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CAST

Final report on C-14 released from irradiated Zircaloys in NaOH solution: quantification and speciation of C-14

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Date of issue of this report: 14/12/2017

The project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no. 604779, the CAST project.

Dissemination Level		
PU	Public	×
RE	Restricted to the partners of the CAST project	
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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 in underground geological disposal facilities. The project focuses on the release of carbon-14 as dissolved and gaseous species from irradiated metallic materials (steels, Zircaloys), irradiated graphite and from ion-exchange resins.

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

For more information, please visit the CAST website at:

http://www.projectcast.eu

CAST		
Work Package: 3	CAST Document no. D3.18	Document type: R
Task: 3.3		R = report,
Issued by:	CEA / SUBATECH	Document status:
Internal no.: NA		Final

Document title
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Executive Summary

CEA and Subatech developed analytical methods to determine C-14 speciation and quantify the inorganic / organic partition released in NaOH solution pH 12 from M5-type and D4R-type Zircaloy hulls. The leaching experiments were carried out for 14 days and 6 months.

CEA activities focused on determining the inorganic / organic partition as well as detecting the presence of organic molecules by the use of ion chromatography.

Subatech activities focused on developing a filtration technique by the use of resin. In addition, Subatech worked on the identification of carboxylic acids.

Both CEA and Subatech used the liquid scintillation technique to quantify C-14. Due to low concentrations of C-14 released in solution, it was not possible to use liquid scintillation counting (LSC) to quantify precisely the concentration of a given molecule. Therefore, attention was driven to accelerated mass spectrometry measurements. The analytical development is in progress.

Two different laboratories are involved in this task.

Overall the results have revealed both discrepancies and similarities between CEA and Subatech experiments. Indeed, CEA has found significantly lower C-14 concentrations than Subatech.

By contrast, the inorganic / organic partitions revealed consistency of the results with slightly more inorganic molecules than organic molecules.

In terms of organic molecules, CEA and Subatech found oxalate, formate and propionate. CEA found two more molecules as yet unidentified, and Subatech identified propionate.

CEA results highlighted a potential instability of the molecule speciation overtime. Another assumption could be a contamination of the leaching reactant, possibly during the measurements.

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1. Activities performed by CEA

1.1 *Introduction*

Leaching experiments have been carried out by CEA Marcoule on irradiated M5-type (UOX) and D4R-type (also known as Zy-4-type) (MOX) Zirconium-based alloy (Zircaloy) hulls supplied by AREVA. The hull samples were taken from fuel rods discharged from PWR reactors and reprocessed in AREVA-La Hague following the industrial process of shearing/dissolution/rinsing. Details on the experimental conditions and characteristics of the Zircaloy hulls are presented in the D3.2 report [Caron et al., 2014]. Leaching experiments have been carried out in alkaline NaOH solution at pH 12 and room temperature (25°C) under anoxic atmosphere. Samplings were conducted after 14 days and 6 months of leaching (Figure 1).

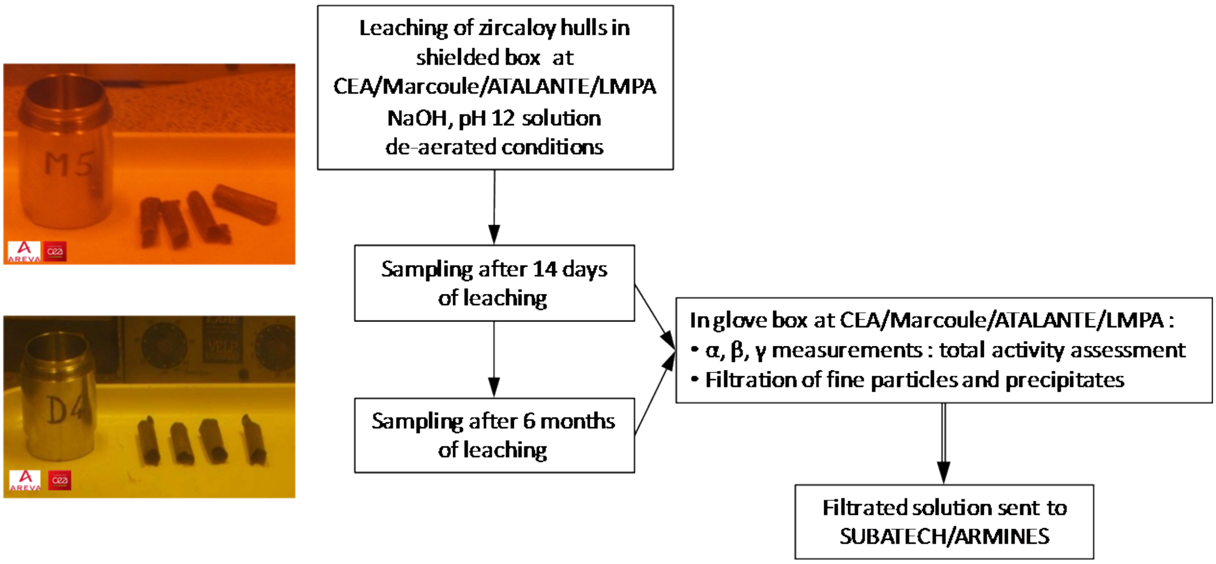

Figure 1: Leaching experimental conditions and sampling conditions. ATALANTE: ATelier Alpha et Laboratoires pour ANalyses; LMPA: Laboratoire d'études des Matériaux et Procédés Actifs

The goal of work reported herein is to have a quantification of organic and inorganic ^{14}C potentially released from irradiated Zr fuel claddings in a cementitious environment (NaOH solution, pH 12) leaching solution. The strategy has focused on the total ^{14}C analysis and organic /inorganic ^{14}C partition. Quantification of total ^{14}C was carried out by pyrolysis followed by Liquid Scintillation Counting (LSC), Partition of inorganic and organic ^{14}C was performed based on a method developed by the LASE laboratory.

1.2 *Materials*

Table 1 presents the materials' history. The hulls were subjected to an industrial treatment in AREVA-La Hague. Moreover a second rinse with nitric acid was also performed at Atalante facility in order to limit the activity of the leaching samples.

Table 1: Hulls irradiation characteristics.

Hulls reference	M5	MOX D4
Cladding material	M5	Inner layer = Zy-4 outer layer Zr-0.8%Sn
Fuel type	UOx (3.88% ^{235}U)	MOX (7.2% Pu)
Irradiation time	1937 days	2293 days
Mean Burn up	46570 MWd/t$_{HM}$	54500 MWd/t$_{HM}$
Reactor (PWR)	EDF Nogent 2	Gösgen (Switzerland)
Discharged from reactor	June 2004	June 2002
Output of AREVA	October 2009	Sept. 2008

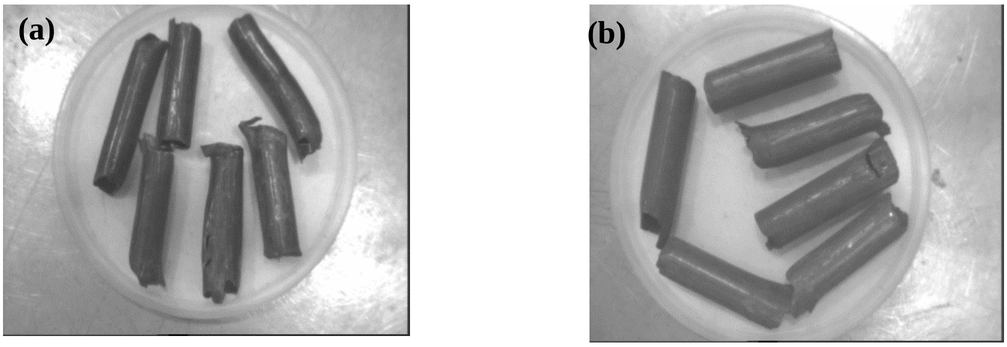

Figure 2: Image of the two batches of 6 Zircaloy-based alloy hulls (a) M5-type (UOX) and (b) D4R-type (Duplex, MOX).

As shown in Figure 2, the selected samples have a defined geometry with a cylindrical shape of claddings in order to have the same surface in contact with the leaching solution.

Consequently, the kinetics of C-14 released in solution can be compared. The general characteristics of the selected hulls are presented in the Table 2.

Table 2: General characteristics of the selected hull.

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

In order to characterise the oxide layer formed at the metal surface, RAMAN spectroscopy was used in a hot cell of Atalante Facility (DHA lab). Figure 3 shows representative spectra obtained for M5-type hulls. The Raman bands correspond to ZrO_2 monoclinic phase [BAR, 1997]. Moreover the spectra are very close to the one obtained after zirconium alloy oxidation in PWR primary water conditions [VER, 2015]. Consequently, the acidic treatments performed in Areva La Hague and in Atalante did not change the structure of the oxide layer already formed in reactor.

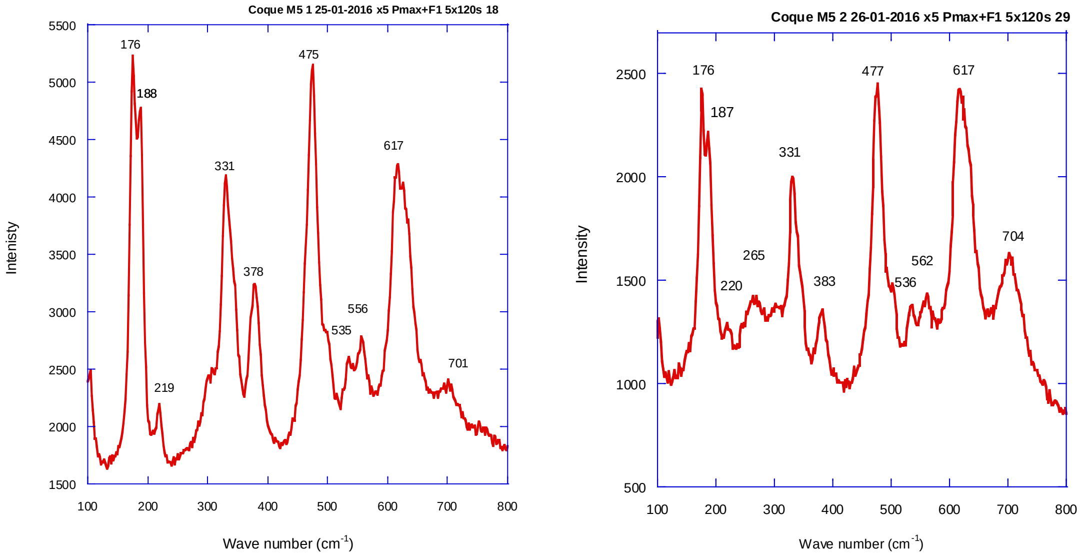

Figure 3 : Raman spectra on M5 hulls before leaching

1.3 *Preliminary test*

Before starting the leaching tests, a preliminary test was conducted in aerated and alkaline (NaOH) conditions at pH 12 has been carried out with a M5-type hull during 14 days in a volume of 235 mL of water. The aim of this experiment was to check the feasibility of the radiochemical analysis in NaOH solution. In addition, to ship the leachates to CEA Saclay and SUBATECH, the activity of the solution had to be known. The experimental parameters (volume, time, number of hulls…) were subsequently determined. After each sampling, βγ activity and α activity were measured by radiochemical counting. Results are shown in Figure 4 for two hulls in 30 mL. The maximum βγ activity is about 840 $Bq.mL^{-1}$ which represents an activity of 50.6 kBq. As shown in Figure 4 (red line), this value is less than the activity limit accepted to ship samples to SUBATECH (1Mbq). The α activity is maximum at the beginning of the experiment (about 30 $Bq.mL^{-1}$). For two hulls and 30 mL sampling the activity calculated is equal to 1800 Bq which is still below the activity limit of SUBATECH (2000 Bq).

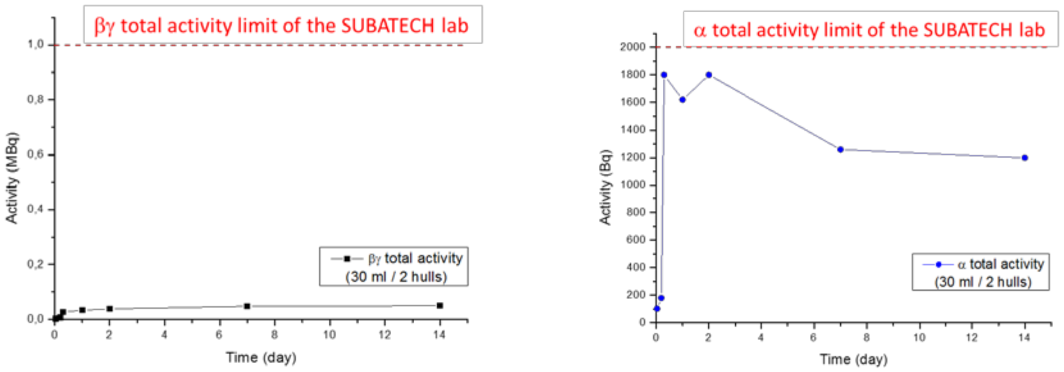

Figure 4 : Evolution of the βγ activity (left) and α activity (right) during the preliminary test

The preliminary leaching test has confirmed the experimental conditions for the leaching test (2 hulls, 30 mL sampling at the end of the test).

1.4 *Leaching experiments*

The leaching experiments were carried out with two types of hulls (7,7g of M5 Zircaloy and 8,8g of MOX D4R Zircaloy). They were placed in a reactor (235 mL) in an alkaline NaOH 10^{-2} $mol.L^{-1}$ solution, (reference groundwater, pH 12) under anoxic conditions (4.6 bar of argon) (Figure 5 and Figure 6). After static leaching (without solution renewal) in a hot cell at room temperature (28 ± 2°C), two samplings were performed after 14 days and 6 months. Samples were filtered before analysis (millipore IC Millex-LH, PTFE hydrophilic 0.45 µm filter). Two “blanks” of alkaline solution (NaOH 10^{-2} $mol.L^{-1}$ filtered) were also sampled after 1 hour and 5 hours in hot cell conditions in order to take into consideration the background in the measured C-14 concentrations.

After 14 days, only 20 ml of filtered solution was withdrawn in order to maintain the volume of solution relatively constant during the leaching test. After 6 months all the solution was withdrawn (about 200mL).

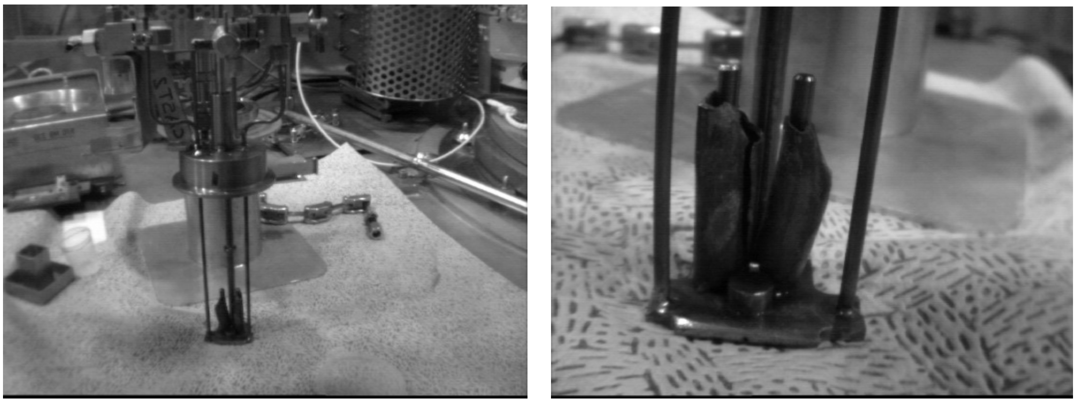

Figure 5 : Photograph of the hulls on the oxidized sample holder

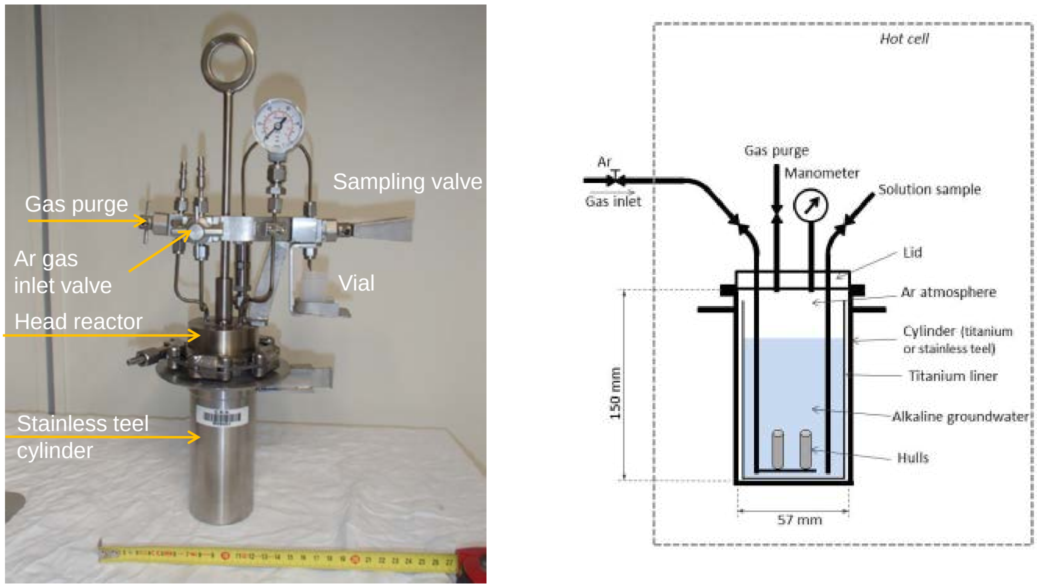

Figure 6 : (a) Photograph and (b) schematic diagram of the experimental setup for static leaching tests in NaOH solution

After each sampling and transfer to the radiochemical analysis laboratory, α and βγ activities were measured. The results are presented in Table 3 and Table 4 for the M5-type and D4R-type hull leaching tests respectively.

Table 3 : Radiochemical analysis of sampling for M5 hulls leaching test

M5-type hulls (start 02/02/16)	**14 days (16/02/16)**	**6 Months (02/08/16)**
α activity (Bq/mL)	59 (±24)	42 (±17)
β activity (Bq/mL)	2300 (±460)	2310 (±462)
γ activity (Bq/mL)	2430 (±251)	2280 (±241)

According to the results, presented in Table 3, activities do not vary between 14 days and 6 months showing that radioactive species are released at the beginning of the test. Moreover activity values are in good agreement with the acceptance limits of the laboratories in charge of the analyses.

Table 4 : Radiochemical analysis of sampling for D4R hulls leaching test

D4R-type hulls (start 20/09/16)	**14 days (4/10/16)**	**6 Months (23/03/17)**
α activity (Bq/mL)	727 (±145)	631 (± 126)
β activity (Bq/mL)	4420 (±302)	6404 (± 640)
γ activity (Bq/mL)	4290 (±302)	6000 (±389)

After radiochemical analysis, samples (about 5 mL after 14 days and about 50 mL after 6 months) as well as the blanks of the NaOH solution were sent to the three laboratories in charge of C-14 analyses (CEA/DEN/DPC/SECR/LRMO, CEA/DEN/DPC/SEARS/LASE and SUBATECH).

1.5 *Surface characterisations*

Raman spectroscopy was carried out before and further to the leaching experiments. Between 20 and 30 grains were analysed on each sample. Results are presented in Figure 7.

Highly luminescent spectra were observed on the M5-type and D4R-type hulls, indicating the presence of metallic zones.

Monoclinic zirconia was identified as expected in the temperature and pressure conditions of the leaching experiments.

Moreover, several spectra show a band defects around 710 cm^{-1}. This band appears on irradiated zirconia either in reactor or under heavy ions beam. The intensity of this defects band may vary along with the irradiation damage, but also with the orientation of the zirconia grains. This defect band was attributed to oxygen vacancies.

Time exposure did not seem to influence the oxide layer according to the Raman observations.

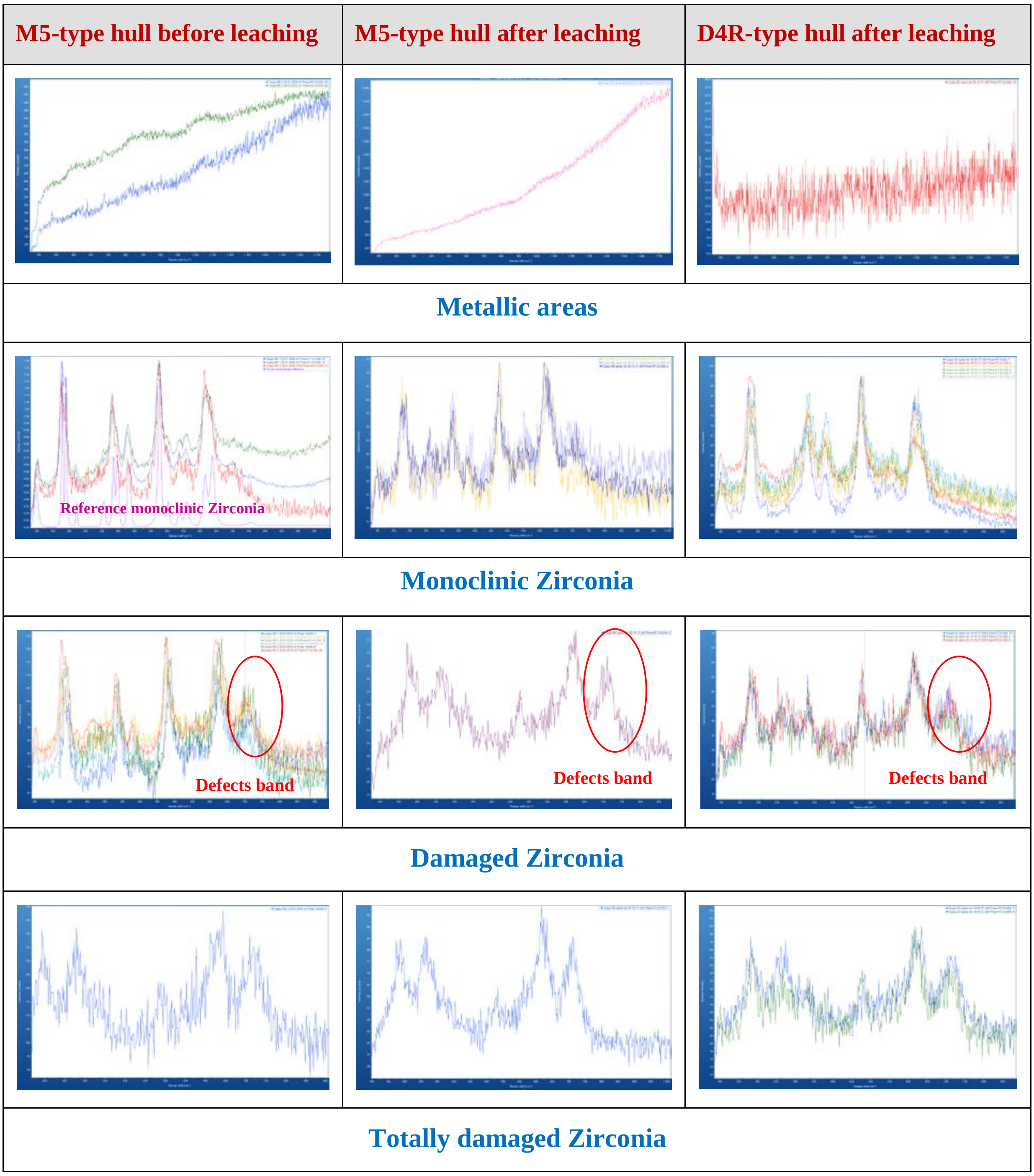

Figure 7 : Raman spectra obtained on M5 and D4R hulls

1.6 *Analytical methods for C-14 analyses*

1.6.1 Total C-14 determination

The determination of total ^{14}C in the leachate sample has been realised on a tri-tube pyrolysis furnace manufactured by ERALY et associés (Noisy le roi, France) (Figure 8).

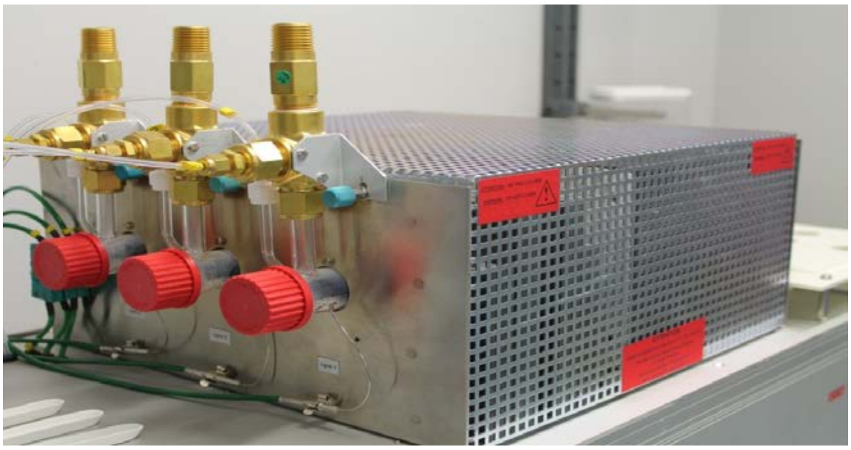

Figure 8: Tri-tube pyrolysis furnace.

The furnace has two independent heating zones. The first one, where the sample is placed, is programmable (temperature gradient), whereas the second heating zone remains at 950°C. The sample in the first zone is under nitrogen atmosphere during the heat-up, while the second zone is under N_2 + O_2 atmosphere. This is carried out in order to ensure the complete combustion of the gases released during the pyrolysis taking place in the first zone. The gas flow rate is 150 mL/min in both zones. The leachate sample (between 0.1 and 0.5 mL) is placed into the cold furnace in ceramic boats as shown in Figure 9.

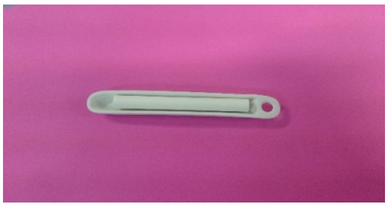

Figure 9: Ceramic boat.

As the temperature rises, the given off gases are trapped in 3 successive bubblers. The first one containing 0.1M HCl traps ^{3}H and the last two, containing CarboSorb trap ^{14}C (Figure 10).

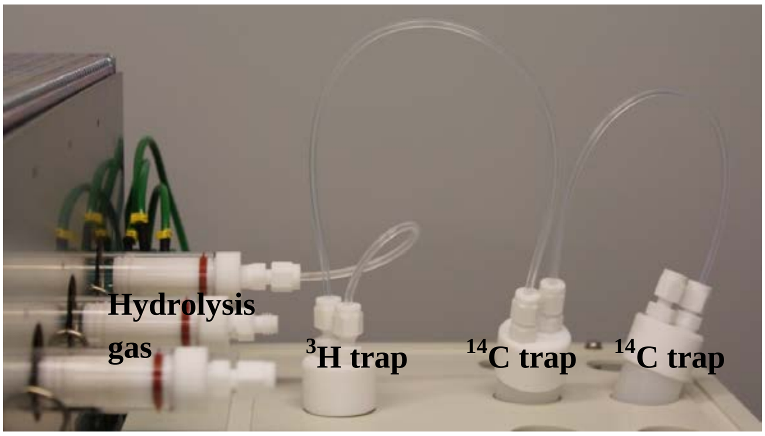

Figure 10: system to trap the pyrolysis gases.

The applied temperature gradient is shown in Figure 11. The temperature program has been optimised to ensure a recovery of both ^{3}H and ^{14}C above 90 % for liquid samples.

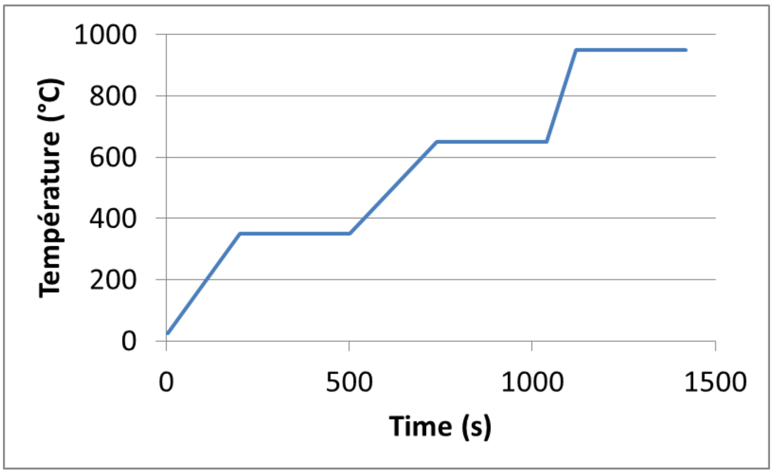

Figure 11: Temperature program used for leachate solution pyrolysis.

^{14}C trapped in the CarboSorb solution has been measured by Liquid Scintillation Counting on a Tricarb 2910TR apparatus calibrated by the establishment of a quenching curve.

In the tested conditions, the detection limit of ^{14}C is around 0.3-0.5 Bq/mL of sample in the ceramic boat.

1.6.2 Organic and inorganic C-14 partition

The LASE laboratory had no previous experience on the analysis of ^{14}C partitioning. Based on the reaction used to make organic / inorganic partition in commercial apparatus, a method has been developed. A small volume of the leachate solution (1 mL) was treated with a solution of H_3PO_4 25 % under N_2 bubbling to guide the CO_2 produced from inorganic C in a trap solution (NaOH) (Figure 12). Organic carbon is retained in the reaction vessel.

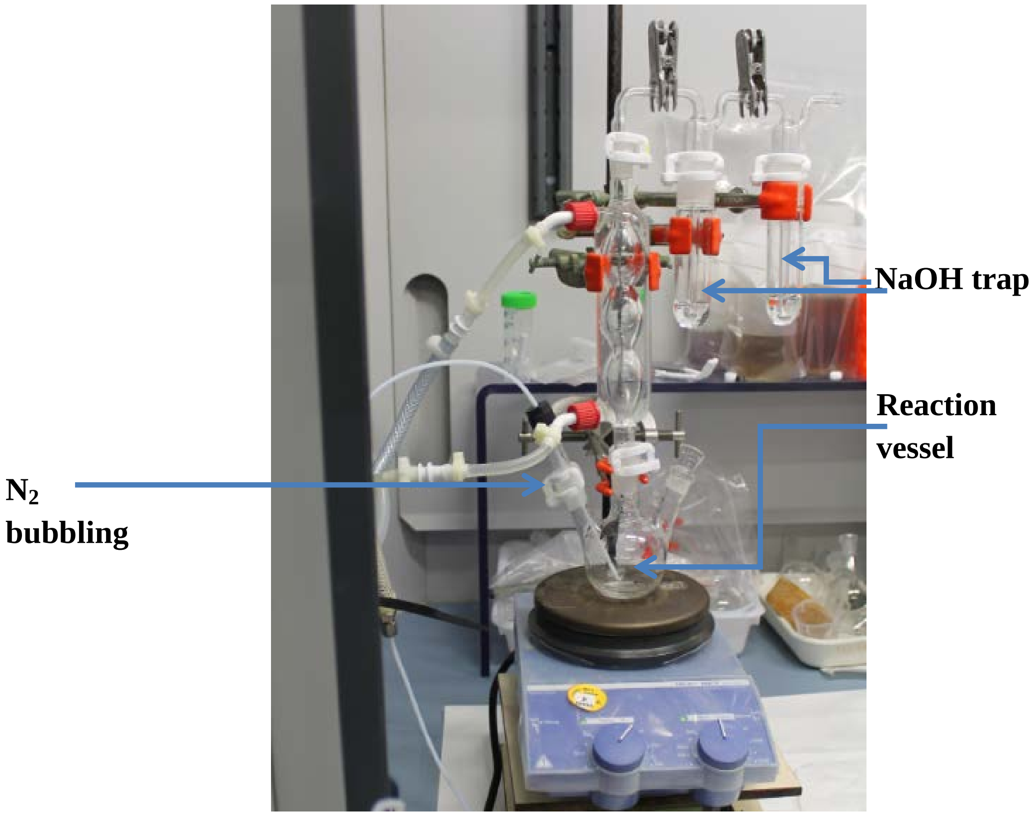

Figure 12: Organic and inorganic partition of ^{14}C

An aliquot of the NaOH trap solution was measured by LSC to determine the amount of inorganic ^{14}C. The remaining solution in the reaction vessel was pyrolysed to measure the concentration of organic ^{14}C.

This procedure has been tested on an individual solution and on a mixture of two labelled organic and inorganic molecules (glucose $^{14}C_6H_{12}O_6$ and $Na_2{}^{14}CO_3$).

The organic and inorganic ^{14}C partition results for the tests with the labelled molecules are presented in Table 5.

Table 5: Organic and inorganic ^{14}C partition results of labelled molecules

Sample	Inorganic ^{14}C	Organic ^{14}C
$Na_2{}^{14}CO_3$	85 %	0 %
$^{14}C_6H_{12}O_6$	0 %	100 %
$Na_2{}^{14}CO_3$ + $^{14}C_6H_{12}O_6$	70 %	100 %

85 % of the inorganic ^{14}C was trapped in the NaOH solution from the solution containing only ^{14}C-carbonate and 70 % for the mixture. 100 % of organic ^{14}C was detected by this method for the solution containing only ^{14}C-glucose and for the mixture of the two labelled molecules. The organic ^{14}C is not overestimated as, when a carbonate solution is used alone, all the ^{14}C is

detected in the trapped solution and no inorganic ^{14}C is kept in the vessel reaction. These tests showed that acidification by H_3PO_4 has no effect on organic ^{14}C, releasing inorganic ^{14}C as CO_2 with none remaining in the vessel.

Inorganic ^{14}C concentration of leachate samples could not be measured in the NaOH trap solution due to dilution. The results were below the detection limit of the LSC.

Therefore, inorganic ^{14}C was determined by the subtraction of the measured organic ^{14}C to the total measured ^{14}C in the leachate sample.

1.6.3 Results

1.6.3.1 Total C-14 determination

The total ^{14}C results of blank and leachate samples are presented in Table 6.

Table 6: Total ^{14}C results of blank and leachate samples

Samples	**Total ^{14}C**			
	Bq.g^{-1}	**ng.g^{-1}**	**Bq per gram of hull**	**Bq per cm^2 of hull***
Blank (10^{-2} M NaOH in hot cell)	**< 0.3 (LD LSC)**	**< 1.8.10^{-3} (LD)**	**< 9 (0.05 ng) (LD)**	**< 2 (0.01 ng) (LD)**
Leachate M5-type hull 14 J	6.1 ± 0.4	3.7.10^{-2}	190 (1.1 ng)	37 (0.217 ng)
Leachate M5-type hull 6 M	6.3 ± 0.2	3.8.10^{-2}		
Leachate D4R-type hull 14 J	1.5 ± 0.2	9.1.10^{-3}	44 (0.3 ng)	10 (0.06 ng)
Leachate D4R-type hull 6 M	1.8 ± 0.3	1.1.10^{-2}		

* *The hulls surface in contact with the medium is estimated to 40 cm^2.*

There is no evolution of ^{14}C released in leachate between 14 days and 6 months. Release of total C-14 by M5-type hull is higher by a factor of 4.5 than D4R-type hull. Based on a calculation to determine the total C-14 inventory, D4R-type hulls and M5-type hulls contain 1.8E+04 and 3 E+04 Bq/g C-14 respectively (Appendix 1). In other words, in the early stage C-14 release is significantly less for D4R-type than M5-type hulls.

1.6.3.2 Partition of organic ^{14}C and inorganic ^{14}C

Organic and inorganic ^{14}C partition results of blank and leachate samples are presented in Table 7.

Table 7: Organic and inorganic ^{14}C partition results of blank and leachate samples of M5-type and D4R-type hulls

Sample	Organic ^{14}C *(measured)*		Inorganic ^{14}C *(calculated)*		Partition Organic / Inorganic
	Bq.g^{-1}	Bq per gram of hull	Bq.g^{-1}	Bq per gram of hull	%
Blank (10^{-2} M NaOH in hot	**< 0.3 (LD LSC)**	**< 9 (0.05 ng)**	**< 0.3 (LD LSC)**	**< 9 (0.05 ng)**	**Not possible**
Leachate M5-type hull 14 J	2.8 ± 0.4	86 (0.5 ng)	3.3 ± 0.4	101 (0.6 ng)	46/54
Leachate M5-type hull 6 M	2.7 ± 0.4	83 (0.5 ng)	3.6 ± 0.4	110 (0.7 ng)	43/57
Leachate D4R-type hull 14 J	**≤ 0.3 (LD LSC)**	**≤ 9 (0.05 ng)**	***< 1.2***	**< 32 (0.2 ng)**	**20/80**
Leachate D4R-type hull 6 M	**≤ 0.3 (LD LSC)**	**≤ 9 (0.05 ng)**	***< 1.5***	**< 40 (0.2 ng)**	**17/83**

There is no evolution of ^{14}C organic released in leachate between 14 days and 6 months. Release of inorganic ^{14}C by M5-type hull is higher by a factor 2.5 than D4R-type hull.

Organic ^{14}C released by D4R-type hull could not be detected because the results are below the detection limit of the LSC. A method has been developed to quantify ^{14}C in the leachate samples by Accelerator Mass Spectroscopy (AMS) after pyrolysis. Results are ongoing.

1.7 *Analytical method for identification of organic matter*

1.7.1 Objectives

The analytical approach has been developed by CEA-LRMO. This analytical strategy has been already demonstrated for the study of uranium carbide dissolution [LEGAND, 2014].

The sample's activity has limited the analytical possibilities. The final strategy focused on the global organic carbon analysis by different techniques:

1. partition of organic and inorganic total carbon by Total carbon analyzer (TC),
2. quantification of low molecular mass carboxylic acids by anionic chromatography (aIC),

3. detection of low molecular mass molecules by Gas Chromatography coupled with Mass Spectrometry (GC-MS).

1.7.2 Organic and inorganic total carbon partition

The concentration of Total Organic Carbon (TOC) and Total Inorganic Carbon (TIC) in solution is determined on a total carbon (TC) analyzer in a glove box (Figure 13). This quantification is the way to control the carbon mass balance of each sample at the end of the experiment.

Figure 13: TOC analyzer in a glove box

1 mL of sample is injected into a chamber. After acidification with phosphoric acid, the TIC dissociates into CO_2. The CO_2 produced is quantified by infrared spectroscopy. Then, the TOC is oxidised with sodium persulfate to produce CO_2, also quantified by infrared spectroscopy.

In the tested conditions, a detection limit around 1 $mgC.L^{-1}$ in TOC and TIC (without sample dilution) was obtained. The quantification limit is determined by the lowest measurement for which the signal to noise ratio is above 5. The available volume of sample and the background noise of the device are the limiting factors. Reproducibility and repeatability were considered (Figure 14).

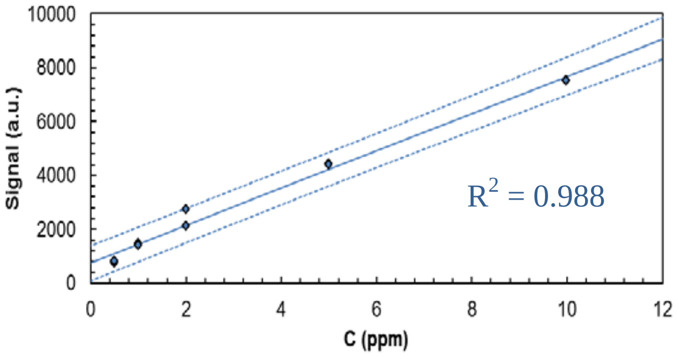

Figure 14 : TOC Calibration curve

1.7.3 Ionic chromatography

Ion chromatography is used to quantify low molecular mass carboxylic acids and inorganic anions. This device is equipped with a conductimetric detector (Figure 15). The eluted compounds are identified by comparison of retention times of the pure similar compounds.

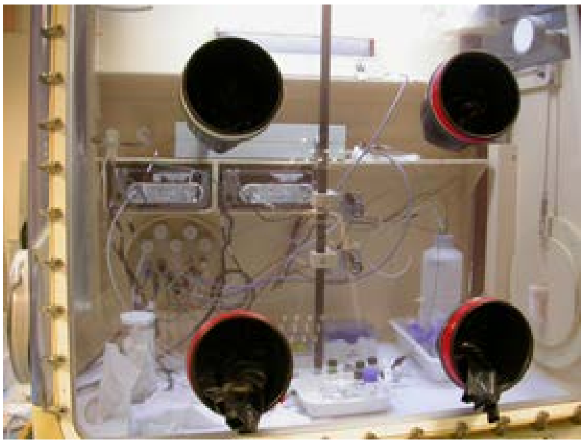

Figure 15 : Ionic chromatography in glove box

A method has been developed for the detection of carboxylic acids in high NaOH concentrations, and inorganic anions in aqueous solution.

The chromatographic system used was an ICS-3000 High Performance Ion Chromatography System (Dionex, Sunnyvale, CA, USA). The sample was diluted in water before analysis. The chromatographic separation of carboxylic acids was performed on an IonPac AS15

Hydroxide-Selective Anion-Exchange analytical column (250 mm × 2 mm i.d. Dionex) and an IonPac AG15 guard column (50 mm × 2 mm i.d. Dionex) with KOH as eluent at a flow-rate of 0.3 mL min^{-1}. The sample injection volume was fixed at 10 µL. The carboxylic acids were detected and identified by comparison of retention times with pure similar compounds. The separation was performed with a gradient elution:

(1) 0 - 7.5 min with 10mM KOH, 7.5-8 min 10-15mM KOH , 8-13 min 15-25mM KOH and 13-39 min 25mM. (Figure 16)

(2) 0 - 7.5 min with 10mM KOH, 7.5-8 min 10-15mM KOH, 8-13 min 15-40mM KOH and 13-39 min 40mM.

Two methods were tested to detect the maximum number of compounds. The first method allowed separation of the rapidly eluted compounds on the column, while the second method was more relevant to elute compounds with a higher retention on the column.

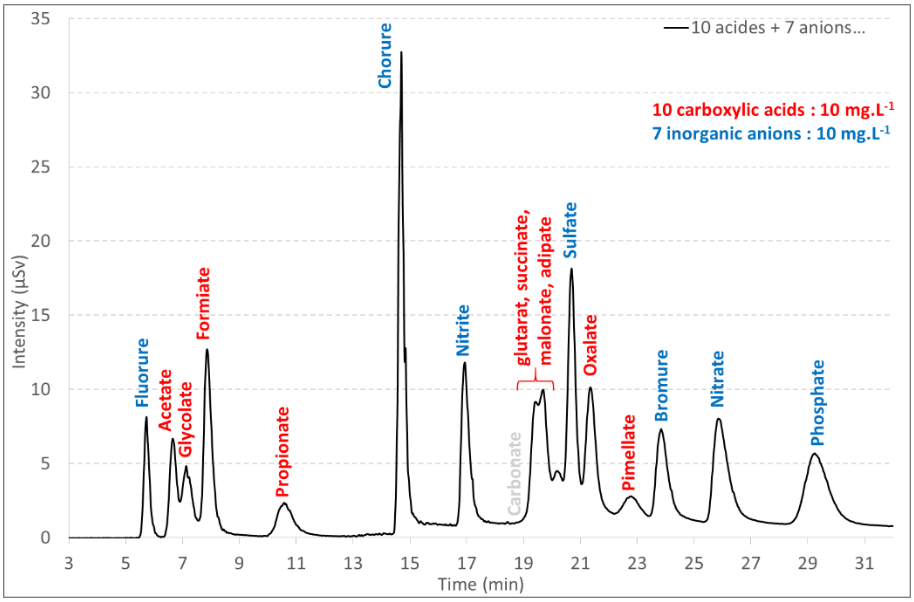

Figure 16 : Example of chromatogram obtained with the method (1): 10 carboxylic acids at 10 mg/L and in red and 7 inorganic anions at 10 mg.L^{-1} in blue. (Carbonate, in grey, not included in this solution so the retention time is given on an indicative basis)

In the tested conditions, a detection limit around 0.1 $\text{mg}_{\text{acid}}/\text{L}^{-1}$ was obtained. The quantification limit was determined by the lowest measurement for which the signal to noise ratio was above 5 (Figure 17).

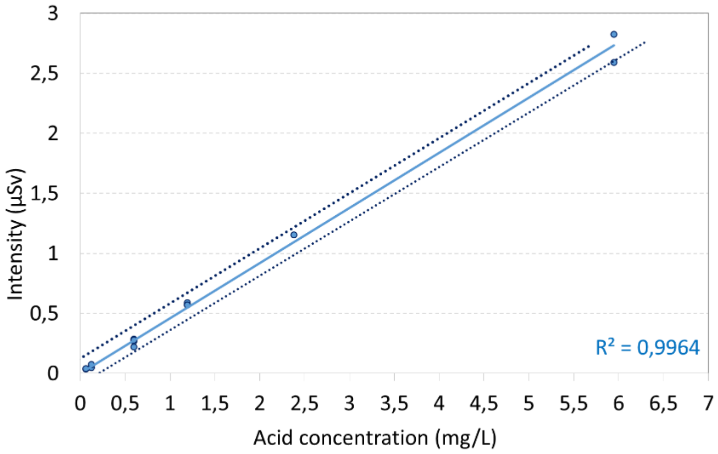

Figure 17 : example of calibration curve (Formic acid)

1.7.4 Gas chromatography coupled with mass spectrometry

To identify semi-volatile organic compounds with mass between 100-500 g.mol^{-1}, the sample was analyzed by Gas Chromatography (GC) coupled to Mass Spectrometry (MS). The system used was a “Trace ultra GC” coupled with a DSQII MSD equipped with an electron impact ionization source.

Gas chromatographic separations were performed on a TR1-MS capillary column (30 m length, 0.32 mm i.d., 0.20 µm df, Thermo). The oven was maintained at the initial temperature of 50 °C for 10 min, heated to 250 °C at the rate of 10 °C.min^{-1}, and then held at 250 °C for 20 min. The inlet temperature was 220 °C and the transport line maintained at 300 °C. Helium was used as the carrier gas at a flow rate of 1.6 mL.min^{-1}. The injection volume was 1 µL in splitless mode. The ion source and quadrupole temperatures were 200 °C and 150 °C, respectively. An electron energy of 70 eV was used. The full scan MSD was operated over the range of 10 to 600 amu.

1.7.5 Results

1.7.5.1 Organic and inorganic total carbon partition

All leaching solutions have been analyzed by total carbon analyzer to determine TIC and TOC concentrations (Table 8 and Table 9).

Table 8 : TOC results for M5 hull leaching (in mgC.L^{-1})

		TOC	**TIC**
Blank “M5” NaOH		6	7
Leaching M5	**14 days**	11	18
	6 months	5	29

Table 9 : TOC results for D4R hull leaching (in mgC.L^{-1})

		TOC	**TIC**
Blank “D4” NaOH		< 1	2
Leaching D4	**14 days**	9	18
	6 months	5	31

In all hull leaching solutions, the TIC concentration is higher than the TOC concentration. This high TIC concentration is probably due to carbonation of solutions. It is difficult to reach a conclusion on TOC concentrations coming only from hull leaching because TOC quantities obtained in the blank and sample solutions are very close to each other. Moreover, these blanks were exposed to the hot cell at different times, consequently they only give an indication of the background but not an accurate concentration relevant to the background during the leaching experiment.

These results show a higher TOC concentration after 14 days than after 6 months. It is assumed that either a higher organic contamination occurred for the 14 day sample or an evolution and/or a degradation of organic compounds in alkaline conditions took place after six months.

1.7.5.2 Quantification of carboxylic acids by aIC

All leaching solutions have been analysed by anionic chromatography to quantify carboxylic acids by the methods (1) or (2). Pure molecules were regularly analysed to verify the retention time (Figure 18 and Figure 19).

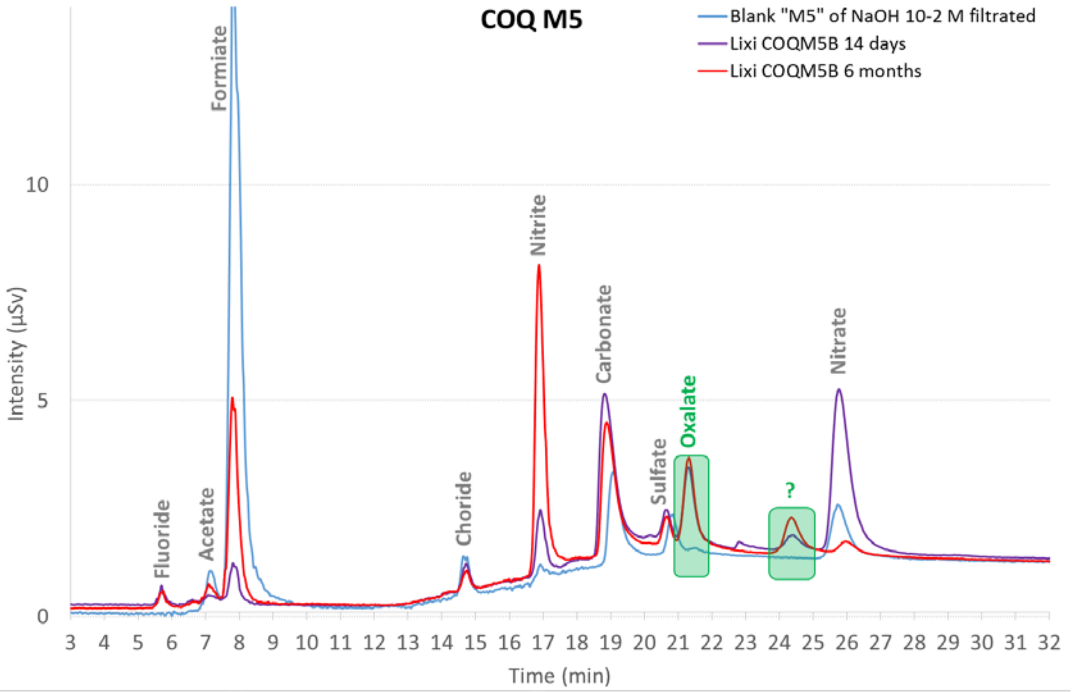

Figure 18 : Chromatograms obtained by aIC with the method (1) (Comparison of NaOH blank in blue, M5 leaching solutions after 14 days in purple and 6 months in red).

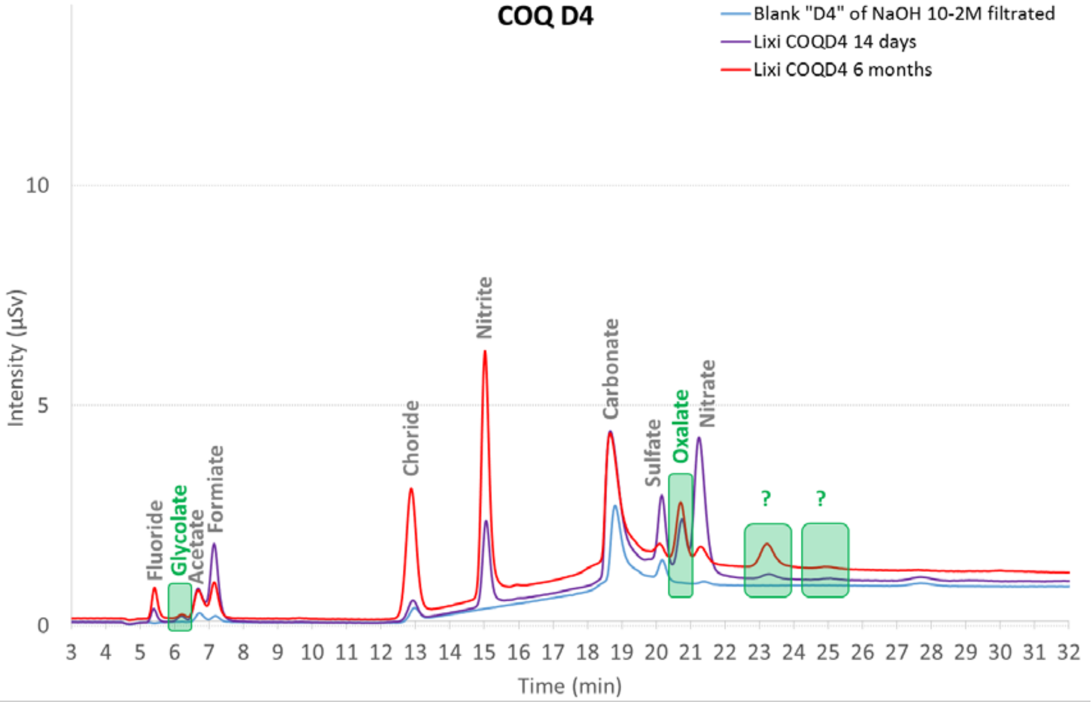

Figure 19 : Chromatograms obtained by aIC with the method (2) (Comparison of NaOH blank in blue, D4R leaching solutions after 14 days in purple and 6 months in red).

In both hulls leaching solutions, various inorganic anions were observed as fluoride, chloride, nitrite, nitrate and sulfate. Carbonate was the only one with inorganic carbon (TIC).

Several organic anions were detected: glycolate, acetate, formate and oxalate. These two first compounds, acetate and formate, were also detected in blank solutions, suggesting a potential contamination. Only glycolate and oxalate seemed to come only from hull leaching solutions. Only oxalate was quantified as glycolate contration was below the detection limit.

In addition, unidentified compounds (t_r = 24 min in M5 and t_r = 23 and 25 min in D4) were detetcted in hull leaching solutions. It was not possible to determine whether they were organic or not.

Quantification was carried out on four carboxylic acids as shown in Table 10 and Table 11.

Table 10 : Carboxylic acids concentrations in M5 hull leaching solutions in $mg_{acid}.L^{-1}$ or $mgC.L^{-1}$ (between brackets) with a measurement error of 15%

		Glycolate	**Acetate**	**Formate**	**Oxalate**
Blank "M5" NaOH		< 0.2	1.5 (0.6)	18.3 (4.8)	< 0,3
Leaching M5	**14 days**	< 0.2	0.4 (< 0,1)	2.0 (0.5)	1.9 (0.5)
	6 months	< 0.2	0.9 (0,4)	5.8 (1.5)	2.0 (0.5)

Table 11 : Carboxylic acids concentrations in D4R hull leaching solutions in $mg_{acid}.L^{-1}$ or $mgC.L^{-1}$ (between brackets) with a measurement error of 15%

		Glycolate	**Acetate**	**Formate**	**Oxalate**
Blank "D4" NaOH		< 0.2	< 0.6	< 0.4	< 0 .5
Leaching D4	**14 days**	< 0.2	1.2* (0,5)	1.3*(0.3)	1.1 (0.3)
	6 months	< 0.2	1 (0.4)	0.6 (0.2)	1.3 (0.3)

* Measurement error of 50 %, *not very reproducible probably due to contamination (filtration or bottle)*

1.7.5.3 Analyses by GC-MS

The leaching of D4R hulls (6 months) was analysed by GC-MS.

One separation process, a liquid -liquid extraction (or solvent extraction) was carried out to extract organic compounds from the aqueous solution. Chloroform was chosen for the high polarity and immiscibility with water. The organic phase was then analysed by GC-MS. No organic compounds have been detected (Figure 20).

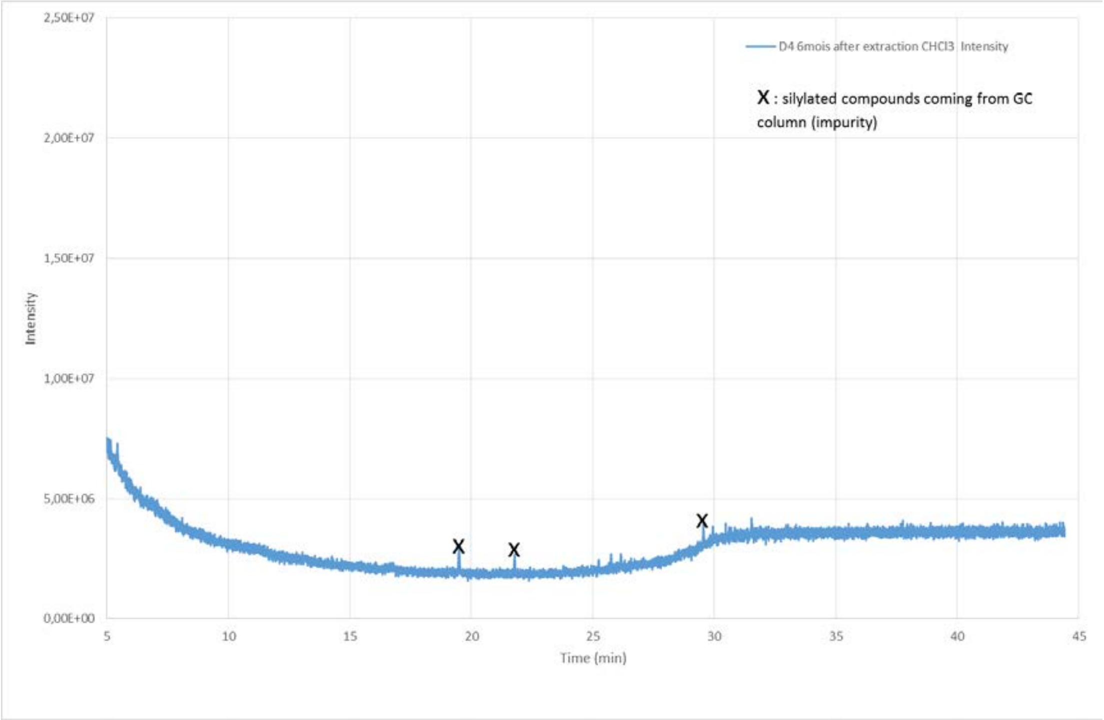

Figure 20 : GC chromatogram of CHCl3 organic phase after liquid extraction with the leaching of D4R- type hull after 6 months

2 Activities performed by SUBATECH/ARMINES

2.1 *Introduction*

The radiochemical composition and the activity of the leaching solution depend on several factors related to the cladding material, fuel type, the number of irradiation cycles, irradiation time, and mean burn up. Leaching experiments carried out in the framework of the CAST project on irradiated Zircaloys show that leachates contain actinides, fission products and activation products besides C-14 [Gras, 2014; Herm et al., 2015]. Some radionuclides are present with a significant activity level compared to C-14; i.e. several Bq/mL of leaching solution. [Yamaguchi et al., 1999] reported the presence of Co-60, Ru-106/Rh-106, Sb-125, Cs-134, Cs-137 and Eu-154 in the leachates of Zircaloy-4 cladding from a PWR. Subatech focused on the characterization of carbon-14 organic fraction released in the leaching solution, and particularly on the analysis of ion carboxylic acids having a short carbon chain ≤ 5. Characterization of carboxylic acids with a low carbon chain length is of importance, since they are preferentially released compounds from Zircaloy alloys.

Ion Chromatography (IC) has been used to separate carboxylic acids and Liquid Scintillation Counting (LSC) for the quantification of C-14 in the IC collected fractions. A method to extract radionuclides having significant activities from solution is described as follows. The proposed method is based on the use of inorganic ion exchanger $K_2[CuFe(CN)_6]$ without binding polymer resin, characterized by its selectivity regarding radionuclides and the absence of interaction with targeted C-14 carboxylic acids. The decontaminated solution from resin is thereafter separated by two types of chromatographic columns (ion exclusion, anion chromatography) in order to fractionate and collect the carboxylic acids compounds. The fractions are then analysed by LSC and accelerated mass spectroscopy (AMS). Detailed information on the methodology and tests conducted to assess the decontamination methods is given in [Bahri et al., 2017]. The Figure below (Figure 21) presents the strategy to separate carboxylic acid compounds as well as their quantifications.

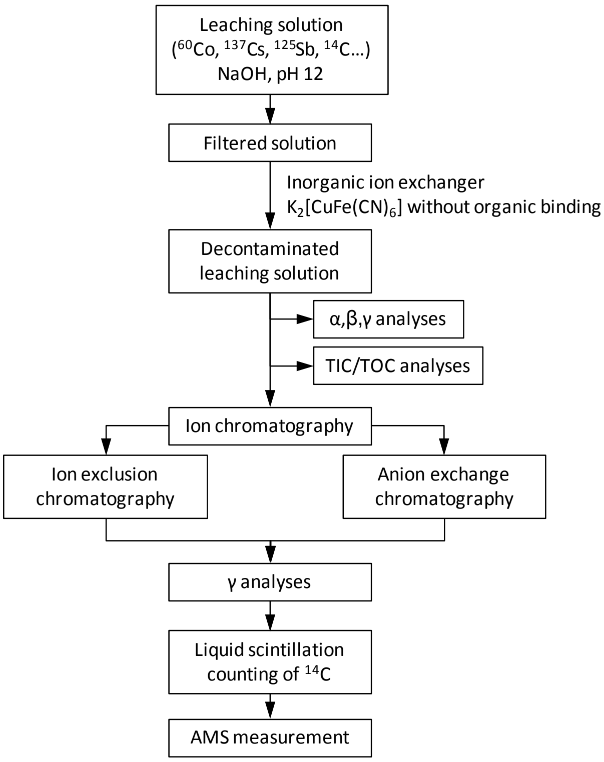

Figure 21 Outline of the general analytical strategy developed at SUBATECH/ARMINES for C-14 released in solution

2.2 *Decontamination of the leaching solution*

Decontamination of two leaching solutions containing M5 and D4R hulls was performed. After contact with $K_2[CuFe(CN)_6]$, actinides were removed efficiently as shown by a significant decrease of the total alpha activity (Table 12). Likewise, the total beta activity was considerably lowered down to 50 Bq/mL. For gamma emitters initially present in the leaching solution, it is obvious that the remaining activity is due to Sb-125; this is substantially decreased with the addition of $K_2[CuFe(CN)_6]$.

Figure 22 presents the radiochemical composition from gamma spectrometry measurements of leaching solution before and after treatment for the two leaching samples. One can observe that the activity level at 14 days and 6 months of M5-hulls alteration does not change and remains in the same order of magnitude. In addition, after 14 days of alteration, the comparison between M5 and D4R hulls shows that the leaching solution composition (radionuclide species, activity level) does not differ significantly and remains of the same order of magnitude, despite their different histories (burn up, fuel type, cladding composition).

Table 12: Radiochemical composition of 14-days leaching solution of M5-type (UOX) Zircaloy hulls before and after contact with $K_2[CuFe(CN)_6]$.

Activities in the leaching solution	**Before $K_2[CuFe(CN)_6]$ contact**	**After $K_2[CuFe(CN)_6]$ contact**
alpha counting		
Total activity	**59**	**0.07**
Accuracy (Bq/mL)	24	0.03
beta counting		
Total activity	**2300**	**50**
Accuracy (Bq/mL)	115	4
gamma spectrometry		
Total activity (Bq/mL)	**2430**	**60.6**
^{134}Cs	30	< LD
^{137}Cs	996	2.1
^{125}Sb	691	54.7
^{241}Am	12	< LD
^{106}Ru-^{106}Rh	659	3.4
^{60}Co	5.1	< LD
^{155}Eu	<0.5	< LD
^{154}Eu	6.4	< LD
^{51}Cr	33	0.4

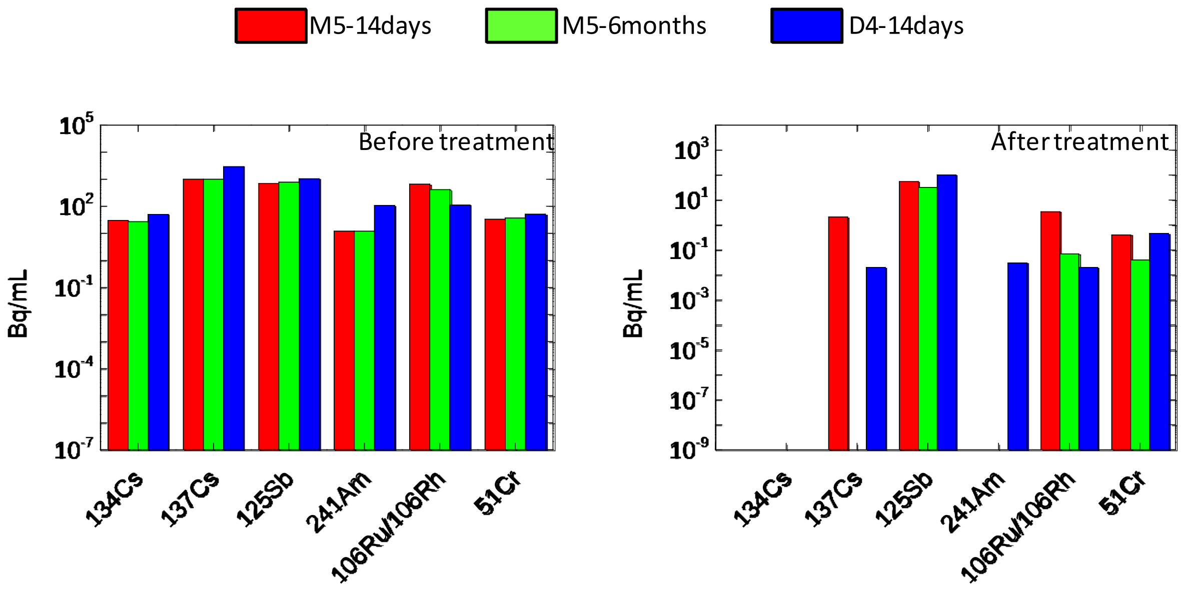

Figure 22: Radiochemical composition of leaching solution of M5-, D4R-type Zircaloy hulls in NaOH pH 12, before (left) and after (right) resin treatment for sampling at 14 days and 6 months, filtration with PTFE 0.45 µm.

2.3 *Ion chromatography*

Among the carboxylic acids compounds, four molecules were targeted: formate, acetate, propionate and oxalate, because they are the first molecules constituting the carboxylic acids family. To identify their retention time, separation tests were performed with standard solutions. The first three molecules were collected by ion exclusion column, specific to low molecular weight organic acid (Figure 23-a), and the last one was collected by anion column (Figure 23-b). Figure 24 shows an example of a chromatogram obtained after decontamination of Zircaloy leaching solution using an ion exclusion column. One can identify the presence of formate and acetate. The presence of chloride is due to the acidification step to adjust the pH in order to optimize the decontamination.

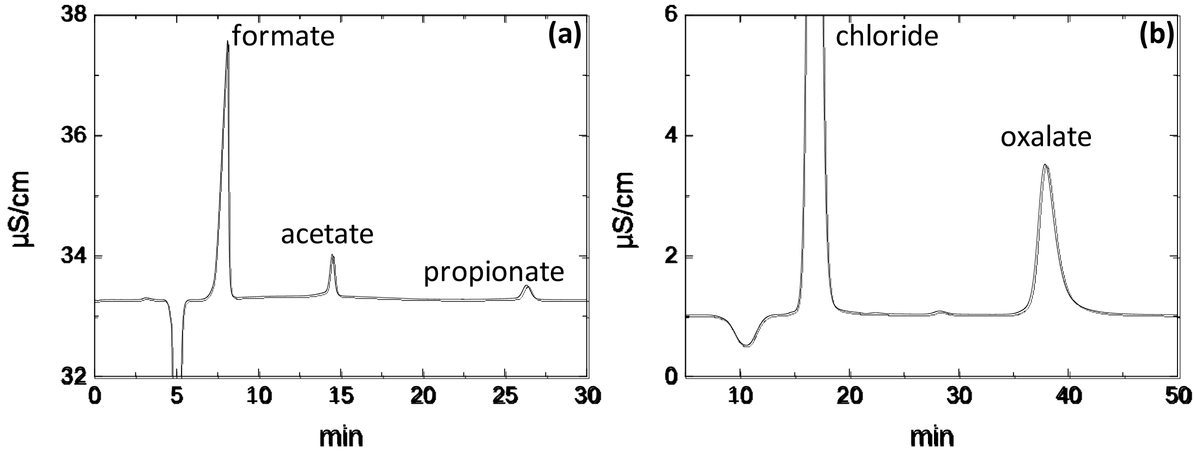

Figure 23: Radiochemical composition of leaching solution of M5-, D4R-type Zircaloy hulls in NaOH pH 12, sampling at 14 days and 6 months, filtration with PTFE 0.45 µm: a) results obtained by ion exclusion column; b) results obtained by anion column

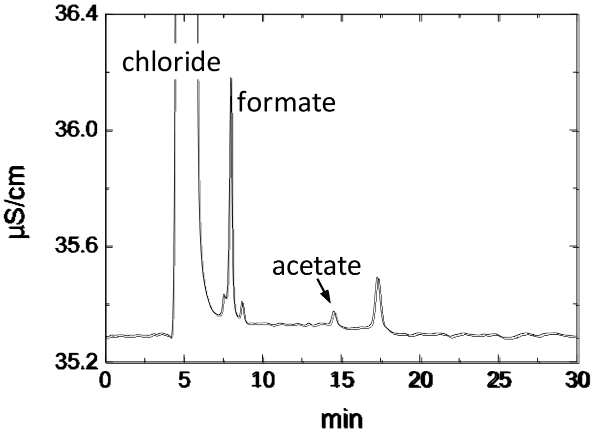

Figure 24: Radiochemical composition of leaching solution of M5-, D4R-type Zircaloy hulls in NaOH pH 12, sampling at 14 days and 6 months, filtration with PTFE 0.45 µm.

2.4 *Radiochemical analyses*

Each fraction was collected and analysed by liquid scintillation counting (LSC), with results that were close to the detection limit (0.02 Bq/mL). This gave the maximum activity value measured in the collected fraction and the highest activity level released in the leaching solution. Gamma spectrometry analyses do not indicate any radionuclide such as ^{137}Cs, ^{60}Co, ^{125}Sb and ^{106}Ru/^{106}Rh, confirming the efficient decontamination process. Only ^{40}K released from the ion exchanger resin was detected. Table 13 shows the results for each fraction collected in terms of mass activity (Bq/g hulls) and mass concentration (g of carboxylic acid / g hulls) from liquid scintillation results. The results show an increase of mass activities or mass concentration in the case of D4R-type Zircaloy hulls. This may reveal a link between the burn-up rate (given also by the fuel type which is MOX in contact with D4R and UOX with M5) and the mass concentration of carboxylic acids released.

Table 13: Radiochemical composition of the leaching solution of M5-, D4R-type (UOX) Zircaloy after contact with $K_2[CuFe(CN)_6]$.

C-14 carbox. acids	**COQM5 / 6 months**		**COQD4R / 14 days**	
Formate	179 Bq/g hulls	1.1×10^{-9} g/g hulls	394 Bq/g hulls	2.4×10^{-9} g/g hulls
Acetate	71 Bq/g hulls	4.3×10^{-10} g/g hulls	265 Bq/g hulls	1.6×10^{-9} g/g hulls
Propionate	65 Bq/g hulls	3.9×10^{-10} g/g hulls	127 Bq/g hulls	7.7×10^{-10} g/g hulls
Oxalate	19 Bq/g hulls	1.2×10^{-10} g/g hulls	15 Bq/g hulls	9.2×10^{-11} g/g hulls

TIC/TOC measurements were carried out on M5-type Zircaloy hulls after 6 months of leaching (Figure 25). The figure below gives the proportion of organic fractions with regard to the total carbon based on ion chromatography results, and the proportion of ^{14}C-carboxylic acid content in total organic carbon. The results confirm the weak contribution of total organic carbon in the inventory (TOC = 7% TIC), similar to the results found in [Yamaguchi et al., 1999]. Furthermore, almost 83% of total organic carbon is identified as carboxylic acids. The contribution of carbon 14, based on LSC measurements, shows a very weak contribution.

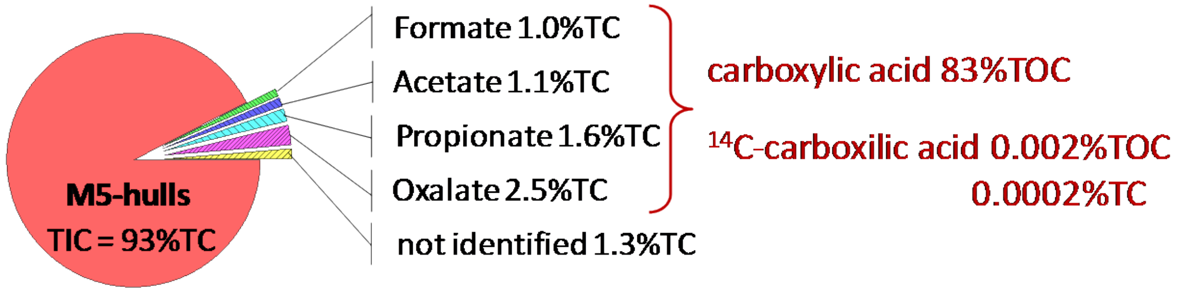

Figure 25: Carboxylic acid distribution in leaching solution of M5-type Zircaloy hulls in NaOH pH 12, sampling at 14 days and 6 months.

2.5 *Inventory of hulls waste in repository*

In France, the inventory of hulls considers the wastes produced between 1990 and 1995, which represents 2,277 m^3, and those produced from 2002 with the compaction technology, which represents 1,337 m^3 in 2007 [ANDRA, 2009]. The estimations for 2030 give a total of

4,566 m^3 of compacted hulls wastes. As one does not know the exact contribution of the M5- and D4R-type hulls in the waste, one can consider two scenarios:

– considering that all carbon 14 stems from M5 hulls, then the maximum quantity of carbon 14 released would be about 90 g,

– considering that all carbon 14 stems from D4R hulls, then the maximum quantity of carbon 14 released would be about 220 g.

These values are only assumptions and consider 100% of M5 or 100% of D4R types hulls to be disposed of. In addition, these results are based on LSC measurement, which over-estimates the results due to the activity levels being close to the detection limits. This explains why the uncertainties are so high. To be more accurate, AMS measurements have been performed. AMS consists of a selective technique compared to LSC. AMS measurements on mass 14 should give more precise results and confirm the presence of carboxylic acid molecules in the collected fraction.

2.6 *AMS measurements*

The AMS instrument is usually used in archaeological and environmental fields to quantify very low-level concentrations of carbon 14 in samples. In that scope, the strategy developed by SUBATECH/ARMINES was to decontaminate the leaching solutions by inorganic ion exchanger to remove the major radionuclides (^{137}Cs, ^{60}Co, ^{125}Sb and ^{106}Ru/^{106}Rh) and collect only organic carboxylic acids after the separation by ion chromatography. Presently, there are two principal methods to measure carbon 14: graphitisation of carbon 14 into solid form and conversion into $^{14}CO_2$ gaseous form.

Due to the liquid form of the samples and the limited collected volume, the method by graphitisation was not required. Therefore, the method of conversion has been preferentially chosen. Depending on AMS facilities, some pre-treatment may be required. Discussions with Dr. Peter Steier from the VERA facility (Vienna Environmental Research Accelerator, University of Vienna, Austria, https://isotopenforschung.univie.ac.at/en/vera/) opened the possibility for the quantification of organic fractions by AMS measurement. The sample preparation is based on the oxidation of organic carbon by UV light inside closed quartz vials.

The oxidation process formed CO_2(g) and the fraction released in the head volume was extracted for AMS measurements. The chemical yield of this method is 50-70%. Preliminary tests were performed on the oxalate fraction (6 months leaching experiment on M5 hulls). Because the total amount of carbon was low (a few µgC) and the ratio $^{14}C/^{12}C$ was about 10^{-6}, which is 6 orders of magnitude higher than the acceptable ratio, the typical measurement $^{14}C/^{12}C$ was not performed, preventing a possible underestimation of carbon 14. Therefore, the ratio $^{14}C/^{13}C$ was measured, considering the addition of an isotopic pure carbon 13.

The comparison between LSC and AMS results on the same oxalate fraction is presented as follows:

COQM5 / 6 months	**LSC measurement**		**AMS measurement**	
Oxalate	19 Bq/g hulls	1.2×10^{-10} g/g hulls	9 Bq/g hulls	5.5×10^{-11} g/g hulls

AMS measurements confirmed the presence of carbon 14 in the sample, which should correspond to oxalate molecule and validate the experimental methods to collect fractions. The result also confirmed the sensitivity of the technique which allows more accurate measurements of the activity level for carboxylic acids.

Collected fractions from leaching solutions of M5 (6 months leaching) and D4R (14 days and 6 months leaching) hulls were sent to AMS VERA and results are planned to be obtained before the end of 2017.

3 Summary

Overall, the TC concentration increased within 6 months and the TIC increased significantly as a consequence of potential carbonation of the solution. By contrast, the TOC concentration decreased due to potential organic contamination or an evolution of organic compounds in alkaline conditions after one month of leaching (Figure 26 and Figure 27).

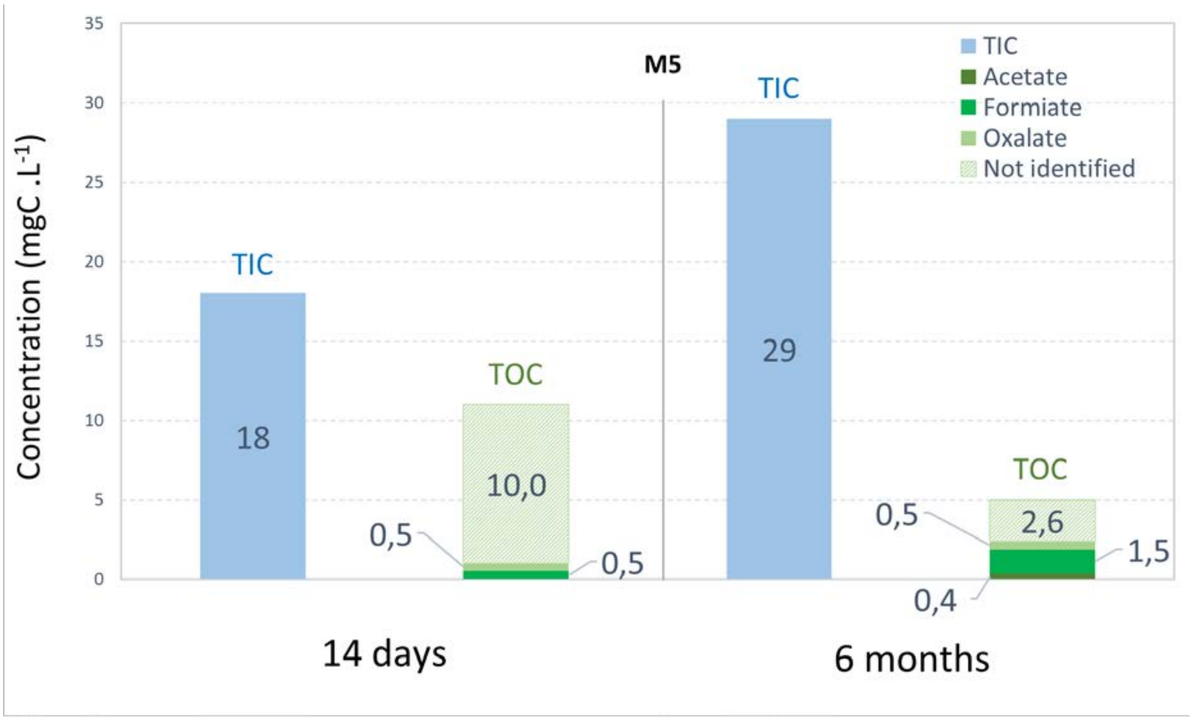

Figure 26 : Total carbon mass balance of the leaching experiments on the M5 after 14 days and 6 months in mgC.L^{-1}

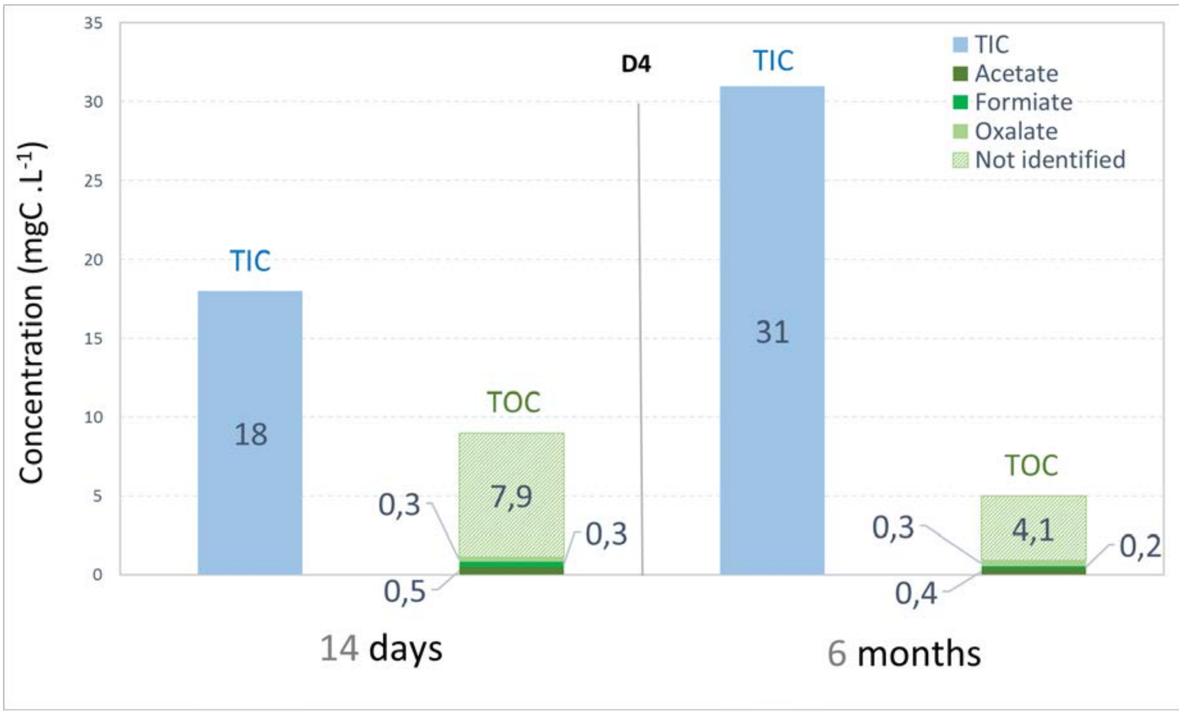

Figure 27 : Total carbon mass balance of the leaching experiments on the D4R hulls after 14 days and 6 months in mgC.L^{-1}

Concerning total C-14 released in leachate and organic / inorganic partition of ^{14}C, there is no evolution between 14 days and 6 months (Figure 28 and Figure 29). Releases of total 14C and organic ^{14}C by M5-type hull are respectively higher by a factor 4.5 and 2.5 than D4R-type hull.

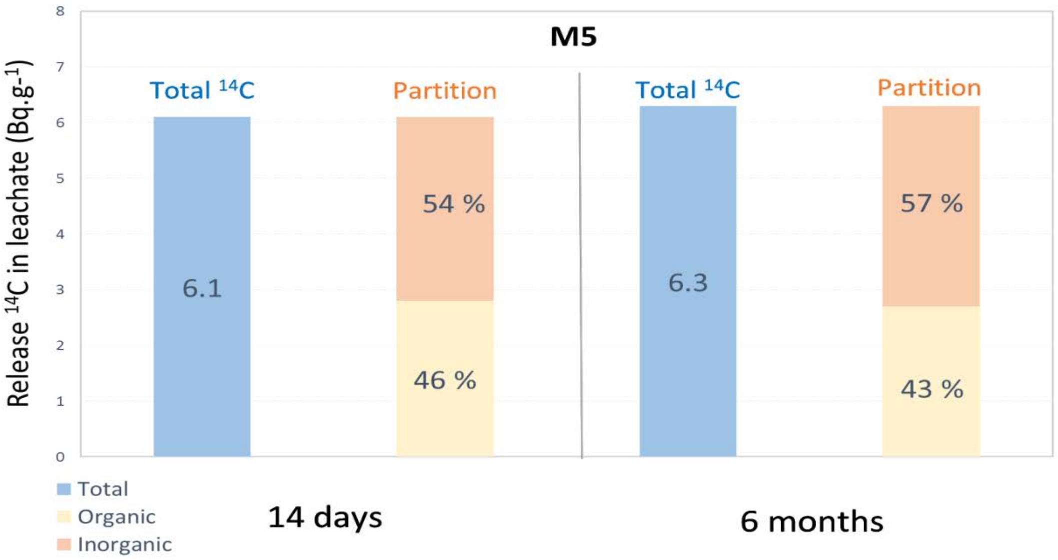

Figure 28: ^{14}C release in leachate by M5-type hull leaching after 14 days and 6 months in Bq.g^{-1}

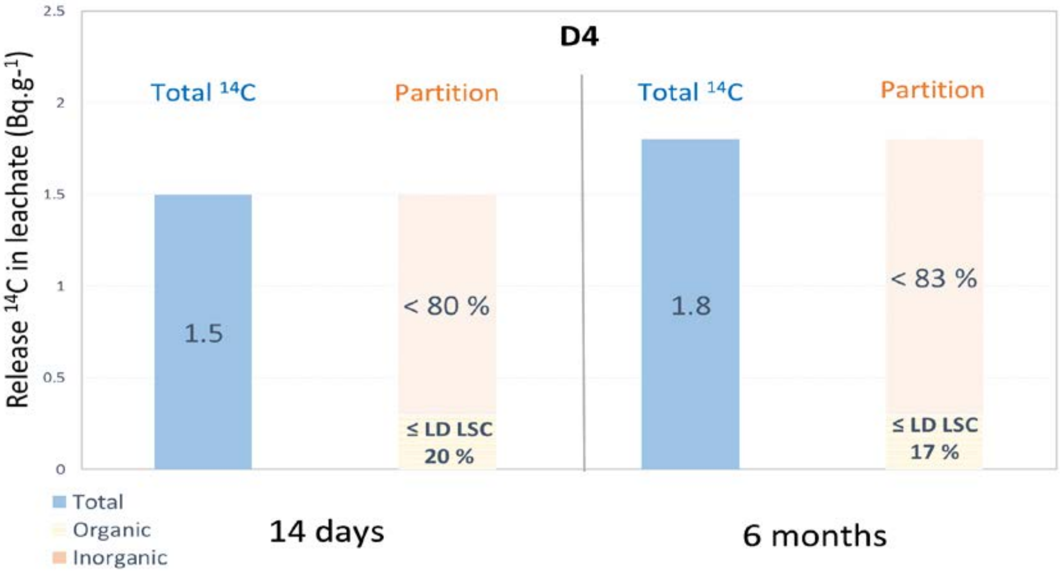

Figure 29: ^{14}C release in leachate by D4R-type hull leaching after 14 days and 6 months in Bq.g^{-1}

Organic ^{14}C released by D4R-type hull could not be detected because the results were below the detection limit of the LSC (< 0.3 Bq.g^{-1}). A method has been developed to quantify ^{14}C in the leachate samples by Accelerator Mass Spectroscopy (AMS) after pyrolysis. Results are in progress. Most of the ^{14}C released by D4R-type hull seems to be inorganic ^{14}C.

For D4R-type hulls, a Japanese team [GRAS, 2014; YAMAGUCHI, 1999] found that ^{14}C released from PWR samples was detected mainly in the liquid phase and most of the ^{14}C was in the organic form (78.9 % of total ^{14}C after 6 months). In the presented conditions, less than 20 % of organic ^{14}C was released after 6 months. It should be noted that various parameters are different:

- The burn-up: 47.9 GWd.t^{-1} Japan / 54.5 GWd.t^{-1} Switzerland (presented study),
- The rinsing procedure (our hulls) or not rinsed hulls,
- The fuel type of the PWR (MOX with 7.2 % Pu for our hulls),
- The oxide layer thickness,
- The geometry of hulls,
- The composition of the leaching solution: SGW Japan (Sea water derived groundwater equilibrated with cement), NaOH France.

Different organic anions were detected in the leaching solution. Acetate and formate were likely from contamination, while glycolate (below the detection limit) and oxalate (between 1 and 2 mg$_{acid}$.L^{-1}) were properly released from hull leaching solutions. Other organic compounds could be detected but not identified.

In this study, the total ^{14}C represents less than 8.10^{-4} % of each TOC or TIC parts.

The only carboxylic acid (oxalic acid) that was quantified in the M5-type hull solution after 6 months represents 0.5 mgC$_{acid}$/L as around 1.10^{-4} % of ^{14}C according to the AMS results obtained by Subatech (6.10^{-7} mg^{14}Cacid/L).

Concerning the quantification of ^{14}C by AMS, SUBATECH has shown that, in the oxalate fraction, 8.5 Bq (5.1.10^{-2} ng) of ^{14}C were released per gram of M5-hulls within 6 months. It is equivalent to 4.5 % of total ^{14}C released by M5-hulls.

From theory calculations, the diffusion coefficient of ^{14}C within Zr-metal and Zr dioxide is very low. However, measurements of ^{14}C in solution indicate its possible diffusion through Zr metal and/or Zr oxide layer by another mechanism, such as diffusion through grain boundaries.

SUBATECH/ARMINES optimized a method of decontamination (based on inorganic ion exchanger) in aqueous media to analyse and separate organic carbon-14. Fractions of organic C-14 were collected by ion chromatography and measured by liquid scintillation counting. However, due to the very low quantity of organic C-14 in collected fractions (below the detection limit of LSC), additional development is needed to measure and quantify precisely the carbon-14 present. Preliminary test using AMS on the oxalate fraction were carried out, which has given promising results. Collected fractions from leaching solutions of M5 (6 months leaching) and D4R (14 days and 6 months leaching) hulls were sent to AMS VERA and results are planned to be obtained before the end of 2017.

4 Acknowledgments

The authors acknowledge C. Mérignac for ion chromatography analyses, SMART laboratory (Le Service de Mesure et d'Analyse de la Radioactivité et des éléments Traces) for the radiochemical analyses by gamma spectrometry and by alpha/beta counting, J. Molina (Areva STMI), and Dr. Peter Steier from the VERA facility for AMS measurements.

The presented research activities have received funding from the European Union’s European Atomic Energy Community’s (Euratom) Seventh Framework Programme FP7/2007-2013 under grant agreement no. 604779, the CAST project.

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6 Appendix 1: Activation calculations and model for the prediction of the radionuclide inventory

Method:

A generic PWR 15x15 UOX assembly [with uniform fuel enrichment 3.5 %] and a generic PWR 15x15 MOX assembly [with three different fuel compositions] models were created in SCALE 6.2.2 TRITON/CENTRM-NEWT with the following settings:

- the ENDF/B-VII.1 252-group cross section library was used;
- Convergence criteria for fluxes and the eigenvalue were set as 1E-5;
- Global grid contained one computational cell per a pin cell, and a 4x4 grid was defined for each pin cell;
- Mirror boundary conditions were used to simulate the infinite 2D lattice;
- Level symmetric quadrature with order sn=6 was used;
- Scattering order was assumed to be pn=2 in the coolant, pn=1 everywhere else;
- To decrease the calculation time, ¼-symmetry was assumed, CMFD acceleration using the global grid was applied, and the inter-assembly gap was omitted, ensuring a perfect overlapping of the global mesh with the mesh introduced by pin arrays (reduction of the number of computational cells);
- Constant representative values were assumed for temperatures, densities and boron concentration.

These models were then depleted with a generic irradiation history (up to the assembly burnup of 81 MWd/kgHM), using uniform burnup steps. However, finer steps were applied at the Begin of Life (BOL). MATREX method was used to solve the Bateman equations and the predictor-corrector approach was utilized. Moreover, addnux=4 option was applied to correctly track all nuclides in ORIGEN.

Both fuel and cladding zones were depleted, fuel in the constant power mode and cladding in the constant flux mode. Using results of these simulations, generic SCALE 6.2.2 ORIGEN macroscopic cross section libraries were created for cladding activation: integral burnup values were linked to integral cladding fluence values, which then formed the bases of the libraries. In the MOX case, three different cladding libraries were created, one for each fuel type. Further description of the methodology for generating activation libraries using generic material compositions is illustrated in [Caruso]. In this study, customized linear interpolation grids were created for the burnup-cladding fluence pairs.

Based on the provided input data (mean burnup, irradiation time, number of irradiation cycles, cooldown duration), approximate irradiation histories were constructed for both samples:

- burnup and irradiation time were distributed evenly among irradiation cycles;
- 30-day-long inter-cycle cooldowns were assumed;
- for each cycle, the burnup-fluence interpolation grid was used to deduce the cycle integral cladding fluence;
- using cycle lengths, average flux values were calculated for each cycle;
- cycles were further subdivided to avoid long time steps in Bateman equation solution.

Based on the material composition provided by the technical specification of the benchmark and integrated with Nagra reference values for cladding impurities, material composition vectors for both samples were constructed for the two cases of the benchmark:

1. The created irradiation history and composition vector were used to construct the combined SCALE 6.2.2 ARP/ORIGEN input file.
2. The ARP module used the supplied irradiation history to generate a case-specific ORIGEN activation library from the generic (UOX-cladding or MOX-cladding) one.
3. The ORIGEN module then depleted the loaded materials according to the supplied irradiation history and using the case-specific macroscopic cross section library.
4. The SCALE 6.2.2 OPUS module was finally used to extract the calculated specific activities for the nuclides of interest.

Results

Case	Case1	Case2
NPP	Gösgen (Switzerland)	EDF Nogent 2
Fuel	MOX (7.2% Pu)	UOx (3.88% 235U)
Cladding	Zircaloy-4	M5TM
Cycles	4	3
Code	SCALE 6.2.2	SCALE 6.2.2
Author	Lubomír Bures	Lubomír Bures
Irradiation	2293 days	1937 days
BU (FA)	54500 MWd/tHM	46570 MWd/tHM
Cooldown	1948 days	2284 days
Activity	Bq/g	Bq/g
C-14	1.78E+04	3.03E+04
Fe-55	4.13E+06	2.12E+06
Sb-125	3.47E+07	3.17E+05