

¹⁴C CONTENT IN CANDU SPENT FUEL CLADINGS AND ITS RELEASE UNDER ALKALINE CONDITIONS

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ABSTRACT. The total ¹⁴C content and its partition between inorganic and organic species were measured on irradiated Zy-4 samples from a CANDU spent fuel rod transferred from Cernavoda Nuclear Power Plant (NPP). Long-term leaching tests and accelerated corrosion tests were carried out to measure the ¹⁴C release and corrosion rate, respectively, in chemical conditions relevant to cementitious environment. Experimentally measured ¹⁴C inventory was compared to the theoretically one predicted based on the irradiation history and impurity content of Zy-4 by means of ORIGEN computations. CANDU SF claddings have a ¹⁴C content of around 2×10^4 Bq/g of Zy-4, mainly as organic compounds (more than 99%). The total ¹⁴C content measured by acid dissolution/wet oxidation method is in good agreement with the value estimated by ORIGEN simulations for an average burn-up of 7 MWd/kgU. The total ¹⁴C released as dissolved species after 18 days and 18 months of Zy-4 immersing in alkaline solution are similar, indicating that a small amount of ¹⁴C was available as instant release fraction (0.05% from the initial ¹⁴C content) followed by a very low release rate that could not be measured by liquid scintillation counting. In alkaline conditions, ¹⁴C is released predominantly (~70%) as soluble species, but also inorganic ¹⁴C was measured as gaseous species. From the soluble ¹⁴C released during leaching test, more than 60% was found to be as organic species. Generally, corrosion rates values ranging between 46 and 130 nm/yr were measured by the linear polarization resistance method. In addition, defects and cracks were observed on the oxide layer by scanning electron microscopy (SEM) investigation.

KEYWORDS: ¹⁴C, CANDU irradiated Zy-4, corrosion rate.

INTRODUCTION

In Romania, two CANDU 600 (CANada Deuterium Uranium) reactors are currently in operation at the Cernavoda site and two more CANDU units are foreseen to be commenced in the future. The Romanian strategy for spent fuel and radioactive waste management foresees that the CANDU spent fuel (SF) 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 geological disposal, foreseen to be operational in 2055.

CANDU fuel assembly contains 37 elements made of sintered UO₂ pellets (natural uranium) in Zy-4 tubes. The 37 elements are circularly arranged on three rings of 18, 12, and 6 elements respectively, around a central element. CANDU units are designed such as to load and unload their fuel continuously at full power by disconnecting individual pressure tubes. In CANDU nuclear fuel, Zy-4 is used as fuel cladding, and also for end-caps, end support plate, inter element spacers, and pads.

Due to its long half-life ($T_{1/2} = 5730$ yr), high mobility in groundwater system and easy incorporation into man via the food-chain, ¹⁴C is a radionuclide of concern from a safety point of view. In a nuclear reactor, ¹⁴C is generated mainly by neutron activation of stable nitrogen (¹⁴N), oxygen (¹⁷O) and carbon (¹³C) isotopes that are present in the fuel, core structural materials, and in reactor coolant and are activated by the neutrons generated from nuclear fission reactions (Yim and Caron 2006).

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A particularity of CANDU fuel is the colloidal graphite (CANLUB) deposited on the inside surface of the Zy-4 rods (the average thickness of the graphite layer is 5 μm with a minimum of 3 μm). Therefore, the ^{14}C in CANDU SF claddings is a combination of the ^{14}C formed or attached on the oxide layer, the ^{14}C formed in the Zy-4 metal (mainly from activation of nitrogen impurities) but also small amount of ^{14}C formed in the graphite layer.

MATERIALS AND METHODS

The irradiated Zy-4 samples were obtained from a CANDU spent fuel bundle (GK964F1) irradiated for 1 year in the Cernavoda Unit 2. After a cooling period of around 4 years in the spent fuel cooling pool at the Cernavoda site, the fuel bundle was transferred to RATEN ICN and some fuel elements were extracted for different investigations inside the ICN hot cells. A tube of 10 cm length from one spent fuel element 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 between 0.45 and 0.60 mSv/h, below the acceptable limit to carry out further experiments in a fume hood outside the hot cells.

To have real measurements on 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 (Table 1). Two more small rings originating from the same spent fuel element were also available and used in the leaching/corrosion tests.

The non-irradiated Zy-4 samples were cut from as-received Zy-4 tube with external diameter of 13 mm and wall thickness of 0.4 mm. To obtain a similar oxide film as irradiated Zy-4 claddings, the non-irradiated Zy-4 samples were oxidized in static isothermal autoclaves in representative conditions to CANDU primary circuit (LiOH solution, pH = 10.5, T = 310°C, p = 100 atm). A target value of 2.5 μm was established for the oxide thickness in order to investigate the post-transition regime and complete the current knowledge on the corrosion kinetics at low temperature.

Leaching and Corrosion Tests

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 behavior 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 electrochemical methods (accelerated corrosion tests).

Table 1 Mass and length of the irradiated Zy-4 samples.

Used for ^{14}C measurement			Used for leaching/corrosion tests		
Sample ID	Mass (g)	Length (mm)	Sample ID	Mass (g)	Length (mm)
# 1.1	0.2439	1.71	# 1.2	1.1815	8.29
# 2.1	0.1623	1.14	# 2.2	1.1205	7.86
# 3.1	0.3825	2.68	# 3.2	1.0425	7.31
# 4.1	0.2320	1.63	# 4.2	0.8328	5.84
# 5.1	0.1664	1.17	# 5.2	1.1166	7.83
# 6.1	0.1383	0.97	# 6.2	1.2498	8.77
# 7.1	0.2616	1.84	# 7.2	0.2132	1.50

Static Leaching Tests

Leaching tests were carried out in static conditions (individual samples prepared for each time established to measure the ¹⁴C released in liquid and gas phase: 18 days, 6, 8, 10, 12, and 18 months). Sodium hydroxide (NaOH) 0.01 M was chosen as leachant solution (pH = 12, total dissolved salts of 1100 mg/L, and conductivity of 2.20 mS/cm) relevant for cementitious environment. Even cement pore water contains important amount of dissolved Ca, calcium hydroxide was not chosen as leachant solution to avoid ¹⁴C precipitation as carbonate.

Seven glass tubes with silicon lids were adapted to allow N₂ purging in the space above the liquid level and after the irradiated Zy-4 samples and leachant solution were introduced in each tube the lids were connected to N₂ gas for 48 hr to ensure anoxic conditions. For adequate shielding all the glass tubes with irradiated Zy-4 were placed inside a lead castle during the leaching tests.

At the time interval established to measure the ¹⁴C release, N₂ gas was purged for 2 hr through selected leaching tube and outgases were washed through gas washing bottles for ¹⁴C absorption. After gas collection, the lid was opened, and solution was sampled for ¹⁴C measurement.

Method Used for ¹⁴C Measurement

As ¹⁴C is a pure β-emitter with a fairly low energy compared with the β energy emissions of the other radionuclides it may be difficult to quantify. For ¹⁴C measurement by liquid scintillation counting (LSC) it has to be separated and purified from other potential interfering radionuclides (such as ³H, ¹²⁹I, ¹³⁷Cs etc.) to get accurate results.

The analytical method used for inorganic and organic ¹⁴C measurement in irradiated Zy-4 is based on the acid dissolution and wet oxidation, adapted after the method developed by Magnusson et al. for ¹⁴C measurement in spent ion exchange resins and process waters (Magnusson et al. 2008).

The experimental setup (Figure 1) consists in a reaction vessel, a dropping funnel, a nitrogen supply and a vacuum pump, two gas washing lines with a catalytic furnace between them. An Erlenmeyer flask (300 mL) with a three-hole rubber stopper (two for gas and separatory funnel inlets and one for gas outlet) was used as reaction vessel and a tap-water cooling loop, made of copper tubing that fit the outer side of the Erlenmeyer flask ensured the vapor condensation. The reaction vessel was placed on a heater with magnetic stirring.

To ensure that no gases escaped from the system, all dissolution and wet oxidation experiments were carried out under vacuum (0.2 bar below atmospheric pressure) and the carrier gas (N₂) was introduced into the system with a flow rate between 60 and 80 mL/min (controlled by a flow meter).

The Zy-4 dissolution was achieved by adding nitric acid (20% HNO₃) and diluted fluoridic acid (6% HF). Since the inorganic ¹⁴C compounds (i.e. carbonates and bicarbonates) are easily decomposed by weak acids to carbon dioxide, the inorganic ¹⁴C was released during this acid dissolution mainly as ¹⁴CO₂ and carried out by the N₂ gas and absorbed in the first alkaline gas washing bottles (B3 and eventually B4). The ¹⁴C released as carbon oxide (¹⁴CO) or other organic molecules during acid dissolution, passes through the scrubbing bottles of the first gas washing line and it is oxidized to ¹⁴CO₂ in the catalytic furnace and subsequently absorbed in the scrubbing bottles of the second gas washing line. After the acid dissolution step is accomplished the first gas washing line is isolated from the system by means of three-way valves placed

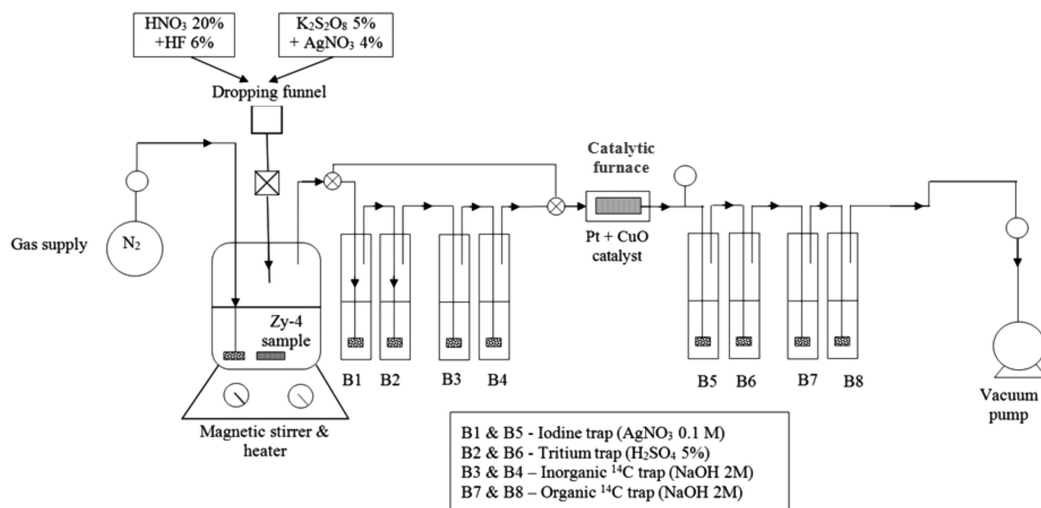


Figure 1 Experimental setup for separation of inorganic and organic ^{14}C .

before the first scrubbing bottle and the fourth one. The ^{14}C released during wet oxidation step (as CO or CH_4) are reduced to CO_2 in the catalytic furnace and subsequently absorbed in the scrubbing bottles of the second gas washing line.

Three wet oxidation steps were carried out in order to ensure the complete decomposition of the organic ^{14}C -labeled compounds, and the carrier gas was purged into the system for 1 hr in each wet oxidation step. This method distinguishes between $^{14}\text{CO}_2$ released during acid dissolution and $^{14}\text{CO}_2$ 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 was measured by LSC using Hionic Fluor liquid scintillation cocktail with a ratio sample to scintillation cocktail of 1 to 10 mL. All samples were kept in darkness over night before their counting to allow for the chemiluminescence decay.

Aliquots from the reaction vessel solution, as well as from all scrubbing bottles were sampled for gamma measurements using an HPGe ORTEC detector and digiDart analyzer for spectra acquisition and Gamma Vision software for radionuclides quantification.

A similar procedure as the one described above was used for inorganic and organic ^{14}C measurements in the alkaline solutions sampled from the leaching tests, except the acid used for inorganic ^{14}C release. In the solution case, the mixture of nitric and fluoric acid used for Zy-4 dissolution and inorganic ^{14}C release was replaced by concentrated sulfuric acid (H_2SO_4 6M).

Accelerated Corrosion Tests

The linear polarization resistance (LPR) method was selected to determine the uniform corrosion rate of the spent fuel claddings. This technique is fast and enables to detect the instantaneous corrosion rate and it was applied on the irradiated Zy-4 samples extracted from the leaching tests after sampling the gas and liquid phases for ^{14}C measurements as well as on non-irradiated Zy-4 samples (with or without oxide layer on their surface).

A potentiostat/galvanostat AUTOLAB 302, with NOVA 1.11 corrosion software, was used for the electrochemical tests. The corrosion cell consists of a glass cell (90 mL), equipped with a five-holed lid: four holes for electrodes (Ag/AgCl reference electrode, two Pt counter electrodes, and the working electrode) and a hole for the bubbling tube. After the electrodes mounting, the vessel lid has been tight by adding resin or glue around them (see Jobbágy et al. 2015 for more details on experimental setup).

All electrodes and the bubbling tube were immersed into 30 mL NaOH 0.01M solution (pH = 12 and conductivity of 2.1 mS/cm). Before starting each experiment, the device was calibrated using an AUTOLAB Dummy Cell 2 and nitrogen gas was bubbled into solution for 2 hr at the beginning of each electrochemical test and also during the test. The electrochemical assembly was mounted into a Faraday cage during all electrochemical tests to protect the experimental setup against electromagnetic interferences from external sources.

Electrochemical tests were carried out both on non-irradiated and irradiated Zy-4 samples by scanning through a potential range around the corrosion potential (E_{corr}). At the beginning of the test, around 2.5 cm² from the Zy-4 sample was immersed in solution and kept for 10 min without electrical connection to stabilize the E_{corr} .

The applied potentials were ± 10 mV and ± 25 mV vs. E_{corr} using a scan rate of 0.16 mV/sec. The polarizing potentials are sufficiently small to avoid disruption of the oxide layer. Following polarization, the Tafel plots were generated using NOVA 1.11 software and corrosion rates were computed (ASTM G 102, 2004).

The Faraday's law was used to calculate the corrosion rate (CR) and mass loss rate (MR), as expressed in Equations (1) and (2)

$$\text{CR} = K_1 * (i_{\text{corr}} / \rho) * EW \quad (1)$$

$$\text{MR} = K_2 * i_{\text{corr}} * EW \quad (2)$$

where: CR is the corrosion rate, mm/yr; MR is the mass loss rate, mg/dm²d (mdd); ρ is the Zy density, g/cm³; i_{corr} is the corrosion current, $\mu\text{A}/\text{cm}^2$; EW is the equivalent weight (dimensionless; for Zy-4 EW = 23); K_1 and K_2 are constants ($K_1 = 3.27\text{E-}03$ mm \times g/ $\mu\text{A}/\text{cm}/\text{yr}$ and $K_2 = 0.0895$ mg \times cm²/ $\mu\text{A}/\text{dm}^2/\text{d}$).

RESULTS AND DISCUSSION

¹⁴C Measurements in Irradiated Zy-4 Samples

From preliminary tests carried out to estimate the volumes of acids used in the dissolution step, it was determined that 20 mL of 20% HNO₃ and 20 mL of 6% HF were enough to completely dissolve the Zy-4 matrix.

To optimize the experimental conditions and chemicals used for inorganic and organic ¹⁴C measurements, a bunch of acid dissolution/wet oxidation tests were carried out in controlled conditions, using non-irradiated Zy-4 samples immersed in solutions with known activities for the radionuclides of interest (¹⁴C in inorganic form as sodium carbonate/bicarbonate and organic forms as sodium acetate and lauric acid, ³H, ¹²⁹I, ⁶⁰Co, ¹³⁷Cs, ²⁴¹Am and ¹⁵²Eu). With these tests, the ¹⁴C recovery, the reproducibility of the results and efficiency of acid dissolution/wet oxidation method to distinguish between inorganic and organic ¹⁴C species were evaluated.

The results show that with this analytical method, good ^{14}C recovery and efficient purification are obtained:

- inorganic ^{14}C recovery: between 96% and 99%, with an average value of 98% and standard deviation of 1.78
- organic ^{14}C recovery: between 94% and 98%, with an average value of 96% and standard deviation of 1.55
- no gamma emitters were identified in the solutions sampled from alkaline gas washing bottles, and ^{14}C specters were free of interferences.

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

The standard deviation of the results of six similar tests carried out in controlled conditions was less than 15%, proving the good reproducibility of the results.

Seven irradiated Zy-4 samples were used to evaluate the ^{14}C content and its inorganic and organic ratio. For this, each irradiated Zy-4 tube was introduced in the reaction vessel together with a solution of 2 M NaOH (10 mL) and the analytical procedure described above was applied. The experimental results obtained for these samples (reported in Table 2) show that the irradiated Zy-4 used for leaching/corrosion tests contains around $2\text{E} + 04$ Bq of ^{14}C per gram of Zy-4, mainly as organic compounds.

Total ^{14}C content measured with this analytical method is in the same order of magnitude as the value estimated by modeling for an average burn-up of 7 MWd/kg U ($1.78\text{E} + 04$ Bq/g of Zy-4). Details on the modeling of the ^{14}C accumulation during CANDU fuel irradiation are given in CAST D3.13 report (Necib et al. 2016).

Since this method also allows measurement of tritium content and of other gamma emitters, the concentration activity of these radionuclides in irradiated Zy-4 samples was measured (see Table 3) in solutions sampled from the acidic scrubbing bottles (for tritium) and from the reaction vessel (for gamma emitters).

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. The preliminary acid dissolution/wet oxidation tests carried out in controlled conditions as well as the results obtained for gamma emitters show that the analytical method used for inorganic and organic ^{14}C allow a very good recovery of the radionuclides contained by the analyzed sample.

^{14}C Release under Alkaline Conditions

Static leaching tests were carried out over a period of 18 months, starting from April 2016. Individual irradiated Zy-4 samples were prepared for each sampling interval (7 samples in total). Before opening the leaching vessels to sample the liquid phase for ^{14}C measurement, N_2 gas was purged in the space above the liquid level and the outgases were washed through gas washing bottles similar with those comprising the gas washing lines in the acid dissolution/wet oxidation method. By this means, the ^{14}C released in gaseous phase was quantified.

Table 2 ¹⁴C content in the irradiated Zy-4 samples used in leaching/corrosion tests.

Sample ID	¹⁴ C activity				
	Bq/g of Zy-4			%	
	Total ¹⁴ C	Organic ¹⁴ C	Inorganic ¹⁴ C	Inorganic ¹⁴ C	Organic ¹⁴ C
# 1.1	$1.64 \times 10^4 \pm 2.46 \times 10^3$	$1.63 \times 10^4 \pm 2.45 \times 10^3$	49.61 ± 7.44	0.3031 ± 0.0455	99.6969 ± 14.9545
# 2.1	$2.16 \times 10^4 \pm 3.24 \times 10^3$	$2.15 \times 10^4 \pm 3.23 \times 10^3$	51.89 ± 7.78	0.2406 ± 0.0361	99.7594 ± 14.9639
# 3.1	$2.12 \times 10^4 \pm 3.18 \times 10^3$	$2.12 \times 10^4 \pm 3.18 \times 10^3$	29.62 ± 4.44	0.1393 ± 0.0209	99.8607 ± 14.9791
# 4.1	$2.47 \times 10^4 \pm 3.71 \times 10^3$	$2.47 \times 10^4 \pm 3.71 \times 10^3$	41.58 ± 6.24	0.1684 ± 0.0253	99.8316 ± 14.9747
# 5.1	$1.87 \times 10^4 \pm 2.81 \times 10^3$	$1.87 \times 10^4 \pm 2.81 \times 10^3$	23.38 ± 3.51	0.1249 ± 0.0187	99.8751 ± 14.9813
# 6.1	$2.22 \times 10^4 \pm 3.33 \times 10^3$	$2.22 \times 10^4 \pm 3.33 \times 10^3$	26.61 ± 3.99	0.1195 ± 0.0179	99.8805 ± 14.9821
# 7.1	$2.35 \times 10^4 \pm 3.53 \times 10^3$	$2.35 \times 10^4 \pm 3.53 \times 10^3$	30.12 ± 4.52	0.1278 ± 0.0192	99.8722 ± 14.9808
Average	2.12×10^4	2.12×10^4	36.11	0.1748	99.8252
St.dev.	2.84×10^3	2.84×10^3	11.49	0.0705	0.0705

Table 3 Radionuclide content in the irradiated Zy-4 samples used in leaching/corrosion tests.

Sample ID	Bq/g of Zy-4						
	^3H	^{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	1.80E + 05	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	1.88E + 05	1.27E + 05
St.dev.	1.38E + 03	1.93E + 05	1.08E + 06	1.02E + 05	2.57E + 06	6.37E + 04	4.68E + 04

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

Sample ID	# 7.2	# 5.2	# 6.2	# 2.2	# 4.2	# 3.2
Leaching time	18 days	6 months	6 months	8 months	12 months	18 months
Inorganic ^{14}C	3.73 ± 0.56	3.18 ± 0.48	3.99 ± 0.60	4.21 ± 0.63	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	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	12.07 ± 1.81	11.36 ± 1.70

The amount of ^{14}C released in liquid phase was measured after 18 days, 6 months, 8 months, 12 months, and 18 months of immersion in alkaline solution, applying the analytical procedure described above in this paper. The measured ^{14}C activities (both as total ^{14}C as well as inorganic and organic fractions) in liquid phase are reported in Table 4.

Beside the ^{14}C released as soluble species during leaching tests, an amount of 4.99 Bq/g of Zy-4 was measured in gaseous phase, as inorganic ^{14}C species (no organic ^{14}C in gas phase was measured).

As it can be observed from the above reported data, similar amount of ^{14}C released in liquid phase was measured after 18 days and 6, 8, 12, and 18 months (an average of 11.42 Bq of ^{14}C /g of Zy-4). These data suggest that very small fraction of ^{14}C is available as instant release, this fraction representing only 0.077% (considering both soluble and gaseous ^{14}C species) from the initial ^{14}C content in irradiated Zy-4. Since the irradiated Zy-4 samples used for leaching tests were pre-washed in 4M nitric acid before their use in the leaching tests, the ^{14}C that was absorbed from the moderator on the oxide layer of CANDU fuel during its irradiation was most likely released during these pre-washed cycles. Consequently, 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 directly to the leaching solution.

By acid stripping/wet oxidation tests carried out on the leachant solutions it was determined that the ^{14}C released in liquid phase is preponderant as organic species (around 64% of the ^{14}C released in solution was in the organic form).

The scanning electron microscopy (SEM) investigations carried out on the irradiated Zy-4 sample after its immersion for 6 months in NaOH solution (Figure 2), evidence large cracks on the oxide surface of irradiated Zy-4 generated probably by the machining of the irradiated Zy-4 samples from the tube. Therefore, fresh Zy-4 metal was likely exposed to the alkaline solution allowing ^{14}C release.

SEM analyses were also carried out on another irradiated Zy-4 sample originating from the same spent tube and not used in the leaching tests. Similar cracks were also observed on this sample confirming that the observed cracks were not induced by sample immersion in NaOH solution.

Corrosion Rates Estimated from Electrochemical Tests

Electrochemical tests were carried out both on non-irradiated and irradiated Zy-4 samples (after gas and liquid phases were sampled from leaching tests for ^{14}C measurement).

Analyzing the Tafel plots obtained for the non-irradiated Zy-4 after 3 and 7 months of immersion in NaOH solution (Figure 3) it can be observed that the specific curve of the sample

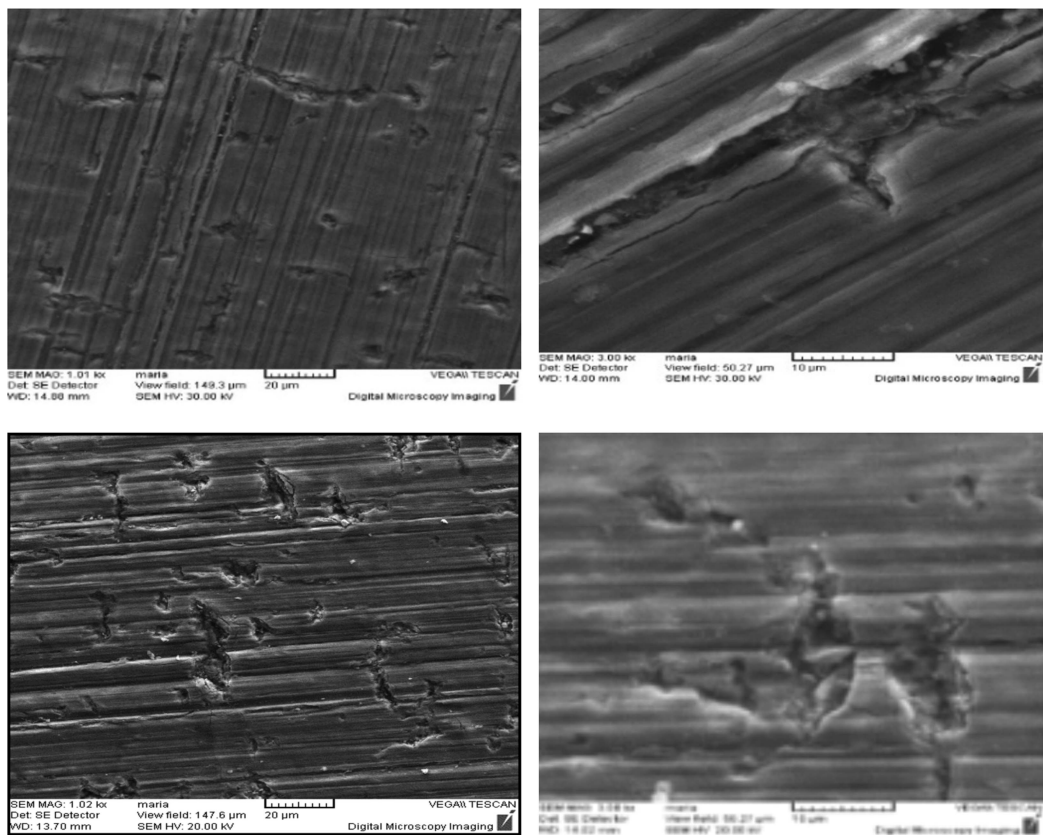


Figure 2 SEM images on irradiated Zy-4 samples: not-immersed in NaOH solution (top) and immersed in NaOH solution for 6 months (bottom).

immersed for 3 months start from more cathodic potential indicating a slightly higher current value than the specific curve of sample immersed for 7 months.

The values obtained for corrosion potentials (E_{corr}), current densities (i_{corr}), polarization resistance and corrosion rates, calculated from the Tafel plots achieved at applied potentials of ± 10 mV vs. E_{corr} , are reported in Table 5.

From the data reported in Table 5, it can be said that the highest value for the corrosion rate was obtained for the non-oxidized non-irradiated Zy-4 sample and the smallest one for the completed oxidized (including edges) Zy-4 sample. Reported to the oxidized Zy-4 sample that was cut at one end (exposing fresh metal at one edge), the corrosion rates obtained for the samples immersed in NaOH solution (to have a comparison with the irradiated Zy-4 samples used in the leaching tests) slowly decrease with increasing the immersing time. This behavior suggests that a thin oxide layer was formed on the fresh surface during immersion in NaOH solution, protecting the metal surface at the cutting edge.

SEM investigations were performed on the surface of the non-irradiated sample not immersed in NaOH solution and on the non-irradiated sample immersed for 7 months in NaOH solution and defects or scratches were evidenced on the oxide layers in both cases (Figure 4). Also, from

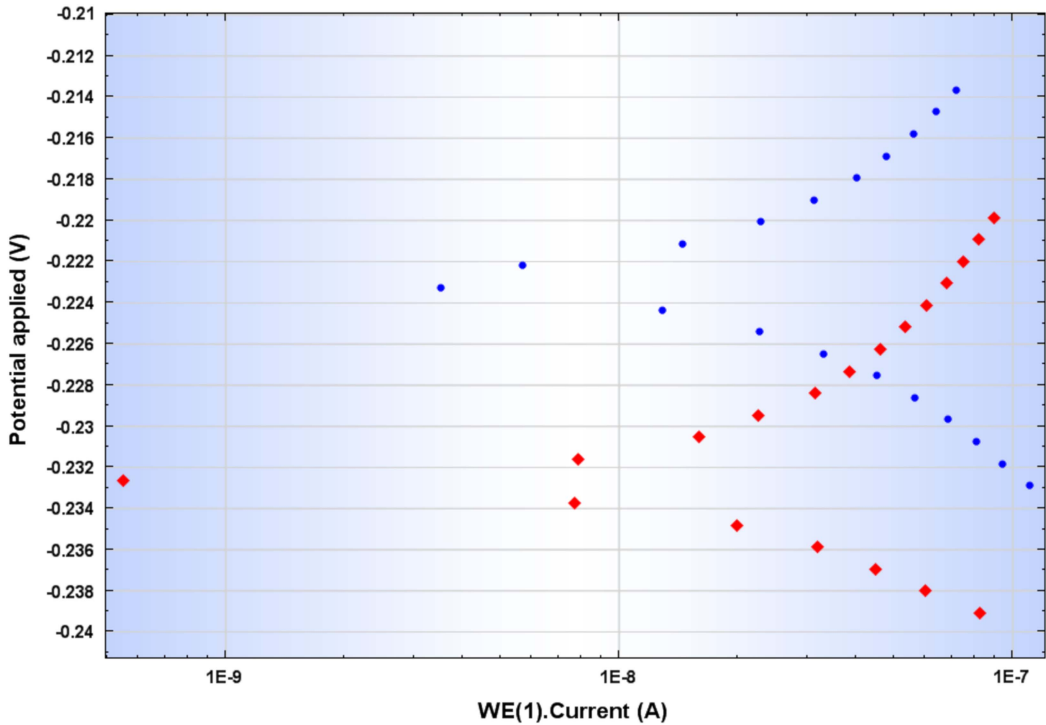


Figure 3 Tafel plots obtained by LPR method for non-irradiated Zy-4 samples immersed in NaOH solution: for 3 months (red curve) and 7 months (blue curve). (Please see electronic version for color figures.)

SEM analysis, on an image taken at the edge part of the oxidized sample (the cutting edge) the presence of some cracks (probably resulting from samples machining) was put in evidence (Figure 4, right image).

For the irradiated Zy-4 samples, after 6, 8, 10, 12, and 18 months of immersion in NaOH solution, the values obtained for corrosion potentials (E_{corr}), current densities (i_{corr}), polarization resistance and corrosion rates, calculated from the Tafel plots (Figure 5) achieved at

Table 5 LPR results for non-irradiated Zy-4 samples, at imposed potentials of ± 10 mV vs. E_{corr} .

Type on non-irradiated Zy-4	E_{corr} (V)	i_{corr} (A/cm ²)	Polarization resistance (Ω)	Corr. rate (nm/yr)
Non-oxidized Zy-4 tube	-0.840	1.0E-08	2.4E + 5	111.0
Oxidized Zy-4 tube (oxide including on the edges)	-0.300	2.7E-10	1.5E + 7	3.2
Oxidized Zy-4 tube cut at one end (with fresh metal exposed at one edge)	-0.220	5.5E-09	1.7E + 5	63.4
Oxidized Zy-4 after 3 months of immersion in NaOH (cut at one end)	-0.233	2.6E-09	1.5E + 5	30.1
Oxidized Zy-4 sample after 7 months of immersion in NaOH (cut at one end)	-0.223	1.5E-09	1.2E + 5	17.2
Oxidized Zy-4 sample after 12 months of immersion in NaOH (cut at one end)	-0.132	1.0E-09	1.0E + 5	12.0

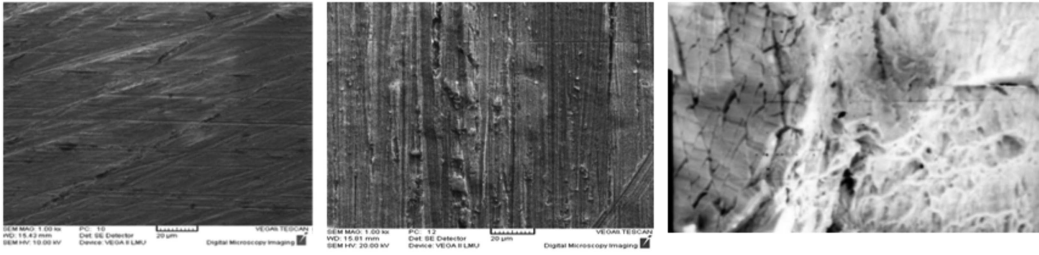


Figure 4 SEM images of non-irradiated Zy-4 samples oxidized and cut at one end: non-immersed (left), immersed for 7 months in NaOH solution (middle) and on the cut part of oxidized Zy-4 sample (right).

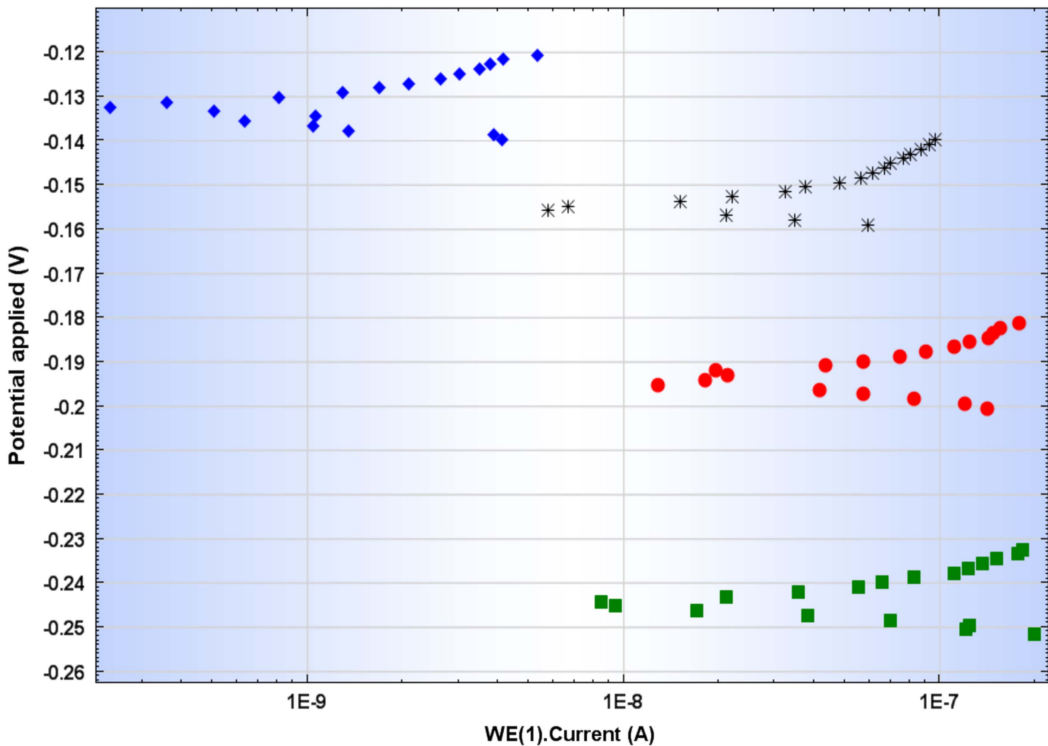


Figure 5 Tafel plots obtained by LPR method for irradiated Zy-4 samples.

applied potentials of ± 10 mV vs. E_{corr} , are reported in Table 6. The values for mass loss rate (MR), computed using Equation (2), are also reported in Table 6.

For all irradiated Zy-4 samples immersed in alkaline solution, the corrosion rates are higher than those obtained for non-irradiated Zy-4 (see Table 5), and for the sample immersed for 6 months in alkaline solution, the corrosion rate is similar with that obtained for non-irradiated and non-oxidized sample.

As for the non-irradiated Zy-4 samples, the corrosion rate decreased with increasing the immersion time. The lower value of the corrosion rate obtained after 12 and 18 months of

Table 6 LPR results for irradiated Zy-4 samples, at imposed potentials of $\pm 10\text{mV}$ vs. E_{corr} .

Type on irradiated Zy-4	E_{corr} V	i_{corr} A/cm ²	Polarization resistance (Ω)	Corrosion rate (nm/yr)	MR (mg/dm ² /d)
After 6 months immersion in NaOH (# 6.2)	-0.245	9.87E-09	6.0E + 5	113	0.0204
After 8 months immersion in NaOH (# 2.2)	-0.194	7.13E-09	6.6E + 5	81	0.014
After 10 months immersion in NaOH (# 1.2)	-0.218	7.53E-09	6.5E + 5	86	0.015
After 12 months immersion in NaOH (# 4.2)	-0.130	4.60E-09	9.4E + 5	52.7	0.0095
After 18 months immersion in NaOH (#3.2)	-0.150	4.01E-09	9.7E + 5	45.8	0.0082

immersion in alkaline solution may indicate that only after a longer period the fresh metal exposed on the edge and in the cracks generated by samples cutting are oxidized.

As observed by SEM investigations carried out on the irradiated Zy-4 samples (Figure 2), the oxide surface of the irradiated samples presents large cracks, which could have initiated because of the samples machining. The highest corrosion rates obtained for the irradiated Zy-4 samples after 6 months of static leaching in NaOH solution could be due to these cracks, by exposing Zy-4 alloy to the solution.

All values obtained by polarizing at $\pm 25\text{mV}$ vs. E_{corr} were much higher than those obtained by polarization at $\pm 10\text{mV}$ vs. E_{corr} (around one order of magnitude higher) and are not presented in this paper.

CONCLUSIONS

The irradiated Zy-4, originating from a CANDU Spent Fuel element, presents a ^{14}C inventory measured experimentally of around $2\text{E} + 04$ Bq per gram of Zy-4, mainly as organic compounds. This content is similar with the value determined by ORIGEN simulation for an average burn-up of 7 MWd/kgU.

The static leaching tests carried out on irradiated Zy-4 samples in alkaline solution (NaOH 0.1 M) indicate that a very small amount of ^{14}C is available as fast release, both in gas and liquid phase, representing around 0.077% (considering both soluble and gaseous ^{14}C species) of the initial ^{14}C content in irradiated Zy-4. After 18 months of immersion in alkaline solution, the amount of ^{14}C released in solution (as well as in gas phase) is similar with the values obtained after 18 days, and the ^{14}C release is likely due to the cracks observed on the surface of the oxide layer (leading to the metal exposure to the leaching solution).

Linear polarization measurements indicated that the irradiated Zy-4 samples are characterized by higher corrosion rates than the non-irradiated samples, with corrosion rates between 46 and 113 nm/yr. In addition, these values decreased as the immersion time increases. Also, these high corrosion rates are assigned to the defects and cracks found in the oxides developed on the samples surface during irradiation.

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