

## <sup>14</sup>C And <sup>129</sup>I Measurements In Spent Fuel

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**Abstract** – Techniques were defined, tested and validated to determine the amount of <sup>14</sup>C and <sup>129</sup>I in spent fuel. Two types of spent fuel were examined: BWR UOX fuel with a burnup of 41.4 GWd/tHMi cooled for 9 years, and MOX fuel with 5.6 wt% Pu/(U+Pu) enrichment and a burnup of 25 GWd/tHMi, cooled for 13 years. The measured values for the UOX and MOX samples were, respectively, 1371 and 1066 Bq <sup>129</sup>I/t<sub>oxide</sub>, 17212 and 6660 Bq <sup>14</sup>C/t<sub>oxide</sub>.

### INTRODUCTION

Within a context of assessing the long-term intrinsic properties of spent nuclear fuel (SNF) of different types and with different burnup values, it is important to quantify their iodine-129 and carbon-14 content, as both of these nuclides have very long radioactive half-lives. The concentrations of these isotopes in SNF must be measured with the greatest possible accuracy for comparison with the values given by calculation codes.

Two spent fuel samples were examined: BWR UOX fuel with a burnup of 41.4 GWd/tHMi cooled for 9 years, and MOX fuel with 5.6 wt% Pu/(U+Pu) enrichment and a burnup of 25 GWd/tHMi, cooled for 13 years.

### THEORETICAL BACKGROUND

#### Isotope characteristics

Iodine-129 is a fission product with a radioactive half-life of  $1.57 \times 10^7$  years. It decays only by  $\beta^-$  emission ( $E_{max} = 150.4$  keV) and has four characteristic X-ray peaks ( $K\alpha_1$  and  $K\alpha_2$  at 29.5–29.8 keV,  $K\beta_1$  and  $K\beta_2$  at 33.7–34.5 keV) and a  $\gamma$  line (39.6 keV).

Carbon-14 has a radioactive half-life of 5730 years and decays exclusively by  $\beta^-$  emission ( $E_{max} = 156.5$  keV). In oxide fuel, it arises from neutron activation of <sup>17</sup>O (about 70% of the total quantity) and <sup>14</sup>N (about 30%). These proportions are only indicative, since <sup>14</sup>N is a fabrication impurity in the oxide. The <sup>14</sup>N concentration in the oxide prior to irradiation is generally considered to range from 0 to 20 ppm.

#### General principle

Direct measurement of <sup>14</sup>C or <sup>129</sup>I in spent oxide fuel or in the dissolution solution is technically impossible today because of the large number of radioelements that interfere with the measurement.

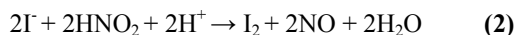
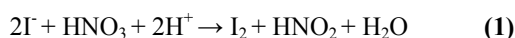
The experimental principle retained consists in isolating the <sup>14</sup>C and <sup>129</sup>I isotopes as selectively as

possible by oxidizing them respectively to CO<sub>2</sub> and I<sub>2</sub> gas and trapping the gas in a concentrated sodium hydroxide solution. The trap was analyzed with or without prior sample treatment depending on the isotope being measured. The main difficulty was to ensure that the experimental technique generates and desorbs the gaseous forms in significant quantities.

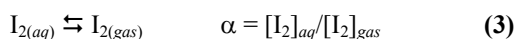
#### Iodine behavior during dissolution of spent oxide fuel in nitric acid

##### Theoretical background

When spent oxide fuel is dissolved in nitric acid, the iodide ions are oxidized by nitric acid and nitrous acid to molecular iodine I<sub>2</sub>:



Molecular iodine is a volatile compound with a distribution coefficient  $\alpha$  between the aqueous phase and the gas phase that diminishes as the temperature increases ( $\alpha \sim 80$  at 25°C et  $\sim 10$  at 100°C) which favors desorption during fuel dissolution.



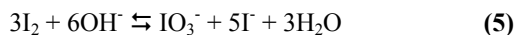
The oxidation of iodide ions may continue to higher oxidation states, however, forming nonvolatile iodate ions. This is a relatively slow reaction, occurring only when nitrous acid has been eliminated from the medium.



##### Experimental findings

During dissolution in boiling nitric acid, iodide is oxidized and iodine desorbs as a gas (Eq. (1) and (2)). Desorption was shown to be quantitatively significant. Sodium hydroxide (2 M) traps were considered sufficient to trap all the iodine in both iodide and iodate forms (Eq. (5)).

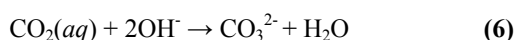
\* The <sup>14</sup>C measurement study was undertaken by A. Vaudano et D. Espinoux



Hydrolysis of  $\text{I}_2$  was complete and rapid. Nitrite ions were added to the dissolution solution to check whether or not the nitrous acid initially present and formed during dissolution was sufficient for quantitative oxidation of the iodide ions to molecular iodine  $\text{I}_2$  and to prevent the formation of iodate ions (Eq. (1) to (4)).

#### Carbon-14 behavior during dissolution of spent oxide fuel in nitric acid

The chemical forms of carbon-14 in the dissolution solution are not well known. In sodium hydroxide media,  $\text{CO}_2$  gas is trapped as a stable carbonate  $\text{CO}_3^{2-}$  (Eq. (6)).



The literature refers to carbon partially oxidized to carbon monoxide  $\text{CO}$ , or desorbed as  $\text{CH}_4$ ; although these are also gases, they cannot be trapped by a sodium hydroxide solution.

## EXPERIMENTAL WORK

### Source of spent oxide fuel

The spent fuel rod segment was selected to ensure it corresponded to a full-flux irradiation zone with homogeneous burnup over the length of the segment. This was important for checking the repeatability and reproducibility of the tests. The selected segment was cut into specimens of about 3 cm. The oxide was mechanically dislodged, mixed and homogenized. The quantities involved represented about 1 g for the tests with  $^{14}\text{C}$  and about 3-4 g for the tests with  $^{129}\text{I}$ .

### Gas trapping

This step was carried out in the C11/C12 shielded cell in the Atalante facilities. The experimental setup was designed to ensure effective gas trapping by controlling and directing the gas stream to the trap through a suction line. The depression was monitored visually with a sparging tube at the air intake. Gas-solution exchange was enhanced by the use of glass frit, and the residence time was extended by the high and narrow design of the trap.

Two trapping flasks containing a 2 N sodium hydroxide solution were mounted in series for all the tests. Both traps were analyzed.

### Iodine trapping

At least 98% of the iodine desorbed during dissolution of spent oxide fuel in boiling nitric acid. Considering the measurement uncertainties (generally

about 10%), an estimate of this order is fully acceptable for consolidating the calculation codes. This method was therefore selected for iodine trapping.

### Carbon-14 trapping

Various experimental routes were tested to oxidize and desorb  $^{14}\text{C}$  as  $\text{CO}_2$ :

1. Dissolution of spent oxide fuel in boiling 3 N  $\text{HNO}_3$ ,
2. Calcining of spent oxide fuel followed by dissolution in nitric acid,
3. Caustic fusion of the oxide with  $\text{Na}_2\text{O}_2$  followed by dissolution of the flux,
4. Caustic fusion of the oxide with  $\text{K}_2\text{S}_2\text{O}_7$  followed by dissolution of the flux.

At each step the gas was trapped in two sodium hydroxide trapping flasks in series for analysis. For both types of spent fuel studied, only the caustic fusion methods were capable of trapping  $^{14}\text{CO}_2$  in significant quantities in a single trap, but not during the same process step (**Figure 1**).

### Traps Analysis

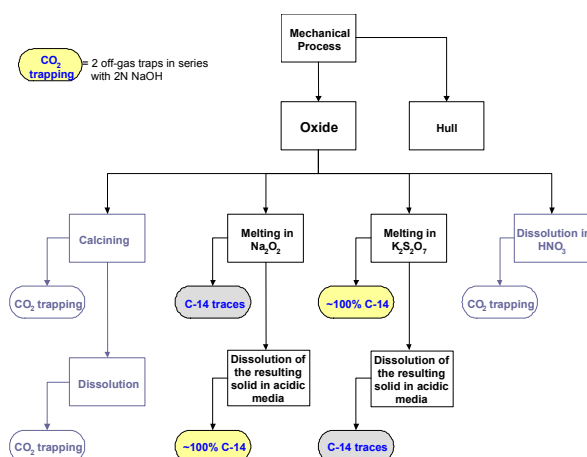
The dose rate in the traps is low enough to allow handling in a glove box.

#### $^{129}\text{I}$ analysis

The trap solutions were analyzed directly by X-ray spectrometry in liquid geometry. The low concentrations required relatively long counting times. The main contaminants in the trap were identified by  $\gamma$  spectrometry analysis.

#### $^{14}\text{C}$ analysis

Unlike  $^{129}\text{I}$ , no X-ray peaks are observable for  $^{14}\text{C}$ , and it can be measured only by  $\beta$  counting. The main contaminants in the traps ( $^{106}\text{Ru-Rh}$ ,  $^{129}\text{I}$ ,  $^{134/137}\text{Cs}$ ) are also  $\beta$  emitters, however, and their continuous spectra interfere with the  $^{14}\text{C}$  spectrum. The  $^{14}\text{C}$  must therefore be isolated for analysis. An aliquot sample from the trap was purified for this purpose in a glove box by carefully acidifying it with  $\text{HNO}_3$  and trapping the gas emission in two traps in series. The first trap was a HAN/ $\text{HNO}_3$  solution used to reduce  $\text{I}_2$  and selectively trap it as  $\text{I}^-$ ; the second trap was a 2 N NaOH solution to solubilize  $\text{CO}_2$ .  $\text{CO}_2$  was desorbed and trapped in appreciable quantities using this protocol. The liquid scintillation analysis sample was then prepared from an aliquot sample taken from the second trap.



**Figure 1.** Experimental methods tested for desorption and trapping of  $^{14}\text{C}$ . Bold text shows the retained ways.

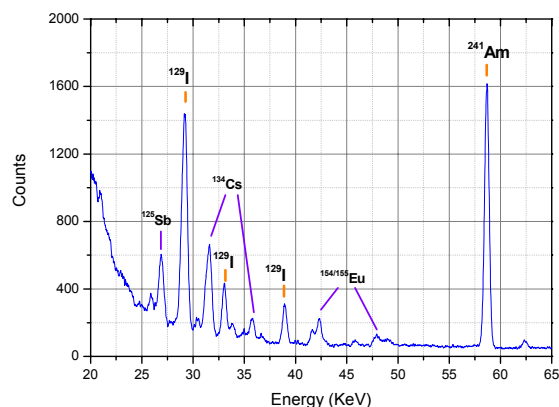
## RESULTS

The uncertainties indicated below correspond to the 5% confidence interval on the mean value. Because of the small statistical population these values are well below the 10% uncertainty generally used for measurements based on high-level tests.

### Iodine-129 measurements

No other radioelements interfered with the X-ray and  $\gamma$  lines of iodine-129 (**Figure 2**). The count rates of the spectrum lines were compared with those obtained from a certified standard solution.

Each test is systematically repeated. The results (**Table I**) are consistent between tests; the mean results are shown in **Table II**.



**Figure 2.** Spectrum of a trap solution

**Table I.** Reproducibility of iodine-129 results

Spent fuel sample	$^{129}\text{I}$ (mol/ $t_{\text{oxide}}$ )
<b>BWR UOX</b>	
First dissolution	1.65 $\pm$ 0.10
Second dissolution	1.60 $\pm$ 0.01
<b>MOX</b>	
First dissolution	1.31 $\pm$ 0.04
Second dissolution	1.21 $\pm$ 0.01

**Table II.** Mean results for iodine-129

Spent fuel sample	$^{129}\text{I}$ (Bq/ $t_{\text{oxide}}$ )	$^{129}\text{I}$ (mol/ $t_{\text{oxide}}$ )
BWR UOX	1371 $\pm$ 42	1.62 $\pm$ 0.05
MOX	1066 $\pm$ 42	1.26 $\pm$ 0.05

### Carbon-14 measurements

Duplicate tests were carried out with carbon-14 for each type of fusion ( $\text{Na}_2\text{O}_2$  or  $\text{K}_2\text{S}_2\text{O}_7$ ). Each trap was analyzed twice (two aliquot samples were purified). Each final sample was counted at least three times. The measurement repeatability and selected process reproducibility were confirmed (**Table III**).

**Table III.** Reproducibility of carbon-14 results

Spent fuel sample	$^{14}\text{C}$ (Bq/ $g_{\text{oxide}}$ )
<b>BWR UOX</b>	
First fusion ( $\text{Na}_2\text{O}_2$ )	17049 $\pm$ 709
Second fusion ( $\text{Na}_2\text{O}_2$ )	17413 $\pm$ 723
Third fusion ( $\text{K}_2\text{S}_2\text{O}_7$ )	17249 $\pm$ 925
Fourth fusion ( $\text{K}_2\text{S}_2\text{O}_7$ )	17154 $\pm$ 941

Additional  $\gamma$  and X-ray spectrometry analysis of purified trap samples showed that:

1. before purification the traps were already partially purified of  $^{129}\text{I}$  by the process itself;
2. the  $^{129}\text{I}$  concentration in the purified trap was below the X-ray spectrometry detection limit and represented less than 5% of the total  $^{14}\text{C}$  activity;
3. the purification step decontaminated the traps of  $^{134/137}\text{Cs}$  and  $^{106}\text{Ru}$ .

The mean results are indicated in **Table IV**.

**Table IV.** Carbon-14 results

Spent fuel sample	$^{14}\text{C}$ (Bq/g <sub>oxide</sub> )	$^{14}\text{C}$ (mol/t <sub>oxide</sub> )
BWR UOX	17212 ± 416	(7.41±0.18) E-3
MOX	6660 ± 200	(2.87±0.09) E-3

## CONCLUSION

The experimental protocols for determining the  $^{14}\text{C}$  and  $^{129}\text{I}$  concentrations in spent oxide fuel were defined and validated by the reproducibility of the initial results obtained for two types of spent fuel.

From the specific characteristics of the test fuel segment (nature, irradiation history and local burnup, position in the fuel assembly), the calculation code estimated the concentrations of both isotopes. These theoretical values can be compared with the experimental values obtained to consolidate the calculation model.