CArbon-14 Source Term

CAST

Final report on experimental results on long-term corrosion tests and C14 release assessment, irradiated Zircaloy (RATEN-ICN)

(D3.16)

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CAST – Project Overview

The CAST project (CArbon-14 Source Term) aims to develop understanding of the potential release mechanisms of carbon-14 from radioactive waste materials under conditions relevant to waste packaging and disposal to underground geological disposal facilities. The project focuses on the release of carbon-14 as dissolved and gaseous species from irradiated metals (steels, Zircaloys), irradiated graphite and from ion-exchange materials.

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

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

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

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Executive Summary

The total ^{14}C content and its partition between inorganic and organic species as well as inventories of ^{60}Co, ^{137}Cs, ^{134}Cs and ^{125}Sb were determined in irradiated Zy-4 samples cut from a CANDU spent fuel rod transferred from Cernavoda NPP to RATEN ICN for different investigations inside the hot cells. Experimentally-measured radionuclide contents are compared to the theoretical inventory predicted for irradiated Zy-4 by means of Origen computations.

Long term leaching tests, also called static corrosion tests, and accelerated corrosion tests were carried out on irradiated Zy-4 in order to measure the ^{14}C release in chemical conditions relevant to cementitious environment and corrosion rate, respectively. Electrochemical measurements were also performed on non-irradiated Zy-4 to identify evidence on the potential effect of irradiation on the oxide layer and consequently on the corrosion rate. The non-irradiated Zy-4 samples were oxidized in simulated conditions representative of primary circuit of Cernavoda NPP to achieve similar thickness of the oxide layer as the irradiated ones.

The irradiated Zy-4 samples have a ^{14}C content of around 2 10^4 Bq/g of Zy-4, mainly as organic compounds (more than 99%). This content is of the same order of magnitude with the value estimated by ORIGEN simulation for an average burn-up of 7 MWd/kgU (1.78 10^4 Bq/g of Zy-4).

The experimental results obtained for the total ^{14}C released as dissolved species after 18 days, 6, 8, 12 and 18 months of Zy-4 immersing in alkaline solution are almost the same, indicating that a small amount of ^{14}C was available as instant release fraction. Both

inorganic and organic ^{14}C were release as dissolved species, but more than 60% from the total ^{14}C released in solution was found to be as organic species.

The corrosion rates measured by electrochemical tests are ranging between 46 and 130 nm/y. The results of the electrochemical tests could be affected both by the cracks likely induced by the sample cutting but also by the non-standard experimental conditions used for these electrochemical measurements.

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1 Introduction

Two CANDU units are currently in operation at Cernavoda NPP (Unit U1 in operation since December 1996 and U2 since November 2007). Two more CANDU units are foreseen to be commenced on Cernavoda site. Each CANDU unit is designed for an operational time of 30 years, but for all four Cernavoda units a refurbishment after 25 years of operation is expected to extend their operational time to 50 years.

The core of the two operational Cernavoda units consists of 380 fuel channels with 12 fuel bundles (FA) on each channel. CANDU fuel FA contains 37 elements comprising of sintered UO_2 pellets (natural uranium) in Zy-4 tubes. The 37 elements are circularly arranged in three rings of 18, 12 and 6 elements respectively, around a central element. More details on CANDU SF are provided in D3.2 report [Caron, 2014].

CANDU units are designed to load and unload their fuel continuously at full power by disconnecting individual pressure tubes. It is expected that each CANDU unit will generate around 4.69E3 FA/year, which means in 50 years of operation for four CANDU units around 9.37E+05 spent FA will be generated. In CANDU nuclear fuel, Zy-4 is used as fuel cladding, and also for end-caps, end support plate, inter element spacers and pads. Each FA contains around 2.155 kg of Zy-4 which means the spent fuel that has to be disposed of in Romania will contain 2.02E6 kg of irradiated Zy-4.

The Romanian strategy for spent fuel and radioactive waste management foresees that the CANDU spent fuel will be disposed of together with other long-lived radioactive waste (such as non-fuel contact spent ion exchange resins, spent filters, pressure tubes and calandria tubes) in a geologic disposal, foreseen to be operational in 2065.

RATEN ICN objective in CAST WP3 was to measure the total C-14 content in irradiated Zy-4 (including its partition between inorganic and organic species) and to perform long-term corrosion tests on non-irradiated and irradiated Zy-4 in chemical conditions relevant to cementitious environment (NaOH 0.01 M, pH 12).

2 Materials and Methods

The corrosion and leaching tests were carried out on non-irradiated and irradiated Zy-4. In the following sections, the available Zy-4 samples are described.

2.1 *Non-irradiated Zy-4 samples*

Generally, the chemical composition of the Zircaloy-4 tubes used in the CANDU active zone, consist of: 1.2-1.7 % Sn, 0.18-0.24% Fe, 0.07-0.13% Cr, 1000-1400 ppm oxygen and Zr balance [TECDOC 2004]. Oxygen is added to increase the yield strength and acts as an α stabilizer, as well as Sn which is added to mitigate the deleterious effects of nitrogen and to improve the alloy mechanical properties. The other elements (Fe, Cr) have very low solubility in α-Zr. Therefore, these elements tend to form various types of second phase particles (intermetallic phases) depending on the composition, the processing and heat treatment history. Most common SPP observed in Zy-4 are $ZrFe_2$ and $ZrCr_2$ [Yan Dong 2017].

According to the specifications provided by the CANDU fuel producer the non-irradiated Zy-4 tubes used in the tests have following chemical composition: around 98 %Zr, 1.6 % Sn, 0.22 % Fe, 0.1% Cr, and 1200 ppm oxygen.

The non-irradiated Zy-4 samples were cut from as-received Zy-4 tube with external diameter (OD) of 13 mm and wall thickness of 0.4 mm, to get samples with length of 5 cm (see Figure 1**Erreur ! Source du renvoi introuvable.**).

Figure 1 Non-irradiatednon-oxidized Zy-4 sample

Before testing, metallographic analyses were carried out to analyse the samples microstructure. For these measurements an optical microscope model OLYMPUS GX71 has been used. For the microstructural investigations the non-irradiated Zy-4 tube was sliced and the resulted pieces were mechanically polished on wet SiC paper with grit sizes from 240 to 4000.

To obtain a similar thickness of the oxide layer as the one formed on the irradiated Zy-4 samples, the non-irradiated Zy-4 samples were oxidised in static isothermal autoclaves (Figure 2) in representative conditions to CANDU primary circuit (LiOH solution, pH=10.5, T=310 ^{o}C, p=100 atm). During the first WP2&WP3 meeting, a target value of 2.5 µm was established for the oxide thickness in order to complete the current knowledge.

Figure 2 Static autoclave used to oxidize the non-irradiated Zy-4 samples

2.2 Irradiated Zy-4

The irradiated Zy-4 samples were obtained from a CANDU spent fuel bundle (GK964F1) that was irradiated for 1 year in the Cernavoda Unit 2. After a cooling period of around 4 years in the Spent Fuel cooling bay, the fuel bundle was transferred to RATEN ICN and some fuel elements were extracted for different investigations inside the ICN hot cells (Figure 3 and Figure 4).

Figure 3 Hot cells from Post Irradiation Laboratory of RATEN ICN

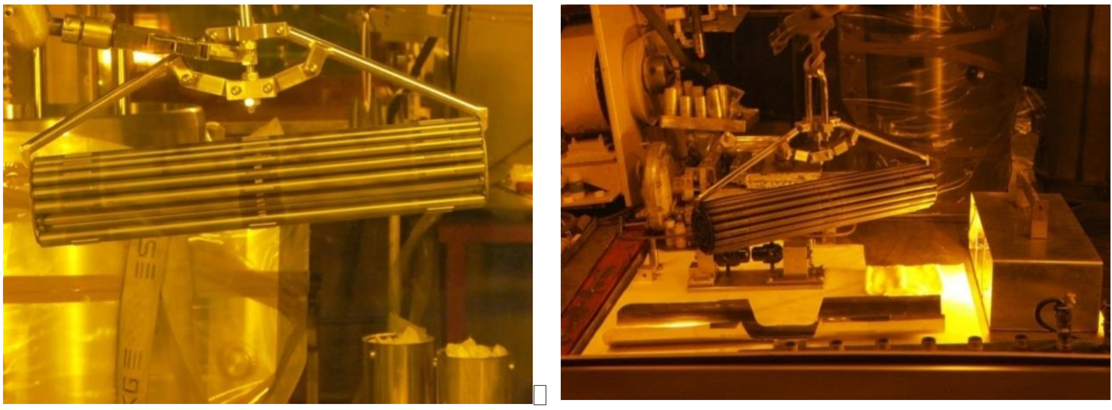

Figure 4 Manipulation of the CANDU spent FA inside the hot cell

At its loading in channel L-02 of Cernavoda Unit U2 (on July 24, 2008) the GK964F1 FA contained 19.208 kg of natural uranium, while at discharge (on August 11, 2009) the spent FA contained 18.958 kg of depleted uranium. The average burn up at its discharge was 210.119 MWh/kg U.

Based on the measurements carried out by the CANDU fuel producer, the Zy-4 used to product the GK964F1 FA contains 30 ppm of N_2.

From one of the spent fuel elements kept in the ICN hot cells for mechanical and radiological investigations, a tube of around 10 cm length (stored inside the hot cell for around 2 years) was available to obtain the irradiated Zy-4 samples for the experimental programme carried out by RATEN ICN under CAST WP3 (Figure 5). This tube was cut in 6 pieces of around 15 mm long each.

After the spent fuel was mechanically removed from these 6 irradiated Zy-4 samples, the Zy-4 tubes were washed in 4M nitric acid (3 washing cycles) and cleaned with deionized water. After air drying, the contact dose rate was below the acceptable limit to carry out the further experiments in a fume hood (between 450 and 600 µSv/h).

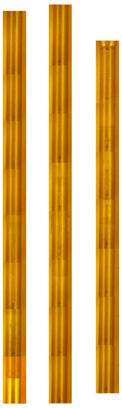

Figure 5 Irradiated Zy-4 tubes cut from one of the CANDU SF element

To have real measurement of the ^{14}C content in the irradiated Zy-4 samples prepared for leaching/corrosion tests, each of these 6 samples was further cut into two pieces, one of around 2 mm long for ^{14}C measurement and one of around 8 mm long for leaching/corrosion tests (Figure 6).

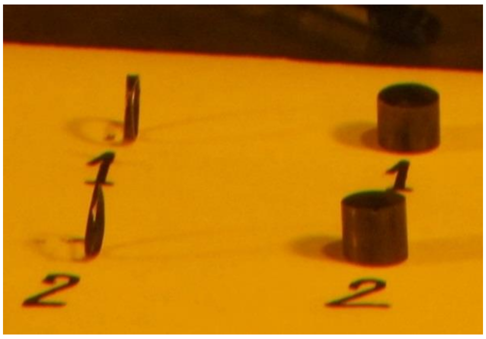

Figure 6 The irradiated Zy-4 samples prepared for ^{14}C measurements and leaching/corrosion tests

The mass and length of the irradiated Zy-4 samples prepared for the RATEN ICN experimental programme are reported in Table 1.

Following the General Assembly Meeting in 2016, it was decided to find one more irradiated Zy-4 sample from the same CANDU spent fuel element to carry out a supplementary leaching test for a shorter period in order to account for the instantaneous ^{14}C release. Two small rings were found (labelled as 7.1 and 7.2 in Table 1). One was used to measure the ^{14}C content and one for leaching test, in the same conditions as described above.

Table 1 Mass of the irradiated Zy-4 samples used for ^{14}C measurement and leaching/corrosion tests

Irradiated Zy-4 for ^{14}C measurement		**Irradiated Zy-4 for leaching/corrosion tests**		
Sample ID	Mass, g	Sample ID	Mass, g	Length, mm
# 1.1	0.2439	# 1.2	1.1815	8.29
# 2.1	0.1623	# 2.2	1.1205	7.86
# 3.1	0.3825	# 3.2	1.0425	7.31
# 4.1	0.2320	# 4.2	0.8328	5.84
# 5.1	0.1664	# 5.2	1.1166	7.83
# 6.1	0.1383	# 6.2	1.2498	8.77
# 7.1	0.2616	# 7.2	0.2132	1.50

Gamma measurements were carried out on the irradiated Zy-4 samples before starting the leaching tests in order to measure the ^{60}Co content and try to see if the release of this radionuclide could be correlated with the ^{14}C release. Gamma measurements were also performed to measure the ^{60}Co content in the leachate solution.

Due to the high content of ^{137}Cs in the irradiated Zy-4 samples, gamma measurements were carried out on small rings cut from the irradiated Zy-4 to be used in the long term leaching tests. An ORTEC Gamma spectrometer with HPGe detector was used for gamma measurements.

2.3 *Corrosion experiments*

To evaluate the ^{14}C release from the irradiated Zy-4 under chemical conditions relevant to cementitious environment, static leaching tests were performed. To assess the behaviour of non-irradiated Zy-4 in the same chemical conditions, leaching tests were also carried out on non-irradiated Zy-4 samples. The corrosion rate was measured both for non-irradiated and irradiated Zy-4 samples by using electrochemical methods.

2.3.1 Static leaching tests

Leaching tests, also called static corrosion tests in this report, were carried out both on non-irradiated and irradiated Zy-4 samples.

The leaching tests started in April 2016 for the irradiated samples and in June 2016 for non-irradiated samples. These leaching tests have been run under N_2 atmosphere at room temperature (23±3°C).

According to the discussions during CAST WP3 meetings, NaOH 0.01 M was chosen as leachant solution (pH = 12, Total Dissolved Salts =1100 mg/l , and conductivity of 2.20mS/cm).

Six glass tubes were adapted to allow N_2 purging for 48 hours in order to ensure anoxic conditions (Figure 7). Due to the high radiation dose, the glass tubes were placed inside a lead castle.

Figure 7 View of the glass bottles prepared for the static leaching tests

After 6 months (October 2016), the first two leaching vessels were opened to sample the leachates and measure the total ^{14}C and its inorganic/organic partition, but also the gamma emitters. Before opening the leaching vessels, N_2 was purged for 30 minutes and the gas was washed through two alkaline gas washing bottles in order to absorb the potential inorganic ^{14}C released in gas phase during the leaching period.

The first leaching vessel was opened after 8 months (December, 2016), the second one after 10 months (February, 2017), the third one after 12 months (April, 2017) and the forth one after 18 months (October 2017. In order to have data for a longer leaching period, it was decided that the last leaching vessel will be opened after 18 months (October, 2017). Also, to account for instantaneous release, a leaching vessel (sample ID 7.2) was opened after 18 days. The leachant solutions were analysed for total ^{14}C content, inorganic and organic ^{14}C partition as well as tritium and gamma emitters.

The corrosion rate was determined on irradiated Zy-4 samples contained in each leaching vessel.

2.3.2 Accelerated corrosion tests/electrochemical measurements

At the first meeting on WP 3 (Paris, June 2014) the Linear Polarization Resistance (LPR) method was selected as the most appropriate technique to determine the uniform corrosion rate of the spent fuel claddings. This technique is quick and enables to detect the instantaneous corrosion rate.

The device used for electrochemical tests was a potentiostat / galvanostat model AUTOLAB 302 (Figure 8) electrically connected to the electrodes immersed in the cell made of borosilicate glass with a 90 ml capacity and equipped with a vessel lid with five openings.

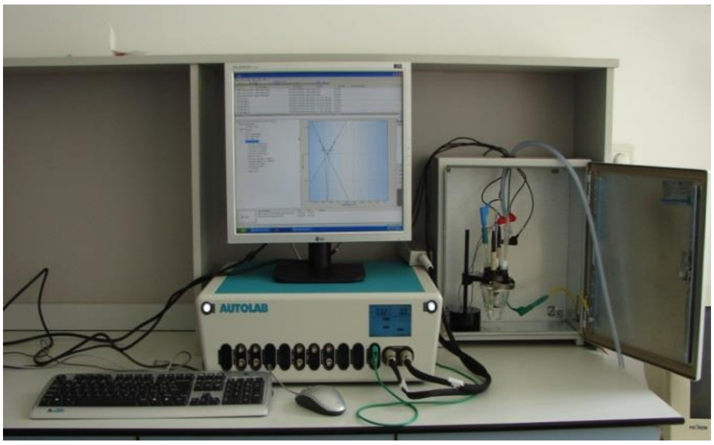

Figure 8 Experimental set-up used for the electrochemical tests (left) and the corrosion cell (right)

Four holes are for electrodes (an Ag/AgCl reference electrode, two Pt counter electrodes, and the working electrode) and a hole for the bubbling tube. Because in time it has been decided to use only 30ml of testing solution, the surface of one rod Pt counter electrode imersed into solution was too small. Consecuently, we used 2 counter electrodes, connected to each other with one cable (the grey cable and black connector in Figure 9). An important parameter of the counter electrode is the surface area, and large enough area is necessary to support the current generated for the working electrode. After mounting the electrodes, the vessel lid was tight by adding resin or glue around them.

All electrodes and the bubbling tube were immersed into 30 ml NaOH 0.01M solution (pH = 12, TDS =1100 mg/l, and conductivity of 2.20mS/cm). Before starting each experiment, the device was calibrated using an AUTOLAB Dummy Cell 2. Nitrogen gas was bubbled into solution for 2 hours at the beginning of each electrochemical test and throughout the duration of the test. The electrochemical assembly was mounted into a Faraday cage during tests to avoid electromagnetic interference from external sources (Figure 9).

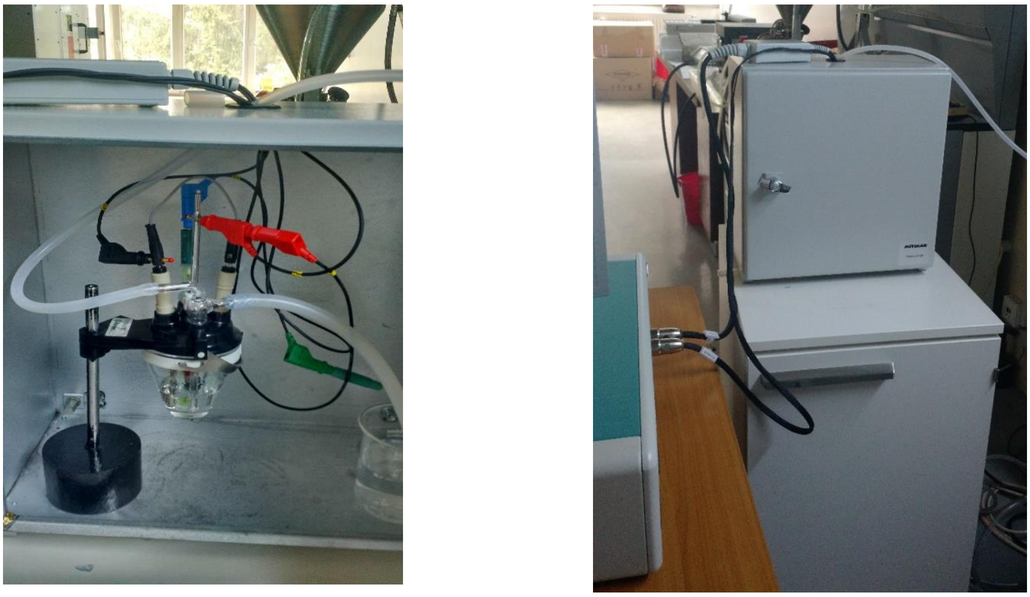

Figure 9 Corrosion cell equipped with electrodes mounted inside a Faraday cage

After testing, the NOVA 1.11 software provides a convenient interface for making Tafel plots, calculating Tafel slopes and corrosion rates. Selecting corrosion rate fit, the analysis tool performs a curve fit based on the Buttler-Volmer equation which allows determination of the corrosion current density (i_{corr}), polarisation resistance (R_p) and corrosion rate.

For reactions under activation control, the polarization resistance can be related to the corrosion current density by the Stern-Geary equation [ASTM G 102, 2004]:

$$R_p = B/i_{corr} = \Delta E/\Delta I \qquad \text{(eq. 1)}$$

where:

R_p = polarization resistance(Ω)

B= Stern-Geary constant (V)

i_{corr} = the corrosion current density (A/cm^2)

The proportionality constant, B, for a particular system can be empirically determined (calibrated from separate weight loss measurements) or, as shown by Stern and Geary, it can be calculated from b_a and b_c, the anodic and cathodic Tafel slopes, as:

$$B = b_a{*}b_c/2.3(b_a+b_c) \qquad \text{(eq. 2)}$$

The Tafel slopes themselves can be evaluated experimentally using real polarization plots. The corrosion currents estimated using these techniques can be converted into penetration rates using the Faraday law or a generic conversion chart.

The study of uniform corrosion or studies assuming corrosion uniformity are probably the most widespread application of electrochemical measurements both in the laboratory and in field. The widespread use of these electrochemical techniques does not mean that they are straight forward. Both linear polarization and Tafel extrapolation need special precautions for their results to be valid. The main complications or obstacles in performing polarization measurements can be summarized as follows:

- Effect of Scan Rate: The rate at which the potential is scanned may have a significant effect on the amount of current produced at all values of potential. The rate at which the potential is changed so-called “the scan rate” must be chosen adequately to avoid misinterpretation of the features.

Effect of Solution Resistance: The distance between the Luggin capillary (of the salt bridge to the reference electrode) and the working electrode is purposely minimized in most measurements to limit the effect of the solution resistance. Solutions with extremely high resistivity may prevent proper electrochemical measurements.

Changing Surface Conditions: Since corrosion reactions take place at the metal surface, when the surface is changed, due to processing conditions, active corrosion or other reasons, the potential is usually also affected enhancing modifications on the polarization curves.

2.4 Method used for ^{14}C measurement on irradiated Zy-4

The analytical method used for ^{14}C measurement on irradiated Zy-4 samples consists of a sequential extraction of inorganic and organic ^{14}C using acid dissolution and wet oxidation, adapted after the method developed by Magnusson [Magnusson et al., 2008] for ^{14}C measurement in spent ion exchange resins and process waters.

The experimental set-up used for release and separation of inorganic and organic ^{14}C is schematically presented in Figure 10. It consists in a reaction vessel, a separatory funnel, a nitrogen supply and a vacuum pump, two gas washing lines with a catalytic furnace between them.

An Erlenmayer flask (300 ml) with a three-hole rubber stopper (two for gas and separatory funnel inlets and one for gas outlet) was used as a reaction vessel and a tap-water cooling loop, made of copper tubing that fit the outer side of the Erlenmeyer flask (Figure 10), ensured vapour condensation. The reaction vessel was placed on a heater with magnetic stirring.

To ensure that no gases are released from the system, all dissolution and wet oxidation experiments were carried out under vacuum (0.2 bar below atmospheric pressure) and the carrier gas (N_2) was introduced into the system with a flow rate between 60 and 80 ml/min (controlled by a flow meter).

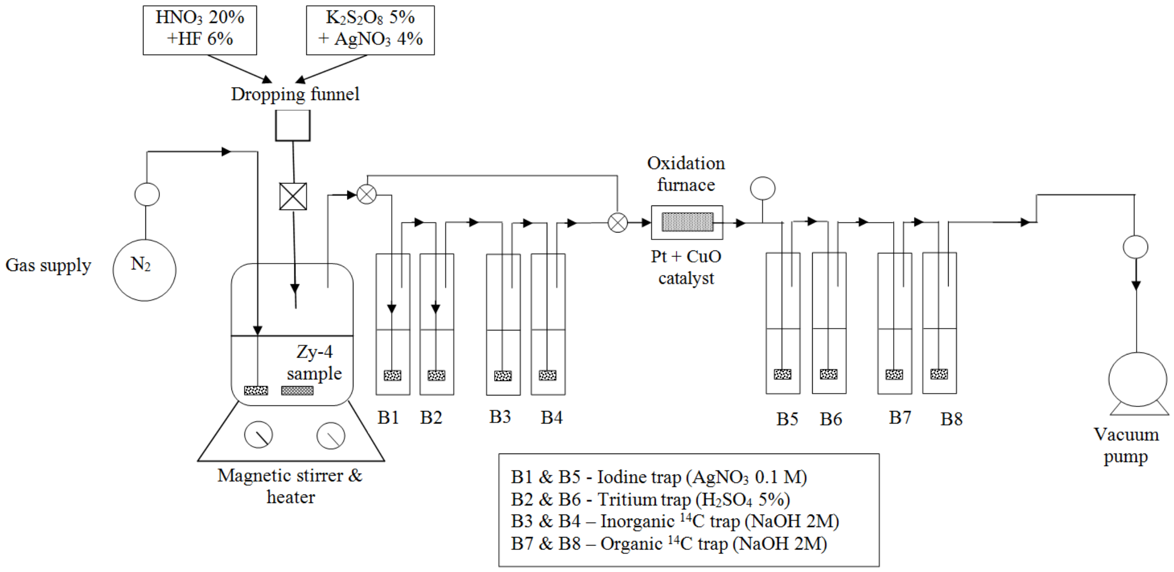

Figure 10 Experimental set-up for separation and purification of inorganic and organic ^{14}C

To absorb the radionuclides that could be released in gas phase during the acid stripping or wet oxidation together with ^{14}C, the gas washing lines consists of iodine traps (0.1 M $AgNO_3$), tritium traps (5% H_2SO_4) and ^{14}C traps (2M NaOH). Other beta-gamma emitters that could be release in gas phase are absorbed in the slightly acidic trap designed also to absorb tritium.

In the first step of the analytical method, the dissolution of Zy-4 was achieved by adding diluted nitric acid (20% HNO_3) and fluoric acid (6% HF). Since the inorganic ^{14}C compounds (i.e. carbonates and bicarbonates) are easily decomposed by weak acids to carbon dioxide, the inorganic ^{14}C was released during this acid dissolution as $^{14}CO_2$ and carried out by the N_2 gas and absorbed in the first alkaline gas washing bottles (B3 and eventually B4).

If any ^{14}C were released during this dissolution step as CO or other organic molecules, it passed through the scrubbing bottles of the first gas washing line and then oxidized to CO_2 in the catalytic furnace and subsequently absorbed in the scrubbing bottles of the second gas washing line. After the acid dissolution step was accomplished the first gas washing line was isolated from the system by means of three ways valves placed before the first scrubbing bottle and the forth one.

Because the organic compounds have high bounding energies between atoms they are decomposed by strong oxidants such as potassium persulphate ($K_2S_2O_8$). The presence of a catalyser such as silver nitrate ($AgNO_3$) enhances the decomposition of the organic compounds. During the wet oxidation step the temperature of the solution resulted in the reaction vessel after Zy-4 dissolution was slightly increased to 90°C.

The mechanism of ^{14}C-labelled organic compounds decomposition is based on the $OH^{(*)}$ radicals and can be expressed by the following equations [Ahn et al., 2013]:

$$K_2S_2O_8 \xrightarrow{H_2O} 2K^+ + S_2O_8^{2-} \qquad \text{(eq. 3)}$$

$$S_2O_8^{2-} + 4H_2O \underset{Ag}{\rightarrow} 2SO_4^{2-} + 2H^+ + 2OH^* \qquad \text{(eq. 4)}$$

$$^{14}C_nH_m + (4n+m)OH^* \rightarrow n^{14}CO_2 + (2n+m)H_2O \qquad \text{(eq. 5)}$$

The ^{14}C released during the wet oxidation step of the analytical procedure (both as CO_2, but also as CO or CH_4) is carried by the carrier gas through a catalytic furnace that ensures oxidation of any reduced compounds to CO_2, which is subsequently absorbed in the scrubbing bottles of the second gas washing line (Figure 10). Three wet oxidation steps were carried out in order to ensure the complete decomposition of the organic ^{14}C-labelled compounds, and the carrier gas was purged into the system for 1 hour in each wet oxidation steps.

This method distinguishes between $^{14}CO_2$ released during acid dissolution and $^{14}CO_2$ released by wet oxidation of hydrocarbons (alcohols, carboxylic acids…) allowing determination of the inorganic and organic fractions of ^{14}C in irradiated Zy-4.

The ^{14}C activity in the alkaline traps as well as ^{3}H activity in solutions sampled from the acid scrubbing bottles were measured by liquid scintillation counting (LSC), using a counter model PerkinElmer Tri-Carb 3100TR (that allows in Ultra Low Level counting mode a count rate between 1 and 20 CPM above the background).

Hionic Fluor liquid scintillation cocktail was used for ^{14}C measurement by LCS, and Ultima Gold AB liquid scintillation cocktail for tritium measurement. The ratio between sample and scintillation cocktail was 1 to 10. All samples were kept in darkness over night before their counting.

Aliquots from the reaction vessel solution, as well as from all scrubbing bottles, were sampled for gamma measurements. The system used for the gamma spectrometry includes the following components: HPGe ORTEC detector, digiDart analyser and GammaVision software. The spectrometer was calibrated in energy and efficiency using a standard liquid source containing ^{60}Co, ^{137}Cs, ^{241}Am, ^{152}Eu in 20 ml glass vials. The same geometry was used for gamma measurements on the sampled aliquots solutions from the acid digestion/wet oxidation experiments. Each sample was counted for more than 4 hours.

2.5 Method for determining the inorganic and organic ^{14}C partition in liquid aliquots sampled from the leaching tests

The liquid aliquots sampled from the static leaching tests were analysed to measure the inorganic and organic ^{14}C, tritium and also gamma emitters.

For inorganic and organic ^{14}C measurement the analytical procedure adapted after that developed by Magnusson [Magnusson et al., 2008] was applied. The same experimental set-up as that described above was used and the procedure is similar with that used for irradiated Zy-4, excepting the first step. For liquid samples the inorganic ^{14}C was released by acid stripping, using concentrated sulphuric acid (H_2SO_4 6M).

For each liquid sample, one acid stripping step and two wet oxidations were carried out (in each the carrier gas was purged for 1 hour) for complete ^{14}C recovery.

The total ^{14}C content in the liquids sampled from the leaching tests was also determined by combustion in an oxygen-enriched atmosphere with a continuous flow of oxygen using Sample Oxidizer, Model 307 PerkinElmer® (Figure 11).

With this method, any hydrogen is oxidized to H_2O and any carbon is oxidized to CO_2. The ^3H_2O is condensed in a cooled coil, washed into a counting vial where it is mixed with LSC cocktail (Monophase®S). The $^{14}CO_2$ is trapped by vapour-phase reaction with an amine

(Carbo-Sorb® E) and the resulting product (carbamate) is mixed with the LSC cocktail (Perma-fluor® E+) directly in the counting vial.

Figure 11 Experimental device used for total ^{14}C measurements in liquid samples

Two separate samples, one for ^{3}H measurement and one for ^{14}C measurement, are trapped at the end of the combustion process at ambient temperature minimizing the cross-contamination. Since the carbon dioxide readily reacts with compounds containing amines, the Carbo-Sorb® E was chosen to absorb the $^{14}CO_2$ released during the combustion process.

The absorption reaction of carbon dioxide can be described as follows [Ahn at al., 2013]:

$$^{14}CO_2 + RNH_2 \rightarrow RNH_2^{+\,14}COO^- \qquad \text{(eq. 6)}$$

$$RNH_2^{+\,14}COO^- + \begin{bmatrix} RNH_2 \rightarrow RNH^{14}COO^- + RNH_3^+ \\ H_2O \rightarrow RNH^{14}COO^- + H_3O^+ \\ OH^- \rightarrow RNH^{14}COO^- + H_2O \end{bmatrix} \qquad \text{(eq. 7)}$$

$$RNH^{14}COO^- + H_2O \rightarrow RNH_2 + H^{14}CO_3^- \qquad \text{(eq. 8)}$$

As shown in eq. 7, the amine contained by the Carbo-sorb E solution reacts with ^{14}C-labelled carbon dioxide to form a zwitterion, which reacts with H_2O to form a stable carbonate compound (eq. 8).

3 Results and discussion

3.1 *Structural characterisation of non-irradiated Zy-4 samples*

Metallographic analyses were carried out to analyse the sample microstructure using an optical microscope model OLYMPUS GX71. For the microstructural investigations a non-irradiated Zy-4 tube was sliced and the resulted pieces were mechanically polished on SiC paper with grit sizes 240 to 4000. To reveal the microstructure, a chemical polishing has been performed for 10 seconds under the fume hood, followed by rubbing the surface with a swab soaked in a mixture of acids (10ml HF, 45ml HNO_3 and 45ml distilled water) [ASTM E 407].

The metallographic analyses performed on the non-irradiated Zy-4 showed uniform distributed small black spots which can be attributed to fine intermetallic secondary phases particles (SPPs) and some black “flakes” which can be attributed to larger SPPs (Figure 12). The type and characteristics of intermetallic secondary phases are dependent on manufacturing heat treatment.

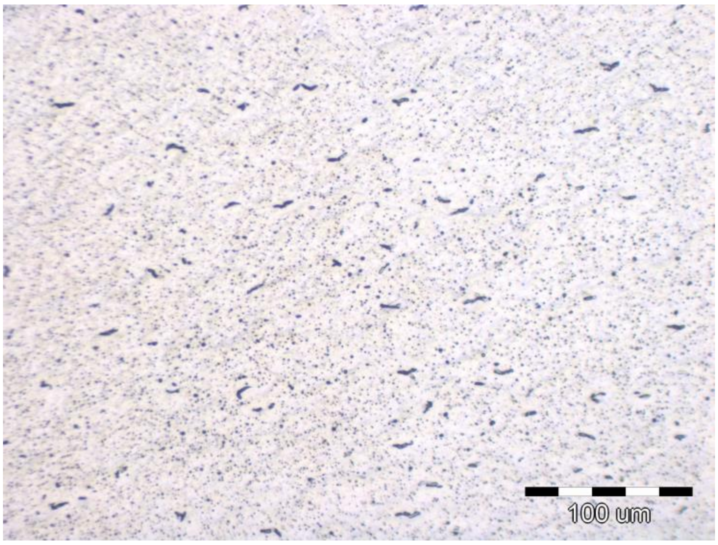

Figure 12 Optical microstructure of as received Zy-4 tube (magnification x200)

After 250 days of exposure inside the autoclave, the non-irradiated Zy-4 samples turned black due to the adherent oxide layer developed on the surface (Figure 13).

Figure 13 Visual aspect of the Zy-4 oxidised sample

The average weight gain of Zy-4 samples after this exposure period was 39 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 Zy-4 oxide represents a thickness of 1µm. In the case of these samples, the average thickness was 2.61µm corresponding to the average weight gain.

Also, the oxide thickness of the non-irradiated Zy-4 samples was measured by optical microscopy. Based on this analyses the oxide thickness was estimated to be between 2.2 µm and 2.7µm (Figure 14).

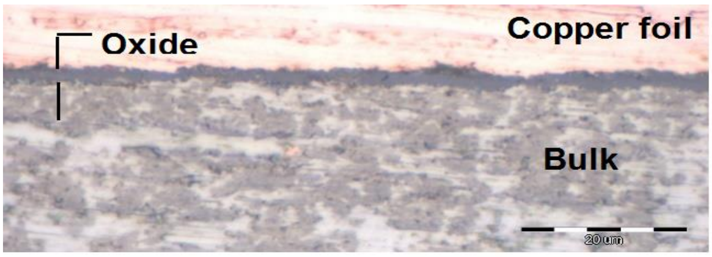

Figure 14 Oxide layer thickness measured by optical microscopy (magnification x1000)

Analysing with optical microscope the microstructure of the non-irradiated Zy-4 samples after oxidation in autoclave, were identified long hydrides (Fig.15a) and a Widmanstatten pattern (Figure 15 b).

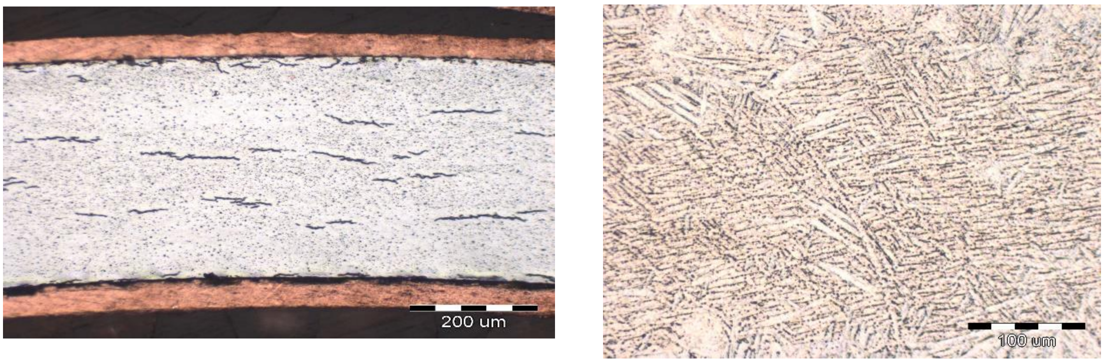

Figure 15 Hydrides and Widmanstatten-basketweave type structure of oxidized non-irradiated Zy-4 samples

3.2 *Characteristics of the irradiated Zy-4 sample*

The outside oxide thickness measured along the CANDU spent fuel element used to cut the irradiated Zy-4 samples was measured inside the hot cells. It was between 2.34 µm and 3.32 µm (Figure 16).

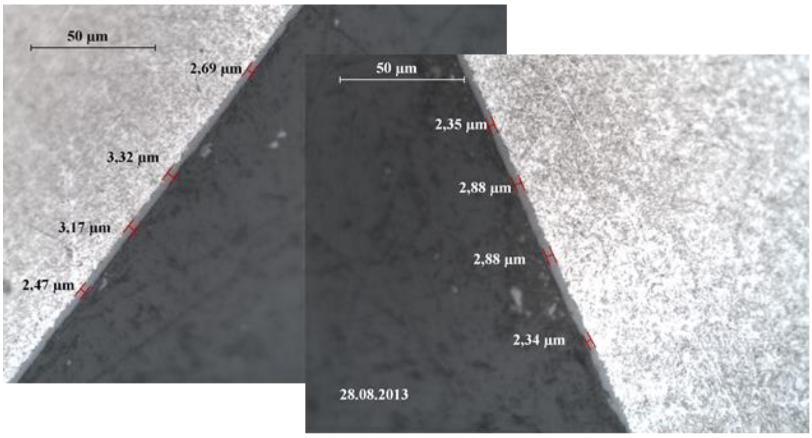

Figure 16 The outside oxide layer along the spent fuel cladding

No continuous oxide layer was observed on the inside surface of the irradiated Zy-4 tube (Figure 17).

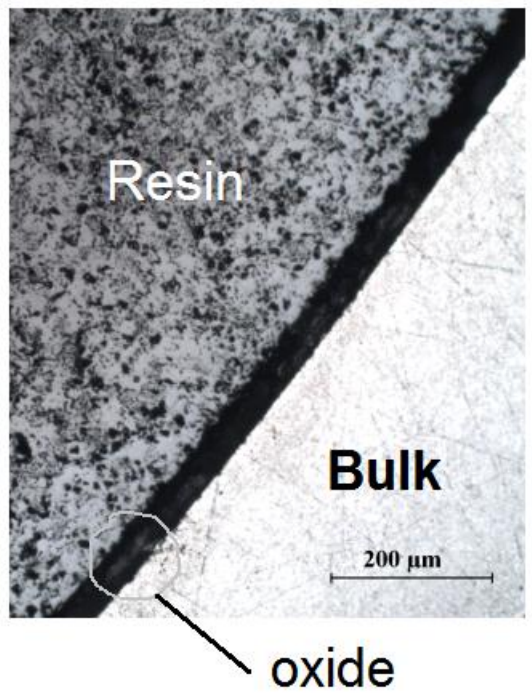

Figure 17 The inside aspect of the irradiated Zy-4 tube

Hydride inclusions and Widmanstatten structure were also observed through optical microscopy on the irradiated Zy-4 tube (Figure 18).

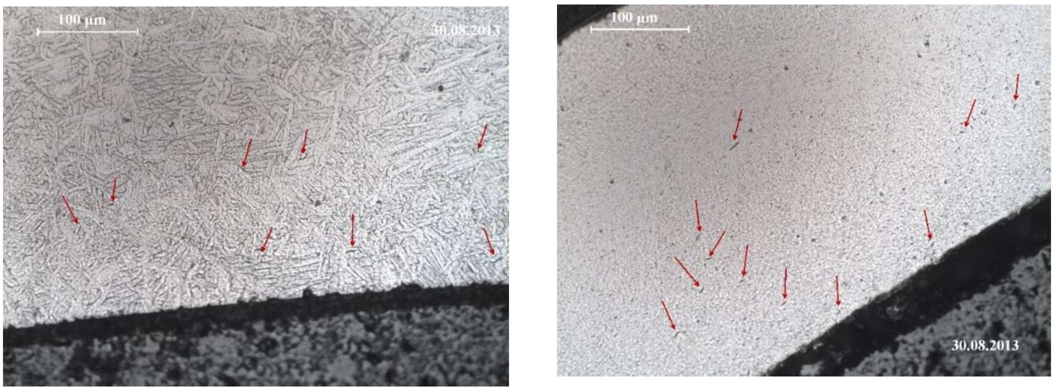

Figure 18 Hydrides and Widmanstatten structure on the irradiated Zy-4 tube

By gamma spectrometry (Figure 19) ^{60}Co concentration activity in the irradiated Zy-4 samples was measured to be around 1E+06 Bq/g of Zy-4 (Table 2).

Table 2 Beta-gamma emitters measured on the irradiated Zy-4

Radionuclide	^{125}Sb	^{137}Cs	^{134}Cs	^{60}Co
Activity, Bq/g	6.19×10^6	5.48×10^6	5.68×10^5	1.60×10^6

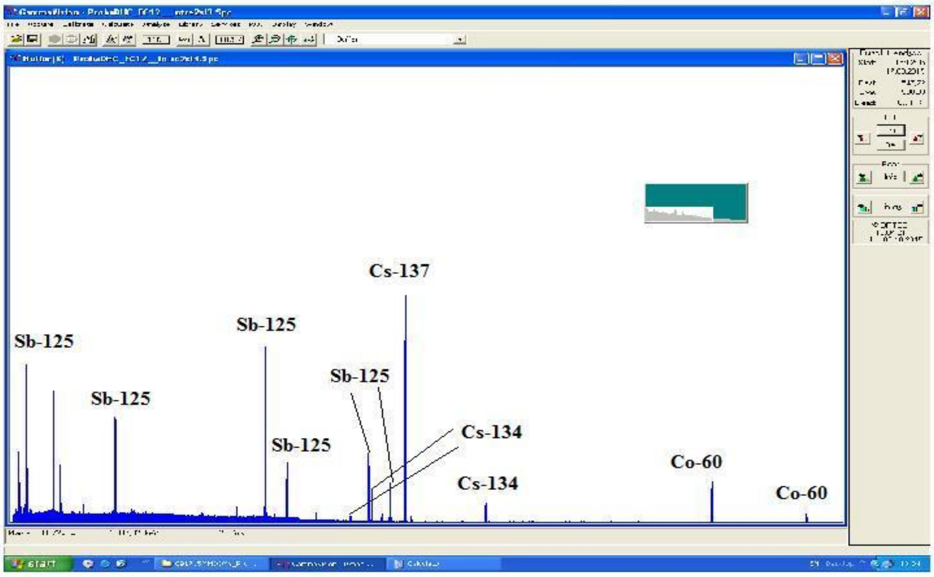

Figure 19 Gamma spectrum for irradiated Zy-4

Also, other relevant gamma emitters were identified in the irradiated Zy-4 samples (Figure 19), with the concentration activities presented in Table 2.

3.3 Tests to assess the ^{14}C recovery and the memory effect of the analytical method for inorganic and organic ^{14}C measurement

Preliminary acid stripping/wet oxidation tests were carried out on aqueous solutions labelled with the radionuclides of interest: inorganic ^{14}C (as sodium carbonate / bicarbonate), organic ^{14}C (sodium acetate and lauric acid), ^{3}H, and gamma emitters (^{60}Co, ^{137}Cs, ^{241}Am and ^{152}Eu).

The available inorganic ^{14}C was a barium carbonate standard with an activity of 1 mCi (3.7 E+07 Bq). The ^{14}C from this barium carbonate was released by acid stripping and absorbed in 2M NaOH solution. By this approach a solution containing ^{14}C in the form of sodium carbonates/bicarbonates with an activity of 37.06E+03 Bq/ml was obtained and further used in the recovery tests. The scrubbing bottles and silicon tubing used to prepare inorganic ^{14}C stock solution were not further used in the recovery tests.

The radionuclides activities in stock solutions used for these experiments are reported in Table 3.

Table 3 The radioactivity of the stock solutions used in recovery tests

Radionuclide	Activity, Bq/ml
^{14}C-labelled sodium carbonate/bicarbonate	$3.34x10^4$
^{14}C-labelled sodium acetate	$8.76x10^4$
^{14}C-labelled lauric acid	$4.13x10^3$
^{3}H	$3.88x10^2$
^{137}Cs	$3.88x10^2$
^{241}Am	$1.11x10^3$
^{152}Eu	$1.22x10^3$
^{137}Cs	$1.19x10^3$
^{60}Co	$1.20x10^3$

In first set of recovery tests only inorganic ^{14}C, ^{3}H, and gamma emitters were used. Five acid stripping tests were carried out to assess the radionuclides recoveries and the reproducibility of the experimental results.

In the reaction vessel, beside the radioactive solutions 100 mg of non-radioactive sodium carbonate and 100 mg of non-radioactive sodium acetate were added as carrier. Also a few drops of methyl orange were added as pH indicator.

After a low vacuum (0.2 bars below the atmospheric pressure) was achieved the nitrogen gas was introduced in the system with a flow rate between 60 and 80 ml/min. The stripping acid (20 ml of H_2SO_4 6M) was dropped into the reaction vessel through the separation funnel and the carrier gas was purged into the system for 1 hour.

Since iodine was not used in these tests, the first scrubbing bottle was used for tritium absorption and the following three were filled with an alkaline solution for $^{14}CO_2$ absorption. The ^{14}C recovery was between 94.79% and 98.32%. The average recovery was 96.97 % with a standard deviation of 1.46 %. From the recovered ^{14}C around 99% was found in the gas washing bottle no. 2, and around 0.8% in the third gas washing bottle. No ^{14}C was found in the fourth scrubbing bottle and it was decided to use only two alkaline gas washing bottles in the following tests. No gamma emitters were identified in any of the scrubbing bottles and the entire activities of ^{60}Co, ^{137}Cs, ^{241}Am and ^{152}Eu were found in the solutions sampled from the reaction vessel (with average recovery higher than 96%). Also the solutions sampled from the alkaline gas washing bottles were counted for tritium (using double labelled mode) but tritium was not detected above the background in these samples. All tritium added in the reaction vessel was found in the acid scrubbing bottle.

An average memory effect of less than 1% was observed. No washing step was performed between the recovery step and the memory one.

In the second set of recovery tests, beside the radionuclides used in the previous tests, organic ^{14}C in the form of sodium acetate was also added in the reaction vessel.

The experimental results obtained for ^{14}C recovery from these tests are reported in Table 4.

After the first test it was observed that the recovery of the ^{14}C-labelled sodium acetate was quite low but in the content of ^{14}C in the gas washing bottles designated to absorb $^{14}CO_2$ released in the acid stripping step, it was higher than the ^{14}C introduced in the reaction vessel as ^{14}C-labelled sodium carbonate/bicarbonate. Since no other radionuclides were identified in the solutions sampled from the alkaline scrubbing bottles, demonstrating that the ^{14}C measurement by LSC was not affected by interferences, the total ^{14}C recovery was computed and it was close to 100%. To confirm these results a second test was carried out in the same conditions with similar results. It was supposed that the sulphuric acid used in the acid stripping step could reduce part of the ^{14}C-labelled sodium acetate, which is present at its release as $^{14}CO_2$ in the acid stripping step.

In the next test the amount of sulphuric acid used as a stripping reagent decreased to 10 ml, but the experimental results were similar to those obtained by using 20 ml. Similar results were also obtained using nitric acid as stripping reagent.

The next test was performed using chloric acid as stripping acid but in this test the chlorine ions inhibit the platinum catalyst and very low ^{14}C was measured in the alkaline gas washing bottles designed to absorbed the $^{14}CO_2$ released during the wet oxidation step.

Table 4 The experimental results obtained in the recovery tests

Test #	^{14}C type	Bq in reaction vessel	Bq recovered in scrubbing bottles	η %
Test 1 20 ml H_2SO_4 6M	^{14}C-labelled sodium carbonate/bicarbonate	5.10E+03	8.50E+03	166.66
	^{14}C-labelled sodium acetate	1.64E+04	1.37E+04	83.22
	total ^{14}C	2.15E+04	2.22E+04	102.99
Test 2 20 ml H_2SO_4 6M	^{14}C-labelled sodium carbonate/bicarbonate	6.06E+04	9.92E+04	163.75
	^{14}C-labelled sodium acetate	1.64E+05	1.17E+05	71.11
	total ^{14}C	2.25E+05	2.16E+05	96.07
Test 3 10 ml H_2SO_4 6M	^{14}C-labelled sodium carbonate/bicarbonate	9.41E+03	1.27E+04	134.75
	^{14}C-labelled sodium acetate	1.05E+04	7.18E+03	68.69
	total ^{14}C	1.99E+04	1.99E+04	99.99
Test 4 20 ml HCl 6M	^{14}C-labelled sodium carbonate/bicarbonate	3.03E+04	5.19E+04	171.36
	^{14}C-labelled sodium acetate	8.21E+04	8.54E+02	1.04
	total ^{14}C	1.12E+05	5.27E+04	46.92

To assess how much from the ^{14}C in the form of sodium acetate is released in the acid stripping step two more tests were carried out only with ^{14}C-labelled sodium acetate solution. Only scrubbing bottles with alkaline solution were used for these tests (three before and after the catalytic furnace). The first two alkaline gas washing bottles were isolated by three ways valves placed before and after them (Figure 20) after the acid stripping step of the analytical method.

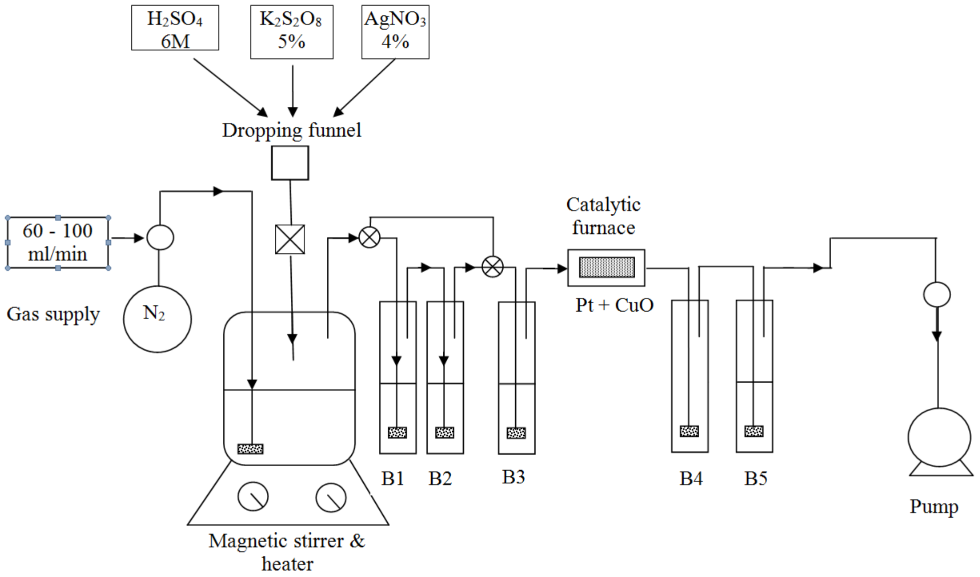

Figure 20. Experimental set-up used to evaluate the ^{14}C released from the ^{14}C-labelled sodium acetate

These tests showed that around 40% from the ^{14}C activity introduced in the reaction vessel was released as $^{14}CO_2$ in the acid stripping step and the rest after oxidation (Table 5).

Table 5 The experimental results obtained in tests for ^{14}C released from the ^{14}C-labelled sodium acetate (no ^{14}C activity was detected in B2, B4 and B5)

^{14}C in reaction vessel, Bq	Total ^{14}C recovered, Bq	Recovery, %	^{14}C in B1, Bq	^{14}C in B3, Bq	Recovered after acid stripping, %	Recovered after wet oxidation, %
548.86	525.40	95.73	202.60	322.80	36.91	58.81
542.08	537.90	99.23	229.30	308.60	42.30	56.93

A hypothesis that could explain the results of these tests was that the ^{14}C-labelled sodium acetate could be degraded and contains not only ^{14}C-labelled sodium acetate but also some ^{14}C-labelled carbonate. To test this acidification of a ^{14}C-labelled sodium acetate solution in fume hood was performed using both sulphuric acid and nitric acid to adjust the solution pH at 5 (assuming that the ^{14}C as sodium carbonate is released as $^{14}CO_2$ at pH around 5.4). By measuring the ^{14}C activity in the initial solution and after its acidification it was observed that indeed around 40% of the ^{14}C activity was released only by adjusting the pH to 5.

To have no doubt in relation to the recovery of the organic fraction of the radiocarbon by the proposed analytical method, a solution containing ^{14}C-labelled lauric acid (even this chemical form is less probable to be present in the irradiated Zy-4 and more in the liquid waste generated by NPP operations, as it is present mainly in soaps and other solutions) was used in another set of acid stripping/wet oxidation experiments.

In these tests, good recoveries were obtained both for ^{14}C in inorganic form (as sodium carbonate/bicarbonate) and organic form (as lauric acid) and no other radionuclides were identified by gamma spectrometry in the solutions sampled from the alkaline scrubbing bottles. The recovery of ^{14}C-labelled lauric acid was around 98% and it was concluded that the proposed analytical method can be used to evaluate the inorganic and organic ^{14}C content in the solutions sampled from the leaching tests as well as to evaluate the ^{14}C content in irradiated Zy-4.

To account for the uncertainty associated to this analytical method, 6 identical tests were carried out using the same ^{14}C activity in the test solutions (both inorganic and organic form). The standard deviation of the results of these tests was less than 15%.

Combustion tests (five tests) were also carried out using the solutions labelled with ^{14}C (in form of sodium carbonate/bicarbonate, sodium acetate and lauric acid), ^{3}H, and gamma emitters.

By this method, the total ^{14}C recovery was between 93.8% and 99.9%, with an average value of 97.5% and standard deviation of 1.24%.

The counting vials obtained after combustion for ^{14}C measurement were also measured by gamma spectrometry and no gamma emitters were identified above the background level even after 12 hours of counting.

3.4 *Inorganic and organic ^{14}C content in CANDU irradiated Zy-4*

Seven irradiated Zy-4 samples were used to evaluate the ^{14}C content and its inorganic / organic partition, using the analytical procedure described in Chapter 2.5.

The experimental results obtained for these samples (reported in Table 6) show that the irradiated Zy-4 used for leaching / corrosion tests contains around 2E+04 Bq of ^{14}C per gram of Zy-4, mainly as organic compounds.

Table 6 ^{14}C concentration activity in the irradiated Zy-4 samples used for inventory measurements

Sample ID	^{14}C activity				
	Bq/g of Zy-4			%	
	Inorganic ^{14}C	Organic ^{14}C	Total ^{14}C	Inorganic ^{14}C	Organic ^{14}C
# 1.1	49.61±7.44	$1.63x10^{4} \pm 2.45x10^{3}$	$1.64\ x10^{4} \pm 2.46\ x10^{3}$	0.3031±0.0455	99.6969±14.9545
# 2.1	51.89±7.78	$2.15x10^{4} \pm 3.23\ x10^{3}$	$2.16\ x10^{4} \pm 3.24\ x10^{3}$	0.2406±0.0361	99.7594±14.9639
# 3.1	29.62±4.44	$2.12x10^{4} \pm 3.18\ x10^{3}$	$2.12\ x10^{4} \pm 3.18\ x10^{3}$	0.1393±0.0209	99.8607±14.9791
# 4.1	41.58±6.24	$2.47x10^{4} \pm 3.71\ x10^{3}$	$2.47\ x10^{4} \pm 3.71\ x10^{3}$	0.1684±0.0253	99.8316±14.9747
# 5.1	23.38±3.51	$1.87x10^{4} \pm 2.81\ x10^{3}$	$1.87\ x10^{4} \pm 2.81\ x10^{3}$	0.1249±0.0187	99.8751±14.9813
# 6.1	26.61±3.99	$2.22x10^{4} \pm 3.33\ x10^{3}$	$2.22\ x10^{4} \pm 3.33\ x10^{3}$	0.1195±0.0179	99.8805±14.9821
# 7.1	30.12±4.52	$2.35x10^{4} \pm 3.53\ x10^{3}$	$2.35\ x10^{4} \pm 3.53\ x10^{3}$	0.1278±0.0192	99.8722±14.9808
average	36.11	$2.12x10^{4}$	$2.12\ x10^{4}$	0.1748	99.8252
stdev	11.49	$2.84x10^{3}$	$2.84x10^{3}$	0.0705	0.0705

Total ^{14}C content measured by this analytical method is in the same order of magnitude with the value estimated by modelling for an average burn-up of 168 MWh/kg U (1.78E+04 Bq/g of Zy-4). Details on the modeling of the ^{14}C accumulation during CANDU fuel irradiation are given in D3.13 report [Necib et al., 2016].

Since this method also allows measurement of tritium content and as well as other gamma emitters, the concentration activity of these radionuclides in irradiated Zy-4 samples was measured (Table 7) in solutions sampled from the acidic scrubbing bottles (for tritium) and from the reaction vessel (for gamma emitters).

Table 7 Radionuclide content in the irradiated Zy-4 samples used in for inventory measurements

Sample ID	Bq/g of Zy-4						
	^{3}H	^{60}Co	^{137}Cs	^{134}Cs	^{125}Sb	^{51}Cr	^{144}Ce
# 1.1	4.35E+04	1.58E+06	5.19E+06	3.18E+05	6.46E+06	2.34E+05	1.23E+05
# 2.1	3.30E+04	1.07E+06	3.57E+06	2.23E+05	4.28E+06	1.68E+05	9.41E+04
# 3.1	4.56E+04	1.57E+06	5.19E+06	2.96E+05	2.24E+05	2.34E+05	1.50E+05
# 4.1	4.95E+04	1.41E+06	4.50E+06	3.00E+05	5.67E+06	N/A	1.50E+05
# 5.1	2.67E+04	1.40E+06	4.55E+06	2.96E+05	5.92E+06	2.30E+05	1.56E+05
# 6.1	1.01E+04	1.57E+06	6.37E+06	4.03E+05	6.53E+06	2.24E+05	1.77E+05
# 7.1	2.67E+04	1.62E+06	3.15E+06	7.53E+04	1.33E+06	4.43E+04	3.96E+04
average	3.36E+04	1.46E+06	4.65E+06	2.73E+05	4.34E+06	1.89E+05	1.27E+05
stdev	1.38E+03	1.93E+05	1.08E+06	1.02E+05	2.57E+06	7.53E+04	4.68E+04

The experimental results for gamma emitters measured in the solution obtained after the irradiated Zy-4 dissolution are similar with those measured directly on the small ring cut from the spent fuel tube (reported in Table 2).

3.5 ^{14}C release during static leaching tests

Static leaching tests were carried out over a period of 12 months starting from April, 2016. Individual irradiated Zy-4 samples were prepared for each sampling interval (7 samples in total).

The amount of ^{14}C released in liquid phase was measured for 18 days, 6 months, 8 months, 10 months, 12 months and 18 months applying the analytical procedure described in Chapter 2.6. The measured ^{14}C activities (both as total ^{14}C and inorganic and organic partition) are reported in Table 8.

Table 8 The amount of ^{14}C released in liquid phase, Bq/g of Zy-4

Sample ID	**# 7.2**	**# 5.2**	**# 6.2**	**# 2.2**	**# 1.2**	**# 4.2**	**# 4.2**
Leaching time	**18 days**	**6 months**	**6 months**	**8 months**	**10 months**	**12 months**	**18 months**
Inorganic ^{14}C	3.73±0.56	3.18±0.48	3.99±0.60	4.21±0.63	120.89±18.13	5.77±0.87	3.68±0.55
Organic ^{14}C	7.26±1.09	7.15±1.07	7.25±1.09	8.31±1.25	196.86±29.53	6.30±0.90	7.68±1.15
Total ^{14}C	10.99±1.65	10.33±1.55	11.24±1.69	12.52±1.88	317.75±47.66	12.07±1.81	11.36±1.70

Since, excepting the sample used for 10 months leaching test, similar results in terms of the ^{14}C release in liquid phase were obtained between 18 days and up to 18 months, it suggests that a small fraction of the ^{14}C is available as instant release fraction. By acid stripping / wet oxidation tests carried out on the leachant solutions it was determined that the ^{14}C released in liquid phase is mainly as organic species (more than 60% from the released ^{14}C in solution was found to be as organic species).

The results obtained for the irradiated Zy-4 samples after 10 months of leaching are higher than those obtained both for shorter and longer leaching time. An explanation for these results could reside in the fact that the irradiated Zy-4 sample used for 10 months leaching test has on its surface two bearing pads that increase the available surface for leaching and on the other hand could be slightly detached from the Zy-4 surface exposing fresh metal to the leachant solution.

Since the irradiated Zy-4 samples used for leaching tests were rinsed in 4M nitric acid before their use in the leaching tests, the ^{14}C absorbed from the moderator on the oxide layer of the CANDU fuel during its irradiation was likely released during the rinsing steps. In this situation, the amount of ^{14}C released during the leaching tests could come from the fresh Zy-4 metal from the edges of the samples created by sample cutting exposed to the leaching solution.

The SEM investigations carried out on the irradiated Zy-4 sample after its immersion for 6 months in NaOH solution (Figure 21), demonstrate that the oxide surface of the irradiated Zy-4 sample presents large cracks which could have occurred after the mechanical cutting of the irradiated samples inside the hot cells. By these cracks, also fresh Zy-4 metal was exposed to the leaching solution, allowing the release of some ^{14}C.

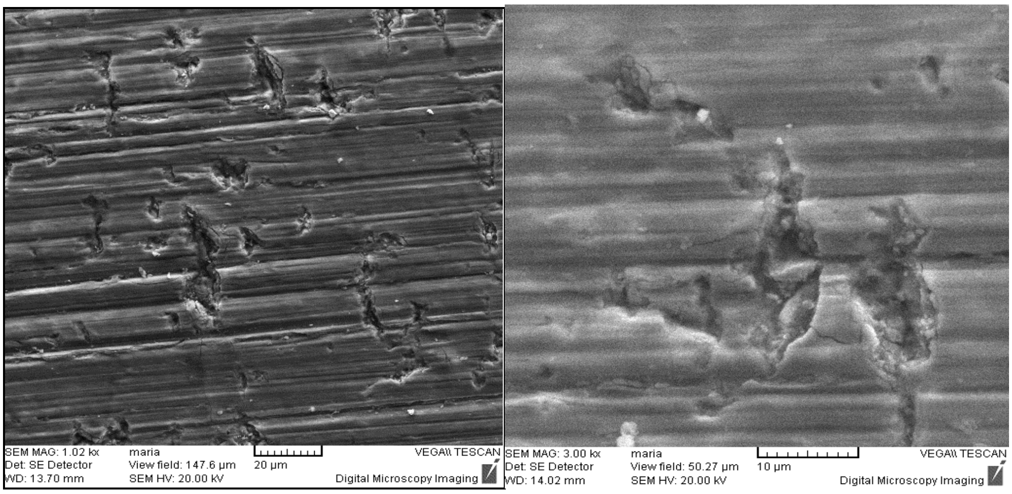

Figure 21 SEM images of irradiated Zy-4 sample after 6 months immersion in NaOH sol (magnification x1000; x3000)

To confirm that these cracks were not induced by the sample immersion in NaOH solution, SEM analyses were also carried out on an irradiated Zy-4 sample (from the same spent fuel claddings as that used for cutting the irradiated Zy-4 samples for leaching tests) (Figure 22).

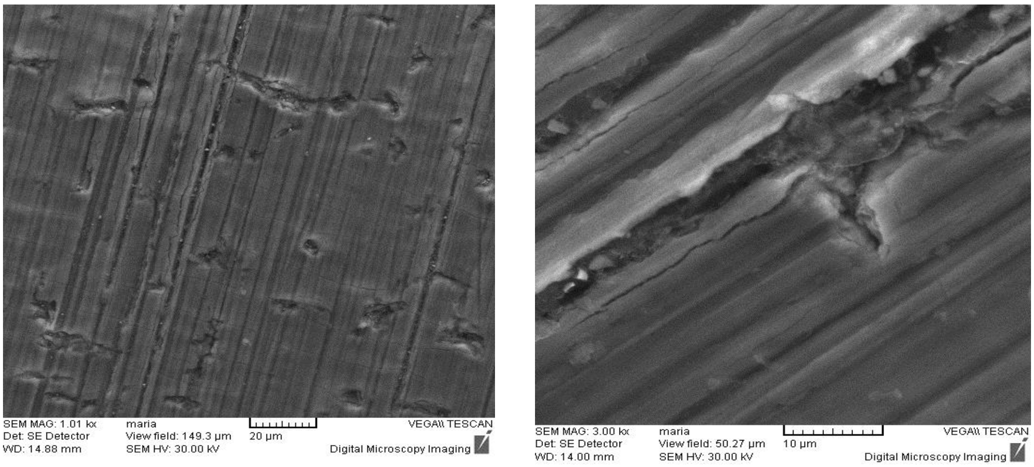

Figure 22 SEM images of irradiated Zy-4 sample non-immersed in NaOH solution (magnification x1000; x3000)

Similar cracks as to those observed for the sample that was immersed in NaOH solution for 6 months were also observed on this sample.

To account for the surface available for leaching and estimate the ^{14}C release rate, the amount of ^{14}C released at each time interval (expressed as g of ^{14}C) was divided by the surface of the Zy-4 tube (cm^2) available for leaching (considering both internal and external surface) and divided by time. The obtained results are reported in Table 9.

Table 9 ^{14}C release rate, g / cm^2 / year

Released rate	18 days	6 months	6 months	8 months	10 months	12 months	18 months
Inorganic ^{14}C	7.93E-11	6.67E-12	8.36E-12	6.62E-12	1.52E-10	6.07E-12	2.58E-12
Organic ^{14}C	1.54E-10	1.50E-11	1.52E-11	1.31E-11	2.48E-10	6.63E-12	5.38E-12
Total ^{14}C	2.34E-10	2.17E-11	2.36E-11	1.97E-11	4.00E-10	1.27E-11	7.96E-12

Gamma measurements were also carried out on the leachant solutions for each tests and no ^{60}Co was measured in the solutions sampled from the leaching tests excepting of that from the 12 months leaching. The ^{60}Co amount measured for this test was around 2.83 Bq/g of Zy-4. A similar value for ^{60}Co in the leachate solution was also measured in the 18 months leaching test. The small amount of ^{60}Co was measured in this solution (0.02 Bq/ml ±0.003 Bq/ml) with a different gamma spectrometer in a smaller background that those used for the previously gamma measurements and for this reason it can be affirmed that this radionuclide was released only after 12 months of immersion of irradiated Zy-4 in NaOH solution.

3.6 *Corrosion rate estimated based on electrochemical tests*

3.6.1 Electrochemical tests on non-irradiated Zircaloy-4 samples

Considering that the uniform corrosion is the only mechanism that can affect the spent fuel claddings under chemical conditions relevant to geological disposal, electrochemical tests have been performed to investigate corrosion mechanisms.

The electrochemical glass cell was filled with 30 ml solution of NaOH (0.01M) at pH=12 with a conductivity of 2.1 mS/cm. As was suggested in the second meeting WP2&3, to determine the uniform corrosion rate, the Linear Polarization Resistance (LPR) method was used.

To establish a working procedure for testing irradiated Zy-4 samples, electrochemical tests on non-irradiated Zy-4 samples were initially performed. In these tests the following types of samples were used: as received Zy-4 tube, oxidised Zy-4 tube, oxidised Zy-4 tube sliced, and oxidised Zy-4 tube sliced and painted on one edge [Figure 23]. Sliced oxidised samples were used to simulate the samples sliced from Zy-4 spent fuel cladding.

Figure 23 Oxidised Zy-4 tube (left), oxidized Zy-4 tube cut at one end (right)

The experimental results obtained from these tests were reported in the D 3.10 report [JOBBÁGY, 2015].

3.6.2 Electrochemical tests on non-irradiated and irradiated Zy-4 samples after their immersion in NaOH solution

Electrochemical tests on the following Zy-4 samples immersed for a long time in NaOH solution were carried out:

- non-irradiated oxidized Zy-4 samples (cut at one end) after 3, 7 and 12 months of immersion in NaOH solution;
- irradiated Zy-4 samples cut from fuel spent cladding immersed for 6, 8, 10, 12 and 18 months in NaOH solution (extracted from the static leaching tests).

The Linear Polarization Resistance measurements have been performed by scanning through a potential range very close to the corrosion potential E_{corr}.

At the beginning of the test, the sample was immersed in solution (around 2.5 cm^2) and kept for 10 minutes without electrical connection to monitor E_{corr} and reach a steady state. The applied potentials were ± 10 mV and ± 25 mV vs E_{corr} using a scan rate of 0.16mV/sec. The polarizing voltage of ±10 mV, has been chosen in agreement with the limits for which the linear relationship between I_{corr} and E/I is valid. Additionally, the value is sufficiently low to produce no significant disruption of the oxide layer. After testing, the NOVA software provided a convenient interface for making Tafel plots, calculating Tafel slopes and corrosion rates. Selecting corrosion rate fit, the analysis tool performed a curve fit based on the Buttler-Volmer expression which allows for more accurate determination of the corrosion current, polarization resistance and corrosion rate.

3.6.2.1 Non-irradiated Zy-4 samples

Non-irradiated oxidised Zy-4 samples cut at one end (to simulate the samples sliced from spent fuel claddings) were immersed for long term in NaOH solution with pH=12, in anaerobic condition. After 3 and 7 months, Zy-4 samples were removed from solution and electrochemically tested. The overlapped Tafel plots obtained by LPR method are presented in Figure 24.

As it can be seen, the specific curve of Zy-4 sample immersed for 3 months start from more cathodic potential and indicates a slightly higher current value than the specific curve of Zy-4 sample immersed for 7 months.

The values of corrosion rates, polarization resistance, corrosion potentials and current densities (i_{corr}) calculated from the Tafel slopes at applied potentials of ± 10 mV vs E_{corr}, are presented in Table 10. For comparison, the values for non-irradiated samples after long term immersion (3 and 7 months) and those obtained for non-irradiated oxidized samples, non-irradiated oxidised samples cut at one end and as received Zy-4 sample are also presented in this table.

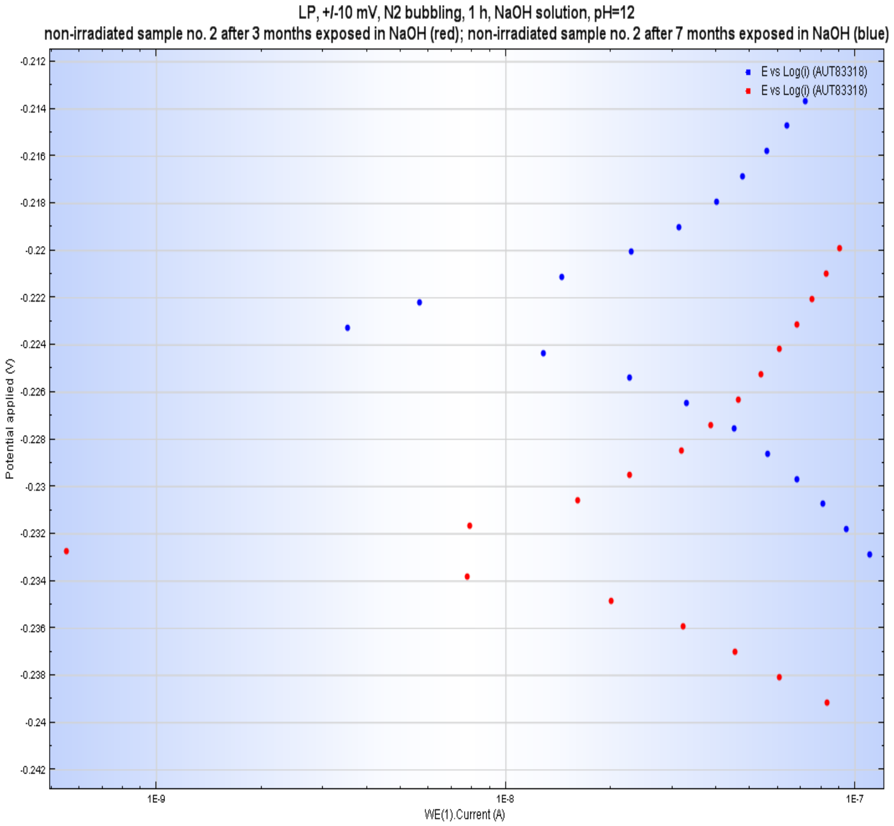

Figure 24 Tafel plots obtained by LPR method for non-irradiated Zy-4 sample immersed for 3 months (red) and 7 months (blue) in NaOH solution

Table 10 LPR results obtained for non-irradiated Zy -4 samples at applied potentials of ± 10 mV vs E_{corr}

Samples	E_{corr} (V)	i_{corr} (A/cm²)	Corr. rate (mm/y)	Corr. rate (nm/y)	Polarization resistance (Ω)
Oxidized Zy-4 sample after 3 months imersion in NaOH (sample cut at one end)	-0.233	2.62E-09	3.01E-05	30,1	1.46E+5
Oxidized Zy-4 sample after 7 months immersion in NaOH (sample cut at one end)	-0.223	1.5 E-09	1.72E-05	17,2	1.19E+5
Oxidized Zy-4 sample after 12 months immersion in NaOH (sample cut at one end)	-0.132	1,04E-09	1,20E-05	12	1.02E+5
As received Zy-4 tube	-0.84	1.0E-8	1.1E-04	111	2.4E+5
Oxidised Zy-4 tube	-0.300	2.7E-10	3.1E-06	0,31	1.5E+7
Oxidised Zy-4 tube cut at one end	-0.220	5.5E-9	6.34E-05	63,4	1.7E+5

The highest corrosion rate was measured for as received Zy-4 sample, followed by the oxidised sample cut at one end not immersed in NaOH solution and the samples immersed for 3, 7 and 12 months.

In the case of oxidised samples immersed for long time in NaOH, can be seen a decreasing of the corrosion rates with the time of immersion. Although the decrease is not significant however, samples immersed in NaOH for a long time had lower corrosion rates.

It is known that the Zr is a highly reactive metal, which can cover spontaneously with an oxide layer (of nm thickness) in air or water at ambient temperature. In this case probably a thin layer of oxide was formed on the fresh surface created by cutting, leading to slowly decreasing corrosion rates with immersing time.

SEM investigations have been performed on the surface of non-irradiated sample not immersed and immersed in NaOH solution. The magnification was the same for both samples (x 1000) and in both cases defects, cracks or scratches were evidenced on the oxides (Figure 25).

Taking into account the studies investigating the cracks in the oxide layer, conclusion could be that the number of cracks is correlated with the number of the intermetallic phases from the bulk metal. Pia Tejland presented a mechanism for crack formation and he concluded that the driving force is the local tensile stress in the oxide, and the initiation sites are the non-oxidized intermetallic phases located within this stress field [Pia Tejland, JNM 2012].

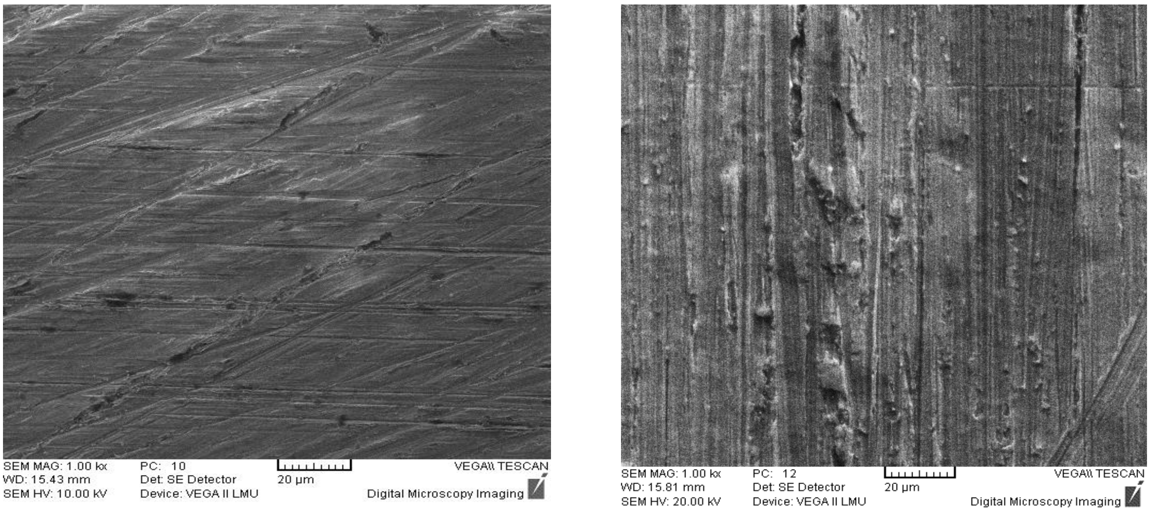

Figure 25 SEM images of non-irradiated Zy-4 samples: oxidised, cut at one end (left), and oxidised, cut at one end and immersed for 7 months in NaOH solution (right)

Also, the image taken by SEM at the cut part of oxidised non-irradiated sample evidenced the presence of some cracks probably resulted from samples cutting (Figure 26).

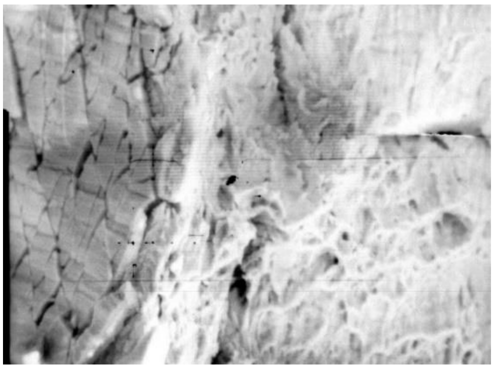

Figure 26 SEM image at the cut part of oxidised Zy-4 sample (2.5 µm thickness of the oxide layer)

All these cracks and fissures induced during samples cutting could influence the corrosion rates obtained by electrochemical measurements since fresh metal could be exposed to the solution.

3.6.2.2 Irradiated Zy-4 samples

The same procedure as for non-irradiated samples was applied in electrochemical testing of irradiated Zy-4 samples extracted from the static leaching tests after 6, 8, 10, 12 and 18 months. After sampling leachant solutions for ^{14}C measurement, the irradiated Zy-4 samples were removed from the NaOH solution and subjected to the linear polarisation resistance tests at applied potentials of ± 10 mV and ±25 mV vs E_{corr}. The surface immersed in the solution (NaOH 0.01M) was similar for all the samples, excepting for the sample extracted after 10 months of leaching due to the two bearing pads placed on this sample.

The overlapped Tafel plots obtained for irradiated Zy-4 samples after 6, 8 and 12 months of immersion in NaOH solution are presented in Figure 27. As it can be seen, the curve specific to Zy-4 sample immersed for 12 months in alkaline solution (blue plot) indicates the lowest current value and the lowest E_{corr} value compared to the irradiated samples immersed for 6 and 8 months.

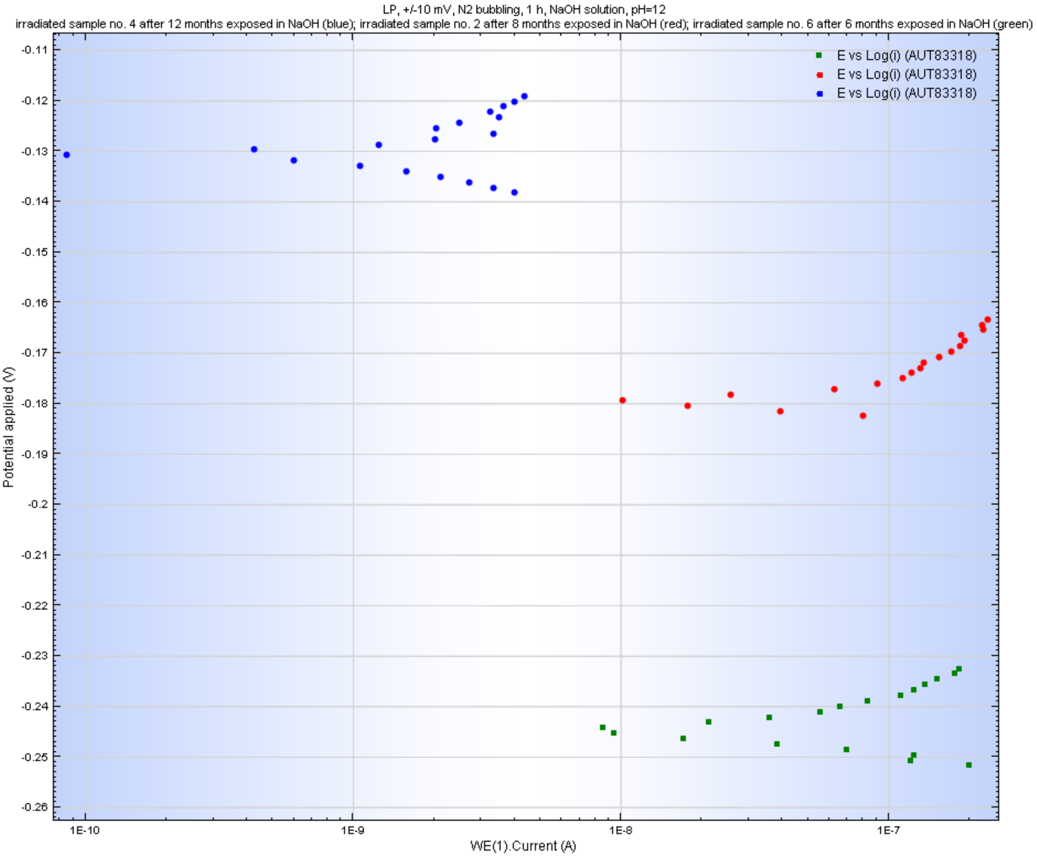

Figure 27 (E vs log(i)) polarization curves for: irradiated sample after 12 months immersion in NaOH (blue); irradiated sample after 8 months immersion in NaOH (red) and irradiated sample after 6 months immersion in NaOH (green)

The corrosion rates, as well as the polarization resistances, corrosion potentials and current densities calculated from the Tafel slopes are reported in Table 11.

Table 11 LPR results obtained for irradiated Zy-4 samples at applied potentials of ± 10 mV vs Ecorr

Samples	Sample surface immersed (cm^2)	E_{corr} (V)	I_{corr} (A/cm^2)	Corrosion rate (mm/y)	Corrosion rate (nm/y)	Polarization resistance (Ω)
Irradiated sample after 6 months immersion in NaOH (# 5)	2.4	-0.2319	1.13E-08	12.906E-05	129	5.9E+5
Irradiated sample after 6 months immersion in NaOH (# 6)	2.6	-0.245	9.87E-09	11.3 E-05	113	6E+5
Irradiated sample after 8 months immersion in NaOH (# 2)	2.5	-0.1936	7.13E-09	8.18E-05	81	6.6E+5
Irradiated sample after 10 months immersion in NaOH (# 3)	3.8	-0.2175	7.53E-09	8.6E-05	86	6.5E+5
Irradiated sample after 12 months immersion in NaOH (# 4)	2.5	-0.1304	4.60E-09	5.27 E-05	52.7	9.4E+5
Irradiated sample after 18 months immersion in NaOH (#1)	2.5	-0,15	4 E10-9	4.58 E-05	45.8	9.7E+5

The corrosion rate is higher than 100 nm/y for both irradiated Zy-4 samples immersed 6 months in NaOH solution and it decreases to around 46 nm/y after 18 months of immersion in NaOH solution.

As it can be seen the irradiated samples immersed in NaOH solution for long time have higher corrosion rates than the non-irradiated oxidised Zy-4 samples. The corrosion rates of two irradiated samples after 6 months of leaching in 0.01M NaOH solution were comparable with the corrosion rates recorded for non-oxidized Zy-4 sample, having fresh surface exposed to the testing solution. For the irradiated Zy-4 samples extracted after 8, 10, 12 and 18 months leaching the corrosion rates are closed to the ones obtained for oxidised Zy-4 samples with a fresh edge (cut at one end).

We suppose that the higher corrosion rates recorded for irradiated samples compared with non-irradiated ones could be attributed to larger cracks observed in oxide layer (Figures 21 and 22).

The results of these tests could be affected both by the cracks likely induced by the sample cutting but also by the non-standard experimental conditions. Standard electrochemical tests are carried out in higher volume of solution (up to 500 ml) but in an attempt to measure the ^{14}C potentially released during the electrochemical tests, the corrosion cell had a smaller volume (a nominal solution volume of 30 ml) and the associated electrodes were adapted for this small volume.

Determination of i_{corr} over a known period of time leads to direct determination of mass loss, so the conversion of corrosion current density values to mass loss rate (MR) or average penetration rates (CR) was carried out using relations from ASTM G 102-2004.

The Faraday's law can be used to calculate the corrosion rate (CR) or mass loss rate (MR) as described in eq.9 and eq.10.

$$CR = K_1 * (i_{corr}/\rho) * EW \qquad \text{(eq. 9)}$$

$$MR = K_2 * i_{corr} * EW \qquad \text{(eq. 10)}$$

where: CR is the corrosion rate, mm/y

MR is the mass loss rate, $mg/dm^2 d$ (mdd)

K_1 and K_2 are constants:

K_1 = 3.27E-03 mm·g/µA/ cm/y

K_2 = 0.0895 $mg \cdot cm^2/\mu A/dm^2/d$

ρ is the Zy-4 density, g/cm^3

i_{corr} is the corrosion current, $\mu A/cm^2$

EW is the equivalent weight (dimensionless); for Zy-4 EW = 23

The corrosion rates obtained using eq. 9 are similar with the corrosion rates calculated from the Tafel slopes (Table 12).

Table 12 Corrosion rates (CR) calculated for irradiated Zy-4 samples after long term immersion

Sample type	E.W	ρ [g/cm^3]	i_{corr} [µA/cm^2]	CR [mm/y]	CR [nm/y]
Irradiated Zy-4 after 6 months immersion in NaOH (# 5)	23	6.56	1.13E-02	1.3E-04	130
Irradiated Zy-4 after 6 months immersion in NaOH (# 6)	23	6.56	9.8 E-03	1.13 E-04	113
Irradiated Zy-4 after 8 months immersion in NaOH (# 2)	23	6.56	7.13E-03	8.18 E-05	81.8
Irradiated Zy-4 after 10 months immersion in NaOH (# 3)	23	6.56	7.53E-03	8.64E-05	86.4
Irradiated sample after 12 months immersion in NaOH (# 4)	23	6.56	4.6 E-03	5.27E-05	52.7
Irradiated sample after 18 months immersion in NaOH (# 1)	23	6.56	4 E-03	4.57E-05	45.7

In Table 13 the values of mass loss rates are presented. Likewise the corrosion rates, the mass loss rate decreases over time.

Table 13 Mass loss rate calculated for irradiated samples.

Sample Type	Jcorr µA/cm2	EW	MR mg/dm^2/d
Irradiated Zy-4, after 6 months immersion in NaOH (#. 5)	1.13E-02	23	0.023
Irradiated, after 6 months immersion in NaOH (# 6)	9.87E-03	23	0.0204
Irradiated Zy-4, after 8 months immersion in NaOH (# 2)	7.13E-03	23	0.014
Irradiated Zy-4, after 10 months immersion in NaOH (# 3)	7.53E-03	23	0.015
Irradiated sample after 12 months immersion in NaOH (#4)	4.60E-03	23	0.0095
Irradiated sample after 18 months immersion in NaOH (#1)	4.0E-03	23	0.0082

The values obtained by polarization at ±25mV vs E_{corr} were much higher than those obtained by polarization at ±10mV vs E_{corr} (around one order of magnitude higher). This data is not presented in this report as it is considered not relevant.

In any solutions after the electrochemical tests no ^{14}C was measured. The LSC detection limit is not as low to measure the very low amount of ^{14}C released during the electrochemical tests (for example, for higher estimated MR, the amount of ^{14}C corresponding to the Zy-4 corroded mass is around 0.004 Bq that could not be measured by LSC).

3.7 Uncertainties

The uncertainty of ^{14}C measurement by LSC was around 7%. To evaluate the uncertainty associated to the analytical procedure for measuring the inorganic and organic ^{14}C, six identical tests were carried out and the standard deviation of the results were below 15% and consequently, a covering uncertainty of 15% was considering for the values reported in Chapter 3.4 and 3.5 for ^{14}C content in irradiated Zy-4 (Table 6) as well as for ^{14}C release during static leaching tests (Table 8).

The measurement error for the experimental device (AUTOLAB 302) used for the electrochemical tests is around 2%.

To assess the global uncertainties associated to the electrochemical tests, 6 identical electrochemical measurements were carried out for three different Zy-4 samples (Table 14) and the measurement uncertainties for the other electrochemical results could be considered the standard deviation of these results (between 31 and 39%).

Table 14 The corrosion rates measured in 6 identical tests to assess the uncertainties

Sample ID	corr rates of oxidised samples, aerob cond., mm/y	corr rates of as received samples aerob cond, mm/y	corr rates of oxidised samples, cut at one end, mm/y
1	3.600E-06	4.800E-04	6.340E-05
2	1.400E-06	4.000E-04	3.740E-05
3	3.720E-06	3.500E-04	6.620E-05
4	2.280E-06	1.600E-04	4.280E-05
5	5.060E-06	6.000E-04	9.800E-05
6	5.300E-06	3.740E-04	7.200E-05
Average, mm/y	3.560E-06	3.940E-04	6.330E-05
Standard deviation, mm/y	1.391E-06	1.335E-04	1.991E-05
Standard deviation, %	39.07	33.88	31.45

4 Conclusions

The irradiated Zy-4 samples available for CAST experiments were obtained from a CANDU spent fuel assembly with a known irradiation history, transferred from Cernavoda NPP.

The Zy-4 samples cut from a fuel element extracted from this CANDU Spent Fuel Assembly have a ^{14}C content of around 2E+04 Bq of ^{14}C per gram of Zy-4, mainly as organic species (more than 99%). This content is of the same order of magnitude with the value estimated by ORIGEN simulation for an average burn-up of 7 MWd/kgU (1.78E+04 Bq/g of Zy-4).

The static leaching tests carried out on irradiated Zy-4 samples in alkaline solution (NaOH 0.1 M) indicate that a small amount of ^{14}C was relatively fast released (same release amount after 18 days, 6, 8, and 18 months). This release could be due to the cracks observed on the surface of the oxide layer that lead to Zy-4 metal exposure to the leaching solution.

From the electrochemical tests carried out under inert atmosphere in borosilicate glass cells, it was found that the irradiated Zy-4 samples had higher corrosion rates than the non-irradiated oxidised samples.

The corrosion rates of irradiated samples dropped to 45.8 nm /y after 18 months of immersion in NaOH.

Generally, corrosion rates values ranged from around 46 to 130 nm /y. These high values of corrosion rates are assigned to the defects and cracks found in the oxides developed on the surface of samples.

The results of the electrochemical tests could be affected both by the cracks likely induced by the sample cutting but also by the non-standard experimental conditions.

The high corrosion rates measured by the LPR method indicate that this method may not be adequate for passivated metals.

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