TOC
BLANK_DW	De-ionized water	< 5	14.1 ± 2.6
BLANK_NaOH	0.032 M NaOH	5.2 ± 2.3	7.6 ± 2.6
BLANK_DW_GB	De-ionized water (glove box)	< 5	< 5
BLANK_NaOH_GB	0.032 M NaOH (glove box)	< 5	< 5

Zry-4-2	Unirradiated Zircaloy-4 (in de-ionized water)	< 5	< 5

Table 12 Carboxylic acid content of the leachates (mg/L).

Sample ID	Electrolyte/Material	acetate	formate	oxalate
Zry-4-2*	Unirradiated Zircaloy-4	< 0.025	< 0.05	< 0.05
Blank-W-GB	De-ionized water	< 0.025	< 0.05	< 0.05
Blank-S-GB	0.032 M NaOH	0.114	0.075	< 0.05
Blank-W	De-ionized water	3.1	< 0.05	< 0.05
Blank-S	0.032 M NaOH	2.9	3.8	< 0.05

It can be concluded that no detectable carbon was released from the Zircaloy sample at neutral pH. However, increased inorganic and organic carbon concentration can be detected in the solutions stored in a regular electrochemical laboratory due to the contamination from the ambient air. Meanwhile, solutions prepared and stored in anaerobic atmosphere, presented values below the detection limits. These results clearly highlight the importance of the electrolyte preparation and storage.

On the basis of the preliminary results, further upgrade / investment will be needed to achieve lower level carbon speciation determination goals by improving the sample preparation, pre-concentration and detection e.g. by using mass spectrometry detection. After the improvement, if carbon species are still undetectable, a laboratory equipped with an accelerator mass spectrometer (AMS) will be contacted as a backup option. It could be at PSI.

2.9.5 Acknowledgements

Thanks are due to the following units/people from SCK•CEN for their collaboration:

- –Structural Materials: Milan Konstantinovic, Luigi Puzzolante, Rik-Wouter Bosch
- –Fuel Materials: Marc Verwerft, Kevin Govers, Rémi Delville
- –Microstructural and Non-destructive Analysis: Wouter van Renterghem
- –Radiochemical Analysis and Processes: Lesley Adriaensen, Göran Verpoucke, Peter van Bree, Arnaud Campsteyn, Patrick Goethals
- –Health Physics: Koen Nijs, Rik Maussen
- –R&D Waste Packages: Bruno Kursten, Wim Verwimp, Steven Smets, Ben Gielen and Regina Vercauter
- –Mechanical Workshop: Jürgen Verlinden
- –Infrastructure Operational Support: Marc Eykmans
- –Performance Assessments: Eef Weetjens
- –Nuclear Systems Measurements: Antonin Krása

The available irradiated Zircaloy-4 specimens originate from two Belgian nuclear reactors (Tihange and Doel) and are ready for experiments.

3 Summary

3.1 *Introduction*

During the second year of the CAST project, the WP3 participants have worked on Tasks 3.2 and 3.3. The analytical strategy has taken an important part of the work already conducted. The experimental setups of the leaching and corrosion experiments have been developed for both, irradiated and unirradiated materials. The different techniques to determine the corrosion rates have been optimised. The following sections present a summary to date.

Table 13 presents the contributions of the partners involved in WP3.

Table 13 Contributions of the different partners

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
Task 3.3 – Characterisation 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

3.2 *Task 3.1*

Task 3.1 was devoted to the State of the Art on C-14 release from Zircaloy and Zr alloys under repository conditions. Deliverable D3.1, completed in 2014, is a part of this Task

(J.M.Gras 2014; S.Necib, D.Bottomley et al. 2014). It highlights some outstanding issues, which are essentially taken into consideration in WP3:

- Inventory of ^{14}C
  - Comparison between modelling and measurements
  - ^{14}C speciation into the metal and oxide layers
- Corrosion of Zircaloy at low temperatures
  - Need to explore the regime of corrosion for oxide thickness (t_{ox}) >> 2.5 µm
  - Consequences of the dense surface layer of hydrides (hydrogen pick-up ratio ~ 90 %)
  - Low dissolution rate of ZrO_2 layers in alkaline solutions in the presence of any complexing species (in relationship with the chemistry of disposal sites' groundwater)
- Leaching
  - Feedback of reprocessing plants (e.g. leaching of claddings in pools)
  - Role of thermal diffusion of ^{14}C in ZrO_2 layers and other possible mechanisms of migration
  - Chemical forms of released ^{14}C
  - Chemical stability of organic compounds in repositories

3.3 *Tasks 3.2 and 3.3*

3.3.1 Materials

In 2015, the availability of the different materials was confirmed and more details could be provided on the history (BU), microstructure, composition, etc.

Table 14 and Table 15 synthetize the available unirradiated and irradiated materials, respectively. These materials have been considered for the leaching and corrosion experiments in alkaline media. Analyses will be conducted on liquid and / or gas samples taken from the leaching solution. C-14 inventory and speciation will be determined subsequently. The principle materials to be studied are Zircaloy – 2, Zircaloy – 4 and M5^{TM}. The nitrogen content should be determined as accurately as possible as it is a precursor of C-14 (J.M.Gras 2014). Metallography has been carried out to identify the microstructure of the materials, both irradiated and unirradiated. Knowing that the dissolution of zirconia is involved in C-14 release, the thickness, properties and microstructure of zirconia has been investigated for irradiated materials. A few groups have decided to oxidise the unirradiated materials in order to form a zirconia layer under autoclave conditions. The oxide thickness should be comparable to that of the irradiated materials. If not, a thickness greater than 2.5 µm is foreseen to complete the current knowledge based on the literature survey. The cleaning of the samples should be minimised in order to be representative of the disposal conditions. Therefore, for unirradiated materials, cleaning with ethanol followed by rinsing with water and air drying is strongly advised. Regarding irradiated materials, cleaning in HNO_3 should be carried out on 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 will be performed.

Table 14 Unirradiated materials

Participants	**Zr alloys types**	**Chemical composition (real N)**	**Metallography**	**Pre-treatment of the surface specimen**	**Oxide thickness (µm)**
ITU/JRC	Zr-4	To be requested	To be done	As-received	~ 3
RATEN ICN **(ex. INR)**	Zr-4	10 ppm	OM, SEM	Sample oxidation to get similar oxide layer thickness as the irradiated one	1.7 – 2.2
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

Table 15 Irradiated materials

Participants	**Zr alloys types**	**Chemical composition (real N)**	**Microstructure**	**Activation history (known)**	**^{14}C Inventory** **(Bq/g)**	**Pre-treatment of specimen, i.e. surface condition etc.**
Areva	Supply the materials to CEA					
CEA	M5 / Zr4(inner layer)Zr-0.8%Sn (outer layer) Tube shape	Incomplete	OM (planned)	46.570 GWd/tHM / 54.500 GWd/tHM	To be done	Industrial treatment (shearing, fuel dissolution in boiling HNO_3, rinsing)
ITU/JRC	Zr-4 with Zr-2.5Nb (external cladding) Ring shape	To be requested	OM + SEM (planned)	Max 100.5GWd/tHM	To be done	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-	Nominal	OM	50.4	Calculated:	wash cycle with

	0.8%Sn (outer layer) Ring shape			GWd/tHM	$3.2(\pm0.3)\times10^4$ Experimental: $3.7(\pm0.4)\times10^4$	ultrapure water / ultrasonic bath
RATEN ICN **(ex. INR)**	Zr-4 Tube shape	10 ppm	OM	7.5GWday/tHM	To be done	spent fuel dissolution using HNO_3; rinsing with pure water
RWMC	Zr-2 STEP3	Not available	OM	39.7 GWd/tHM 3 cycles	Metal ; 1.74 $\times10^4$	Polishing and rinsing with pure water, (removal of the oxide layer)
	Zr-2 STEP1	Not available	OM	41.6 GWd/tHM 5 cycles	Metal ; 2.48 $\times10^4$	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; 3.57×10^4, 1.53×10^4 3.42×10^4	Polishing inner surface and rinsing with pure water. (samples with oxide of outer surface)
	Zr-2 STEP 1	Not available	OM	34.2	Oxide (outer film)	Removed from Zr-2

				41.6 37.4	4.04 x10^4 5.69 x10^4 5.82 x10^4 (Bq/gr)* *Bq/gr is in terms of Zr metal weight, not the weight of ZrO2 (gr-ZrO2 corrected to gr-Zr using each density)	tube
SCK-CEN	Zr-4	17-25 ppm (measured)	OM + TEM	49 GWd/tHM	Calculated: 1.33 x10^4 1.95 x10^4	Rinsing with water + drying in air
Subatech/Armines	Zr-4 (Identical to CEA)					

3.3.2 Task 3.2

Task 3.2 is devoted to the analytical development based on the needs highlighted in Task 3.1. The main contributors to this task are CEA, KIT and Subatech / Armines who are responsible for deliverables D3.3, D3.7 and D3.9 respectively. JRC / ITU, RATEN ICN, RWMC and SCK.CEN are also involved at a lower level.

In 2015, a workshop on analytical development was conducted at PSI. To successfully achieve the chemical analyses, materials preparation and cleaning should be carried out with a great attention. Blank tests should be performed prior to running the leaching and corrosion experiments in order to determine the background C content.

Table 16 and Table 17 summarise the analytical development and the results from the blank tests respectively.

Table 16 Analytical development

Participants	Sampling (gas/liquid)	C-14 speciation	Techniques	Aims
CEA	Liquid	yes	TC analyser (TIC + TOC) LSC or AMS IR IC GC-MS ESI – MS	Total Carbon Quantification of C-14 Speciation (organic molecules) Quantification of carboxylic acids Low molecular weight molecules High molecular weight
ITU/JRC	Gas and liquid	Only gas /liquid phase separation	LSC ICP-MS GC-MS	TIC-14/TOC-14
KIT	Gas and liquid	yes	LSC ICP-MS GC-MS α-γ-spectrometry	TIC-14/TOC-14 Inventory Activity
RATEN ICN	Liquid	Only inorganic/ organic fractions	LSC	TIC-14/TOC-14
RWMC	Gas and liquid	yes	LSC γ-spectrometry IC-MS	Partition Activity Organic/Inorganic
SCK-CEN	Gas and liquid	yes	γ-spectrometry LSC / (AMS) TOC GC IC	Activity Inventory Speciation
Subatech / Armines	Liquid	yes	LSC IC	TIC-14/TOC-14 Speciation

Table 17 Current results on blank tests

Participants	Electrolyte	Temperature	Duration	Materials	Activity	TIC mg/L	TOC mg/L
SCK-CEN	Deionised water pH 7 in GB (deaerated) Deionised water pH 7 (aerated) NaOH pH 12-12.5 in GB (deaerated) NaOH pH 12-12.5 (aerated)	25°C	18 days	Blank test	-	<5 <5 5.2±2.3 <5	<5 14.1±2.6 7.6±2.6 <5
	Deionised water pH 7 in GB (deaerated)			Unirradiated Zr-4	-	<5	<5

3.3.3 Task 3.3

This task involves 15 deliverables (D3.2, D3.4-6, D3.8-D3.19). In 2015, the activities have been focused on the experimental set-up including the purchase, design of equipment, preliminary tests, determination of the reference leaching solution, time duration and temperature. It has been decided to use a reference solution of NaOH at pH = 12 and room temperature. The reference time duration is 6 months. The leaching solution and environmental parameters for the leaching and corrosion experiments are summarized in Table 18 and Table 19. Table 20 and Table 21 summarize the current corrosion experiments planned in WP3 for irradiated and unirradiated materials.

The surface of the samples must be the most representative of the real conditions, therefore polishing should be avoided for irradiated samples. In addition C-14 is present in zirconia, therefore polishing would enhance the removal of zirconia and modify the inventory. Surface characterisation must be conducted prior to running the corrosion experiments.

For sensitivity purposes, gravimetric measurements are no longer considered to measure the corrosion rate (CR). Instead, Co^{60} counting will be attempted. Linear polarisation resistance (LPR) measurements have been maintained. The measurements of the released fractions of C-14 and Zr are strongly recommended to complete the work already undertaken by RWMC.

The results obtained during 2015 in terms of CR and C-14 measurements are summarized in Table 22 and Table 23. The current results on C-14 analyses (inventory and speciation) are summarised in Table 24.

Table 18 Leaching conditions for irradiated materials

Participants	Porewater	pH	Temperature	O_2 measured	Duration
CEA	NaOH	12	~25°C	no	3 weeks -6 months
ITU/JRC	NaOH	~12 (not buffered)	30°C 80°C (possibly)	No	3 months
KIT	H_2SO_4/HF	1–3	ambient	not applicable due to argon / hydrogen overpressure	30 min – 6 hours
RATEN ICN	NaOH	12.5	Room temperature	Monitoring of the O_2 content will be attempted	1 year
RWMC	NaOH	12.5	Room temperature	Eh < -250 mV Calculated by ORP	10 years (max)
SCK-CEN	$Ca(OH)_2$	12.5	ambient	no	1 year
Subatech/Armines	NaOH	12	25°C	ambient	6 -12 months

Table 19 Leaching solution for unirradiated materials

Participants	Porewater	pH	Temperature	O2 measured	Duration
ITU/JRC	NaOH	~12 (not buffered)	30°C	No	~3 months
RATEN ICN	NaOH	12.5	Ambient 80°C	Monitoring of the O_2 content will be attempted	1 year
RWMC	pure water, NaOH, $Ca(OH)_2$,	7 – 8 12.5	30°C, 50°C, 80°C 160°C	< 0.1 ppm	1-60 months
	pure water	7 - 8	180°C, 270°C	< 8ppm	up to 200days (30days interval)

Table 20 Corrosion experiments for irradiated materials

Participants	Corrosion rate
ITU/JRC	Co^{60} counting
RATEN ICN	Co^{60} counting + LPR
RWMC	Estimated by C-14 released fraction
SCK-CEN	LPR

Table 21 Corrosion experiment for unirradiated materials

Participants	Corrosion rate
SCK-CEN	LPR
ITU/JRC	Possible (from H_2 measurements)
RWMC	H_2 measurements
RATEN ICN	LPR

Table 22 Current results on CR for irradiated materials in the reference solution

Participants	Materials	Solution	CR (nm/yr)
SCK-CEN	Zr-4	$Ca(OH)_2$	To be determined
ITU/JRC	Zr-4	NaOH	To be determined
RWMC	Zr-2 Zr-4	NaOH	~10
RATEN ICN	Zr-4	NaOH	To be determined

Table 23 Current results on CR measurements for unirradiated materials in the reference solution (NaOH, pH12, room T)

Participants	Materials	Solution	CR (nm/yr)
RATEN ICN	Zr-4	NaOH	3 – 480 (LPR)
RWMC	Zr-2 Zr-4	NaOH	~ 5nm over 2yrs (H_2 measurements)
SCK-CEN	Zr-4	$Ca(OH)_2$	To be determined

Table 24 Current results on C-14 analyses (inventory + leached in NaOH solution pH 12)

Participants	Electrolyte	Temperature	Duration	Materials	c-14 Bq/gr	Inorganic Bq/gr	Organic Bq/gr
KIT	H_2SO_4/HF (30°C) pH 1-3	30°C	30 min 5 hours	Zr-4	Calculated: $3.2(\pm0.3)\times10^4$ Experimental: $3.7(\pm0.4)\times10^4$(<1%)	Liquid:$1.0(\pm0.1)\times10^1$ (<1%) Gas: $7.2(\pm0.7)\times10^1$ (<1%)	Liquid: $4.0(\pm0.4)\times10^3$ (11.4%) Gas: $3.1(\pm0.3)\times10^4$ (88.4%)
RWMC	NaOHH 12.5	RT	1-5 years	Zr-2	0.007 – 0.1815 Bq/gr of solution	I0.0047 – 0.0153 Bq/gr of solution (18 – 73%)	0.0017 – 0.0357 Bq/gr of solution (27 – 82%)

4 Conclusions

In 2015, WP3 activities have been focusing on Tasks 3.2 and 3.3; aiming towards the analytical development and C-14 analyses from irradiated Zircaloys in disposal conditions.

Five deliverables (D3.6, D3.7, D3.8, D3.10 and D3.11) have been submitted and / or approved. The MS5 milestone was reached with the work accomplished by KIT.

Most materials have been characterised in terms of microstructure, oxide thickness, hydrides, precipitates and composition. The knowledge on the analytical techniques has been optimised and shared with WP2. The reference solution, time duration, temperature… have been set. Most participants have finalised their experimental setup for the leaching and corrosion experiments. Those who have not started yet, are expected to start by the end of this year.

Some results are already available in terms of C-14 inventory and / or corrosion rate measurements in H_2SO_4/HF , NaOH (pH 12), $Ca(OH)_2$ (pH 12) and pure water for irradiated Zr-2 and Zr-4.

2016 will be devoted to continue the work involved in Task 3.3 and start Task 3.4.

A progress WP3 meeting will be held in June 2016 to discuss the ongoing work.

References

ASTM (2004). G102 - 2004 Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements.

ASTM (2013). ASTM E112-13 Standard test method for determining average grain size.

Atkinson, A., D. J. Goult, et al. (1985). "An Assessment of the Long-Term Durability of Concrete in Radioactive Waste Repositories." Scientific Basis for Nuclear Waste Management IX, Material Research Society Symposium Proceedings, Stockholm, Sweden **50**: 239-246.

BGBL (2005). Verordnung über den Schutz vor Schäden durch ionisierende Strahlen (Strahlenschutzverordnung - StrlSchV). BGBl.

J.M.Gras (2014). State of the art of rac in Zircaloy andZr alloys - C-14 release from zirconium alloy hulls, CAST Project. Task 3.1, D3.1 deliverable.

Ken'ichi Ito, Katsumasa Haikawa, et al. (1998). Top Technologies of ABWR Part 2: BWR Core and Fuel Technologies. **47**.

O.Kato, H.Tanabe, et al. (2014). "Corrosion tests of Zircaloy hull waste to confirm applicability of corrosion model and to evaluate influence factors on corrosion rate under geological disposal conditions." Material Research Society Symposium Proceedings **1665**: 195-202.

S.Necib, D.Bottomley, et al. (2014). 1st year Annual WP3 progress report (D3.5) - CAST Project.

T.Sakuragi, H.Miyakawa, et al. (2013). "Long term corrosion of Zircaloy-4 and Zircaloy-2 by continuous hydrogen measurement under repository conditions." Material Research Society Symposium Proceedings **1518**: 173-178.

T.Sakuragi, H.Tanabe, et al. (2013). Estimation of C-14 inventory in hull and end piece wastes from Japanese commercial reprocessing operation paper n° 96110. 15th International conference on Environmental Remediation and Radioactive Waste Management Brussels, Belgium.

W.Van-Renterghem (2015). Microstructure of the RPV- steel and Zircaloy-4 used in the project CAST / Internal SCK.CEN report, Belgian Nuclear Research Centre.

Y.Yamashita, H.Tanabe, et al. (2014). "C-14 release behavior and chemical species from irradiated hull waste under geological disposal conditions." Material Research Society Symposium Proceedings **1665**: 187-194.

Yamaguchi, T., S. Tanuma, et al. (1999). A Study on Chemical Forms and Migration Behavior of Radionuclides in Hull Wastes. 7th International Conference on Environmental Remediation and Radioactive Waste Management - ICEM 1999, Nagoya, Japan.

Glossary

AMS: Accelerated Mass Spectrometer

BWR: Boiling Water Reactor

GC: Gas Chromatography

GMS : Gas Mass spectrometer

HLPC: High Performance Liquid Chromatography

ICP-MS : Inductively coupled plasma mass spectrometry

IR: Infra-Red Spectroscopy

LPR : Linear Polarisation Resistance

LSC: Liquid Scintillation Counting

OM: Optical Microscopy

PWR: Pressurised Water Reactor

SEM: Scanning Electron Microscopy

Zry-2, Zr-2: Zircaloy-2

Zry-4, Zr-4: Zircaloy-4