EUROPEAN
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European
Research Area

CArbon-14 Source Term

CAST

Quantification of C-14 in liquid and gas phases (D3.9)

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Date of issue of this report: 01/03/2017

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

Dissemination Level		
PU	Public	×
RE	Restricted to the partners of the CAST project	
CO	Confidential, only for specific distribution list defined on this document	

CAST – Project Overview

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

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

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

For more information, please visit the CAST website at:

http://www.projectcast.eu

CAST		
Work Package: 3	CAST Document no. :	Document type: R
Task: 3.2	CAST-2016-D3.9	R = report,
Issued by: ARMINES		Document status:
Internal no. :		Final

Document title
Quantification of C-14 in liquid and gas phases

Executive Summary

This report presents the work developed by SUBATECH, CEA and RWMC.

Subatech proposes an analytical strategy for the analysis of the C-14 carboxylic acids released from irradiated Zircaloy (WP3) exposed to a solution of NaOH at pH 12. This strategy is based on the use of Ion Chromatography (IC) for separation of carboxylic acids and Liquid Scintillation Counting (LSC) for the quantification of C-14 in the IC collected fractions. A method for extraction of the main water soluble radionuclides having significant activities is described. The proposed method is based on the use of $K_2[CuFe(CN)_6]$ without binding polymer resin characterized by its selectivity for the identified radionuclides and the absence of interaction with target C-14 carboxylic acids. The experimental protocol combining IC and LSC further to filtration and resin treatment stages of the leaching solution shows that the C-14 carboxylic acid activities are below the detection limits of LSC i.e. around 0.02 Bq/mL. Alternatives methods such as the use of AMS are under investigation. Subatech was not able to develop an analytical strategy for gas analysis and speciation of C-14 because the leaching experiment couldn't be performed at LECI laboratory (Laboratoire d'étude des combustibles irradiés, CEA/Saclay) and had to be transferred to the Laboratory of radioactive materials and vitrification processes (LMPA) hot laboratory (ATALANTE facility, CEA/Marcoule). The existing LMPA facilities do not allow the collection of gas samples.

RWMC have developed methodologies for the determination of C-14 inventory in gas and liquid phases and in the bulk, as well as the inorganic/organic partition in liquid phases of irradiated Zircaloy-2 cladding from a BWR fuel rod. Total digestion of cladding samples and leaching experiments between 6 months and 6.5 years were performed. The main results show (1) an important release fraction of C-14 in gas phase during the first year of leaching experiments which decreases with time, (2) an increasing release fraction of C-14 in liquid phase with time with a ratio inorganic/organic C-14 passing from 2/3 (< 1 year) to 1/3 (at 5.5 years). RWMC compares the effect of the oxide layer at Zr-cladding surface and shows that the majority of C-14 released stems from this oxide layer.

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1 Analytical strategy of SUBATECH/ARMINES

The challenge of the CAST project is the speciation of carbon-14 species released from radioactive waste materials in simulated disposal conditions (reducing conditions, alkaline media, groundwater chemistry, temperature). Work Package 3 (WP3) is investigating the release of C-14 from irradiated Zircaloys and Task 3.2 aims at the development of analytical methods for studying C-14 speciation in solution and gas in collaboration with Task 2.2 of WP2 (Steels).

One of the objectives in Tasks 2.2 and 3.2 is to characterize C-14 organic fraction released in the leaching solution, with a focus on the analysis of ionic carboxylic acids having a short carbon chain ≤ 5. Characterization of carboxylic acids with a low carbon chain length is of importance since they are preferentially released compounds from Zircaloy alloys and steels [Heikola, 2014; Sasoh, 2008; Takahashi et al., 2014]. The combination of Ion Chromatography (IC) and Liquid Scintillation Counting (LSC) will be investigated as a potential characterization method. IC will be used for the separation and the fractionation of the carboxylic acids present in the leachates. However, this technique coupled with non-radiochemical detection is not enough sensitive to quantify the very low concentrations of small carboxylic acids expected in the leaching solution because the detection limit of ion chromatography is around 0.03 ppm for small carboxylic acids. In this perspective, optimization is considered for the separation of a mixture of known concentration of standard carboxylic acids in order to determine the optimal retention time windows related to carboxylic acids to enable their individual collection from real samples. After the chromatographic separation, the collected carboxylic acids will be transferred to an LSC system for the quantification of carbon-14 activity. LSC is a sensitive analytical technique (around 0.3-0.5 Bq/g). However, in case LSC is not sensitive enough to distinguish the C-14 activity from the background noise, the measurement of C-14 in the collected fractions will be conducted by using a technique having an ultra-low detection limit: accelerator mass spectrometry (AMS). For that, the Laboratory of Measurement of Carbon-14 (Laboratoire de Mesure du Carbone 14, LMC 14) has been contacted and meetings took place between July and September 2016 to discuss application of AMS measurements on samples. These discussions have identified that analyses of carbon-14 dissolved in solution is possible only for the inorganic C-14. The feasibility will be checked first on blank solution (NaOH, 0.01M) free from carbon-14 to measure the background level, and then on real samples containing only inorganic carbon-14. This step will be done in collaboration with CEA-LASE (Laboratoire d'Analyse et Soutien aux Exploitants). The remaining question is how to quantify the organic fraction of carbon-14 dissolved in the collected fractions because no treatment of samples is possible at the LMC14 facility to oxidize the organic fraction, trapped in solution, into inorganic form.

A second major objective developed at SUBATECH is to implement a simple and adapted method for the extraction of the main water soluble radionuclides other than C-14 in the leaching solutions using ion exchange resins. The resin treatment stage has several goals: *i*) to reduce the total activity in leachates to avoid the need for further dilution of the leaching solutions to meet activity acceptance limits of the analytical laboratories and to make handling the leachates easier; *ii*) to limit the potential contamination of analytical instruments, especially for AMS analyses because institutions equipped with AMS cannot accept ‘hot’ samples and *iii*) to remove beta-emitting radionuclides that interfere with the measurement of C-14 activity by LSC.

Selective extraction of radionuclides ahead of the chromatographic separation is required and the resin treatment requires the pH of the alkaline leaching solutions to be reduced to ensure optimal extraction efficiency.

Leaching experiments of irradiated Zircaloy cladding for CAST are carried out in the hot cells of ATALANTE facility at CEA Marcoule. The hull samples for the leaching experiments were supplied by AREVA and were taken from fuel rods discharged from PWR reactors and reprocessed in AREVA-La Hague. Leaching experiments are performed in alkaline solution pH 12 at room temperature (25 °C) and anoxic atmosphere. C-14 analysis of the leaching solution is entrusted to two laboratories: SUBATECH/ARMINES for analysis of ionic C-14 carboxylic acids in aqueous media, and CEA/Saclay for the analysis of the total C-14 content, organic and inorganic C-14 partition and the volatile molecules such as alcohols and aldehydes.

Prior to shipping to external laboratories, the leaching solution is filtered to ensure the acceptability limit of the samples by removing metallic particles and oxide precipitates which contribute to increase the total activity level. Sampling of the leaching solutions is considered at two given times of exposure: 14 days and 5.5 months. A first sample of 6 mL after 14 days of leaching was sent to SUBATECH early in March 2016. Test of the leaching solution decontamination protocol and a first evaluation of the carboxylic acids containing C-14 were performed. Figure 1 shows the outline of the general strategy for the characterization of C-14 released from irradiated Zircaloy in solution representative of cement environment, as well as the experimental protocol developed at SUBATECH/ARMINES and CEA to analyze ionized C14-carboxylic acids.

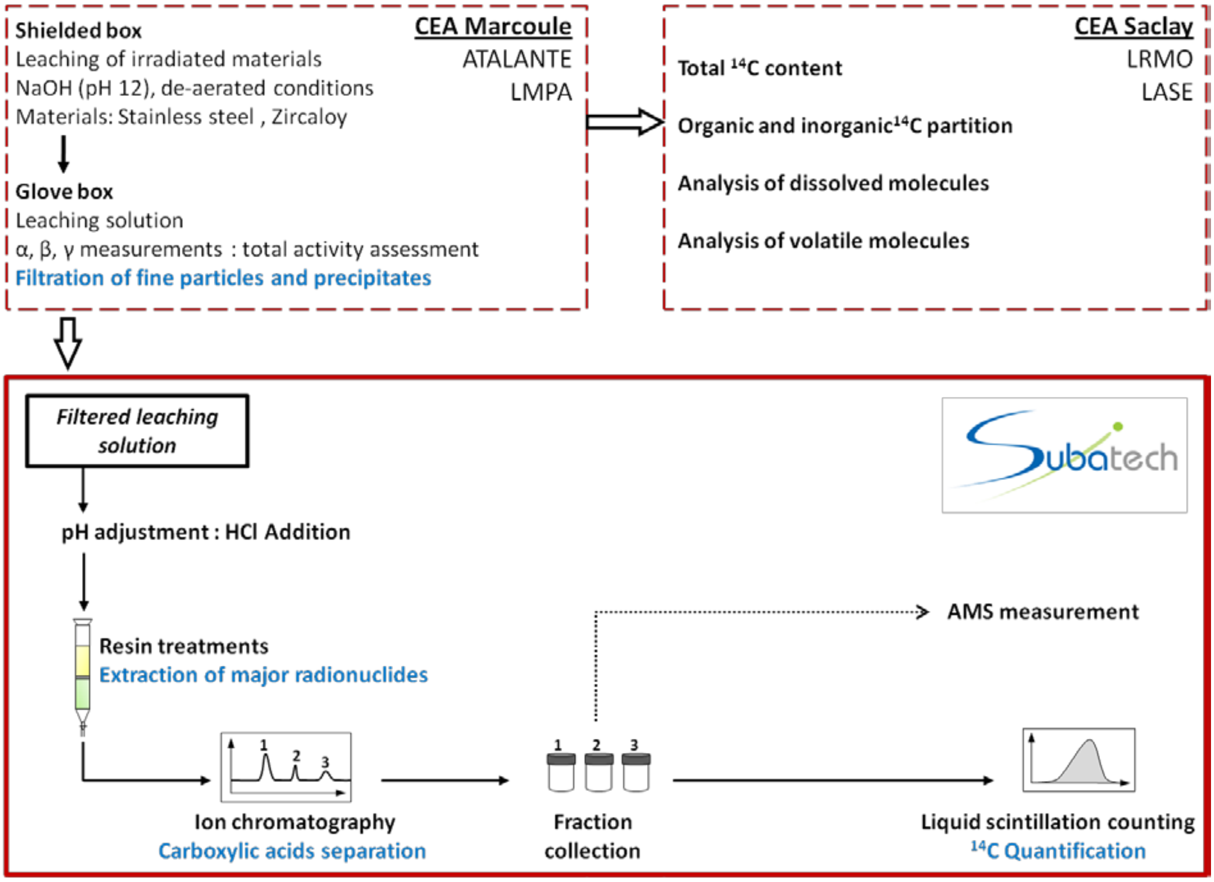


Figure 1. Outline of the general strategy for C-14 speciation in solution developed at SUBATECH/ARMINES and CEA. ATALANTE: ATelier Alpha et Laboratoires pour ANalyses ; LMPA: Laboratoire d'études des Matériaux et Procédés Actifs; LASE: Laboratoire d'Analyse et Soutien aux Exploitants; LRMO : Laboratoire de Radiolyse et de la Matière Organique.

The initial objective of Task 3.2 was to determine the forms of released carbon-14 (organic/inorganic) in solution and gas phases: CEA had to develop analyses for speciation of carbon-14 in cementitious solutions and in gas; SUBATECH/ARMINES had to analyse carbon-14 speciation in solution and in gas phase. For the two laboratories, gas analysis was intended to be developed by SUBATECH/ARMINES and CEA/Saclay based on the availability of the gas samples from the leaching experiments run by CEA. However, due to nuclear safety reasons, the leaching experiment could not be performed at LECI laboratory (Laboratoire d'étude des combustibles irradiés, CEA/Saclay) and was transferred in October 2014 to the LMPA laboratory (Laboratory of radioactive materials and vitrification processes) in ATALANTE facility, CEA/Marcoule [Caron et al., 2014]. However, gas sampling at

LMPA was not possible because the leaching cell was not designed to collect gas samples. The additional development and validation of a new design by the nuclear safety would have delayed the start of the leaching experiments. Therefore no gas samples would be collected: only speciation in solution will be performed. In addition, SUBATECH/ARMINES needed to face another difficulty that was the decontamination of a radioactive leaching solution by disturbing as little as possible carboxylic acids speciation in solution prior sending at the final stage to an AMS facility for quantification. Therefore, here again, the consortium agreed to focus the strength and effort on detection, separation, measurement and quantification of organic carbon-14 [Necib et al., 2016].

2 Current knowledge on the radiochemical composition of the leaching solutions of irradiated Zircaloy

The radiochemical composition and the activity of the leaching solution depend on several factors related to the cladding material, fuel type, the number of irradiation cycles, irradiation time, mean burn up. Leaching experiments carried out in the framework of the CAST project on irradiated Zircaloys show that leachates contain actinides, fission products and activation products besides C-14 [Gras, 2014; Herm et al., 2015]. Some radionuclides are present with a significant activity level compared to C-14; i.e several Becquerels per mL of leaching solution. [Yamaguchi et al., 1999] reported the presence of Co-60, Ru-106/Rh-106, Sb-125, Cs-134, Cs-137 and Eu-154 in the leachates of Zircaloy-4 cladding from a PWR. Leaching experiments at RWMC on irradiated Zircaloy-2 from BWR cladding show a substantial presence of Co-60 in addition to Cs-137 and Sb-125 [Yamashita et al., 2014]. Preliminary leaching experiments carried out by CEA Marcoule for assessing the αβγ activities in leachates from irradiated M5-type (UOX) Zircaloy hulls under aerobic alkaline conditions (pH 12), revealed the presence of additional radionuclides such as Cr-51, Eu-155 and actinides.

3 Leaching solutions of irradiated Zircaloy cladding

3.1 *Experimental conditions*

Leaching tests are carried out at CEA Marcoule using zirconium-niobium M5 hulls supplied by AREVA. The hull samples for the leaching experiments were supplied by AREVA and were taken from fuel rods discharged from PWR reactors and reprocessed in AREVA-La Hague following the industrial process of shearing/dissolution/rinsing. An additional rinse of the Zircaloy M5 hulls was performed by using water and carbonate solution to decrease the total activity of the hulls. Details on the experimental conditions and characteristics of the Zircaloy hulls are presented in the D3.2 report [Caron et al., 2014]. Leaching experiments have been carried out in alkaline solution of NaOH at pH 12 and room temperature (25°C) under anoxic atmosphere.

3.2 *Filtration of the leaching solution*

The filtration of the leaching solution (millipore IC Millex-LH, PTFE hydrophile 0.45µm filter) have been carried out on site at CEA Marcoule in order to eliminate fine particles (e.g. metal oxides) and precipitates and any associated activity. This decreased the activity (in particular the alpha activity) to a suitable level to allow shipping of the samples to SUBATECH. Actinides such as Pu, Am and Cm contained in leachates form precipitates in alkaline hydroxide solutions, thus the alpha activity can be considerably lowered by using suitable filtration. Likewise, some reported lanthanides have high pKs values (e.g. Eu-154 pKs = 25.6 [Martell and Smith, 1974]) and their aqueous concentraions can be considerably lowered by similar filtration. Recovery tests performed at SUBATECH with C-14 labelled carboxylic acids indicate that the PTFE filter does not retain carboxylic acids. According to tests carried out by using formate, acetate, propanoate, butyrate and oxalate tracers, the C-14 recovery was at least equal to 95 % after the filtration of solution containing 100 Bq/mL of C-14 as shown in Table 1.

Table 1: Recovery of C-14 labeled carboxylic acids after filtration with PTFE 0.45µm filter membrane, the initial activity for C-14 labeled carboxylic acids was 100 Bq/mL

Radionuclides	% recovery
C-14 formate	100%
C-14 propanoate	100%
C-14 butyrate	100%
C-14 oxalate	95%

3.3 *Radiochemical composition of the leaching solution after 14 days of exposure*

Table 2 summarizes the radiochemical composition of the leaching solution related to the leaching of two M5-type (UOX) Zircaloy hulls performed at CEA Marcoule. An alkaline solution of NaOH at pH 12 sparged with argon has been used as leachant. The initial leachant volume equal to 235 mL has been used in anoxic conditions under static mode (without solution renewal). Two hulls with a mass equal to 7.70g have been introduced into sealed leaching pots. The leaching solution taken after 14 days of exposure was filtered by using a PTFE 0.45 µm filter.

Table 2: Radiochemical composition of the leaching solution of M5-type (UOX) Zircaloy hulls in NaOH pH 12 solution, sampling at 14 days, PTFE 0.45 µm Filtration.

alpha counting	**Bq/ml**
Total activity	59
accuracy (k=2)	24
bêta counting	**Bq/ml**
Total activity	2300
accuracy (k=2)	115
gamma counting	**Bg/ml**
Total activity	**2430**
^{134}Cs	30
^{137}Cs	996
^{125}Sb	691
^{241}Am	12
^{106}Ru/^{106}Rh	659
^{60}Co	5,1
^{155}Eu	<0.5
^{154}Eu	6.4
^{51}Cr	33

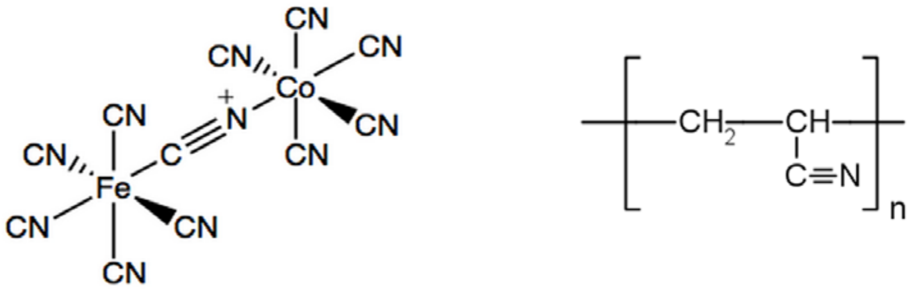
Radiochemical analyses carried out by CEA Marcoule showed a high activity (several hundred of Becquerels per milliliter of leaching solution) related to Cs-137, Sb-125 and Ru-106/Rh-106. Minor activities due to the presence of Cr-51 and Co-60, Cs-134, Eu-154 and Eu-155 were also detected. Moreover, some actinides such as Pu, Am and Cm are detected with an activity up to 10 Bq/mL. A method for extraction of the main water soluble radionuclides encountered in the leaching solution using ion exchange resins (IER) is discussed below. The extraction method based on ion exchange resin meets two essential criteria: i) the minimization of the number of treatment stages that could lead to a loss of C-14 and ii) absence of alteration of the typical C-14 molecules that are expected.

4 Selective extraction of the radionuclides in the leaching solution

4.1 *Tested resins*

4.1.1 Inorganic ion exchanger for cesium extraction

In the literature, several resins and inorganic ion exchangers for cesium extraction are reported [Collins et al., 1995]. Among these, inorganic ion exchanger like potassium hexacyanocobalt(II) ferrate(II), potassium hexacyanonickel(II) ferrate(II) and potassium hexacyanocopper(II) ferrate(II) are good candidates for a rapid and quantitative fixation of cesium. Moreover, these are stable for the entire pH range with a cesium removal efficiency ensured for any pH value ranging from acidic to alkaline [Mimura et al., 1997]. In addition, they have a weak interaction with nonmetallic ions [Kamenik et al., 2013]. The theoretical cesium exchange capacity is about 6 milliequivalents of cesium per gram of dry resin for potassium hexacyanocobalt(II) ferrate(II) [Prout et al., 1965]. For commercial potassium hexacyanocopper(II) ferrate(II), an organic binding polymer based on polyacrylonitrile PAN is added to the active component to improve its mechanical and granulometric properties. Figure 2 shows the structure of the potassium hexacyanocobalt (II) ferrate resin: $K_2[CoFe(CN)_6]$ and PAN.



hexacyanocobalt(II) ferrate(II)

PAN

Figure 2: Structure of potassium hexacyanocobalt(II) ferrate(II) resin and the organic binding polymer based on polyacrylonitrile PAN

The free residual cyano C≡N groups of the PAN polymer support are reactive toward the C=O of the carboxylic acid group [Bashir, 1992; Wu et al., 2012]. This characteristic is confirmed by tests involving labeled C-14 carboxylic acids, in contact with potassium hexacyanonickel(II) ferrate(II) KNiFC-PAN supplied by Triskem. The results showed a significant loss of 94% for carboxylic acids. This result does not support the use of KNiFC-PAN resins for the decontamination of the leaching solution.

For our objective here, $K_2[CuFe(CN)_6]$ without binding polymer supplied by Areva STMI (Sociétés des Techniques en Milieu Ionisant) is considered for the extraction of cesium in the leaching solutions. The ion exchanger is in powdered form with a particle size less than 100 µm. Before use, it was rinsed several times with milliQ water (18.2 MΩ·cm, Millipore, Merck). When immersed in water, the ion exchanger showed a basic pH value of about 11, which can be lowered to pH 7-8 by adding hydrochloric acid. The sorption measurements for cesium were made with batch equilibration tests. A large excess of resins (1g of dry resin) was directly added into the sample containing 100 Bq of Cs-137 in 20 mL of milliQ water. Equilibrium was reached after one hour. After centrifugation (2647g, 10 min), the supernatant was recovered and the remaining activity in solution was measured by LSC. The same experiment was reproduced with C-14 labelled short chain mono- and di-carboxylic acids to verify the absence of interaction between carboxylic acids and $K_2[CuFe(CN)_6]$ without binding polymer resin. Table 3 summarizes the retention of Cs-137 and C-14 labeled carboxylic acid after resin contact. The obtained results validate the quantitative removal of cesium from solution and the non-interaction of the ion exchanger resin with typical short-chain C-14 carboxylic acids.

Table 3: Retention of Cs-137 and C-14 labeled carboxylic acids after 1 hour contact with $K_2[CuFe(CN)_6]$ without binding polymer resin, the initial activity for Cs-137 and C-14 labeled carboxylic acids was 100 Bq

Radionuclides	% retention
Cs-137	> 99%
C-14 formate	< 1%
C-14 propanoate	< 0.5%
C-14 butyrate	< 0.5 %
C-14 oxalate	< 4%

It should be noted that $K_2[CuFe(CN)_6]$ resin, although primarily developed for the cesium removal from solution, also retains divalent or trivalent metals such as Co, Mn, Eu and actinides. The resin supplier (Areva STMI) indicates that $K_2[CuFe(CN)_6]$ retention efficiency depends on pH and is optimal for the neutral pH range.

4.1.2 Chelex-Na resin for transition metal extraction

Chelex 100 resin was used as it has a strong retention of multivalent transition metals and is typically used for the removal of trace metal contaminants in natural waters [Pai, 1988; Pai et al., 1988]. Other interesting characteristics of Chelex 100 are the high exchange capacity (wet capacity 0.4 meq/mL), the stability over the entire pH range and the weak interaction with organic anions species [Nobel, 2000]. Furthermore, Chelex 100 is a radiation resistant resin used for extraction and pre-concentration of radionuclides [Alliot et al., 2013; Pakalns, 1980]. Chelex 100 holds iminodiacetate ions that act as chelating groups for polyvalent metal ions. Figure 3 shows the structure of Chelex 100 resin at two different pH values.

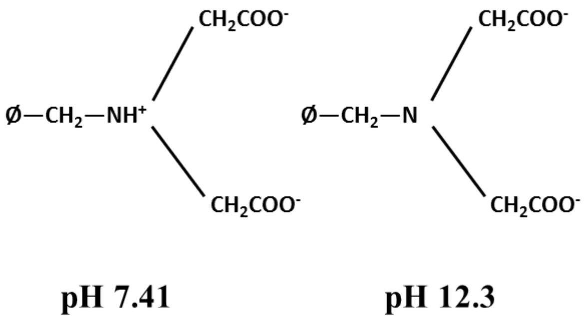


Figure 3: Structure of Chelex 100 resin

In the sodium form, Chelex 100 acts as a cation exchanger and allows the elimination of polyvalent transition metals [Pai, 1988; Pai et al., 1988], specifically Co, Ni, Fe, Cr and Mn, which are detected in the leaching solutions.

Chelex 100 efficiency is strongly pH dependent; and the equilibrium pH value of the batch is a parameter that affects greatly the fixation of polyvalent transition metals [Pai et al., 1988]. For this reason, the pH value of the test solutions requires to be at neutral range to ensure free metal cations and avoid hydroxide complexes that cannot enter the pore structure of the resin [Pai, 1988]. Analytical Grade Chelex 100 Resin (50-100 mesh) supplied by Biorad in the sodium form showed a basic equilibrium pH above 11. Before being used, Chelex 100 was rinsed with copious amounts of MilliQ water and the pH adjusted to 6-8 by adding HCl.

Chelex 100 tests were made with batch method by using 1g of dry resin in 30 mL of solution. Two radionuclides tracers (Co-60 and Ni-63) were used to verify the efficiency of Chelex retention. Contact was performed under agitation for at least 24 hours. After centrifugation, the supernatant was recovered and the remaining activity of each tested radionuclide was quantified by using LSC. Likewise, C-14 labelled carboxylic acids were used to verify the non-interaction of the target molecules. Measurements summarised in Table 4 confirm the high efficiency of the removal of Co-60 and Ni-63 with Chelex 100 as well as the absence of significant interaction with C-14 carboxylic acids.

Table 4: Retention of Co-60, Ni-63 and C-14 labeled carboxylic acids after 24 hours in contact with Chelex 100 resin (initial activity : 100 Bq/mL)

Radionuclides	% retention
Co-60	95%
Ni-63	97%
C-14 formate	1%
C-14 propanoate	7%
C-14 butyrate	2%
C-14 oxalate	2%

4.1.3 Chelex-Fe(III) resin to extract antimony

To remove antimony, Chelex 100 needs to be used in the ferric form. According to Chanda and al. [Chanda et al., 1988], oxoanion species of arsenic (III) and (V) are efficiently removed from aqueous solution by ligand sorption on Chelex (Fe^{3+}) complex. Due to similarities in the coordinating properties between arsenic and antimony, one could expect an efficient removal of antimony by using Chelex 100 doped with Fe(III) cations. The preparation of Chelex 100 doped with Fe(III) is done at SUBATECH laboratory. Antimony is usually found in two oxidation states: Sb(III) for oxygen-depleted media and Sb(V) under oxic conditions [Filella and May, 2003]. When leaching solutions are in contact with air, Sb(V) is probably the predominant form. For antimony diluted solutions, SbO_3^- is the main species present in alkaline conditions [Filella et al., 2002; Pitman et al., 1957; Takeno, 2005].

In order to optimize the pH for Sb(V) retention with Chelex-Fe(III), a solution of Sb(V) was made by oxidizing a solution of $SbCl_3$ dissolved in ultrapure water in the presence of goethite as a catalyst for 3, 4, 5 and 7 days. A solution of 30 ppm Sb(V) was prepared by oxidiation for 4 days (optimal time to get a complete oxidation of Sb), suspensions were then centrifuged and the supernatant filtered with PTFE 0.45µm filter. The pH was then adjusted in the range 5 to 12 by adding HCl and NaOH solutions. The Sb(V) solution was contacted with the Chelex-Fe(III) resin during 4 days and the Sb concentration remaining in solution was measured by ICP-MS (Quadripolaire Xseries 2, THERMOELECTRON). The calibration solution was provided by SCP Sciences. The physical interferences and drift were corrected by the use of internal standardization technique containing a solution of ^{115}In injected simultaneously with the samples in the ICP-MS device. The samples were diluted in 2% high purity HNO_3 solution. The quantification limit with this method is 8.3×10^{-10} mol·L^{-1} and the error is estimated at ±10%. Figure 4 shows the retention of Sb(V) at different pH values ranging from 5 to 12.

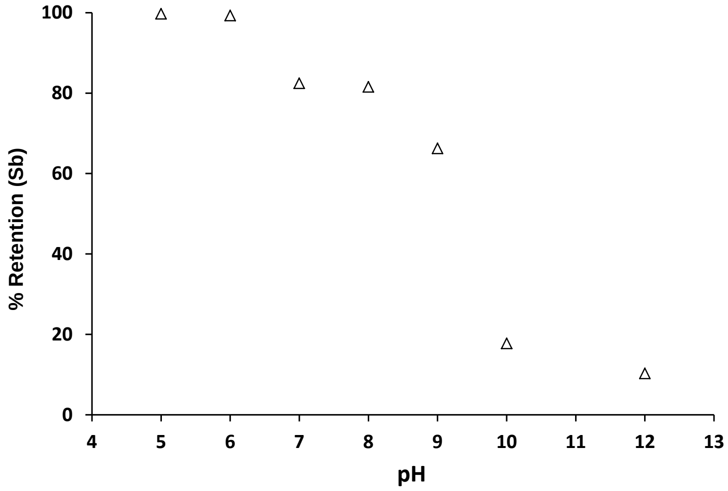


Figure 4: Evolution of the retention for Sb(V) at different pH values ranging from 5 to 12

From Figure 4, we can notice an effective retention of Sb(V) when the pH is in the range 5 and 6. Above these values, the retention of Sb(V) with Chelex-Fe(III) drops dramatically since Chelex-Fe(III) decomposes at high pH extremities and form hydroxide complexes. C-14 labelled carboxylic acids were also in contact with Chelex-Fe(III) at pH 6 to verify the non-interaction with the target molecules. The obtained % retention values are presented in Table 5.

Table 5: Retention of carboxylic acids with Chelex-Fe(III) at pH 6

Carboxylic acids	% retention
Formate	**4**
Propanoate	**25**
Butyrate	**48**
Oxalate	**91**
Sb(V)	> **99**

It can be seen that carboxylic acids are retained significantly with Chelex-Fe(III), up to 91% for oxalate, and therefore, Chelex-Fe(III) cannot be used to remove antimony from leachates containing carbon-14 carboxylic acids.

4.2 Decontamination of the leaching solution using $K_2[CuFe(CN)_6]$ without binder polymer

Among the tested resins, a first decontamination test has been carried out with $K_2[CuFe(CN)_6]$ without binder polymer supplied by Areva STMI. This resin takes a short time to reach equilibrium (one hour) and it has good capacity to remove several radionuclides expected in the leaching solution. The pH value of the leaching solution, initially equal to 12, requires to be adjusted at neutral range by adding hydrochloric acid to ensure an optimal removal of radionuclides. At this acidification stage, carboxylic acids remain ionized as the pH is higher than their pKa (mostly lower than 5). Table 6 shows the results for the decontamination of 1 mL of the leaching solution neutralized to 7 by adding hydrochloric acid. It was also used to lower to 7 the pH of the resin used in excess (50 mg).

Table 6: Radiochemical composition of the leaching solution of M5-type (UOX) Zircaloy hulls before and after contact with $K_2[CuFe(CN)_6]$.

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

After contact with $K_2[CuFe(CN)_6]$, actinides were removed efficiently as shown by a significant decrease of the total alpha activity. Likewise, the total beta activity was considerably lowered down to 50 Bq/mL. For gamma emitters initially present in the leaching solution, it is noteworthy that the remaining activity due to Sb-125 and Ru-106/Rh-106 substantially decreased with the addition of $K_2[CuFe(CN)_6]$. After decontamination, ion chromatography IC technique will be used for the separation and fractionation of the anionic carboxylic acids present in the leachates.

5 Speciation of C-14 carboxylic acids in the leaching solution

5.1 *Ion chromatography of a standard carboxylic acids mixture*

In order to apply the analytical strategy described above, a separation of a mixture of carboxylic acids was carried out by using ionic chromatography. The chromatographic parameters were optimised to enable an individual collection of carboxylic acids fractions. Figure 5 shows the chromatogram related to a mixture of formate, acetate, propanoate, oxalate and butyrate 1 ppm diluted in milliQ water. The solution pH was adjusted to 9 to have the same pH of the eluent. Some HCl was intentionally added to the carboxylic acids mixture to mimic the presence of chlorides in the leaching solution.

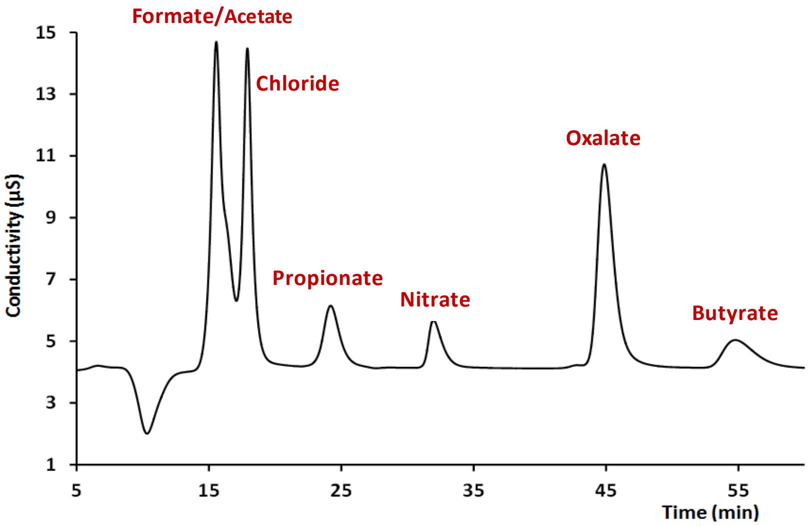


Figure 5: Chromatogram showing the separation of small carboxylic acid (1 ppm) in the presence of chloride. Mobile phase: Na_2CO_3 (7.5 mM) and NaOH (0.75 mM) (Injected volume 250 µL).

Analyses were performed with IC Compact 881 Metrohm liquid chromatography equipped with sequential (Metrohm CO_2 suppressor MCS) and chemical (Metrohm suppressor MSM II) for chemical suppression modules. In this experiment, a solution containing Na_2CO_3 (7.5 mM) and NaOH (0.75 mM) was used as the eluent/mobile phase with suppressed conductivity detection. The separation columns used were Metrosep Asupp 16 250-2.0 columns specifically designed for the separation of inorganic and small carboxylic acids anions; the injected volume was 250 µl. The pump flow was maintained at 0.15 mL/min to maximize the separation peaks; alternatively, one can use a gradient elution to reduce analysis time.

The determination of the optimal separation conditions will enable individual carboxylic acid fractions collection for determining the C-14 activity related to each carboxylic acid present in the leaching solution by using Liquid Scintillation Counting LSC.

5.2 *Ion chromatography of antimony*

Antimony Sb(V) remaining in the leaching solution after decontamination is negatively charged as oxo-anion form and thus may appear in the retention time windows related to carboxylic acids. In order to identify the antimony retention time, a solution containing Sb(V) (see section 4.3.1) and formate was injected in the same chromatographic conditions described for the carboxylic acids separation (section 5-1). The obtained chromatogram is given in Figure 6.

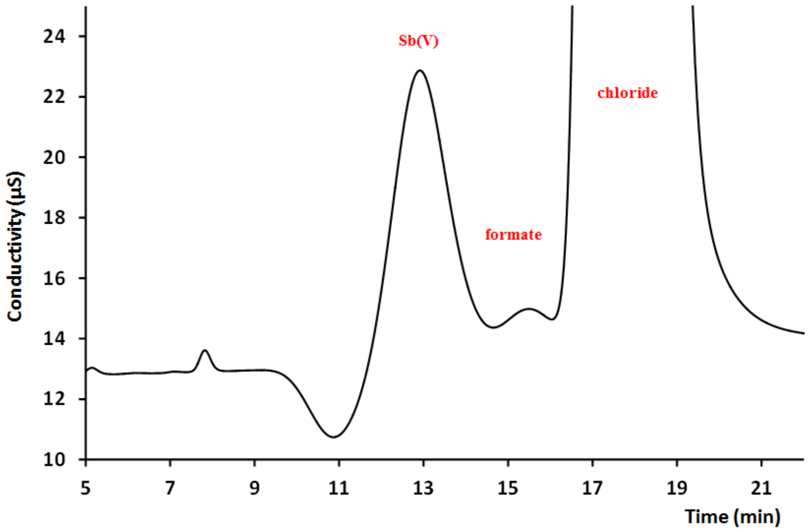


Figure 6: Chromatogram of a mixture of Sb(V) (21 ppm) and formate (0.5 ppm) solution in presence of chlorides. Mobile phase: Na_2CO_3 (7.5 mM) and NaOH (0.75 mM). Injected volume 250 µL.

Figure 6 shows that Sb(V) was weakly retained in the column and was eluted before formate. The eluted volume between 11 to 17 min was collected and ICP-MS was used to ensure the full recovery (99%) of injected Sb(V). Therefore, the presence of Sb in the collected fraction will interfere with the detection of ^{14}C-formate by LSC.

5.3 *Ion chromatography of the decontaminated leaching solution*

Decontaminated leaching solution is injected into the chromatographic system by fulfilling the same chromatographic conditions described for the carboxylic acids mixture separation. The leaching solution injected volume was 250 µL, which is the maximum capacity of the loop injection. To analyse the C-14 related to 1 mL of the leaching solution, fractionation of the decontaminated leachates was repeated four times and the carboxylic acids were collected separately on the basis of the chromatogram shown in Figure 5. Figure 7 shows the chromatograms of the decontaminated leaching solution and the mixture of carboxylic acids.

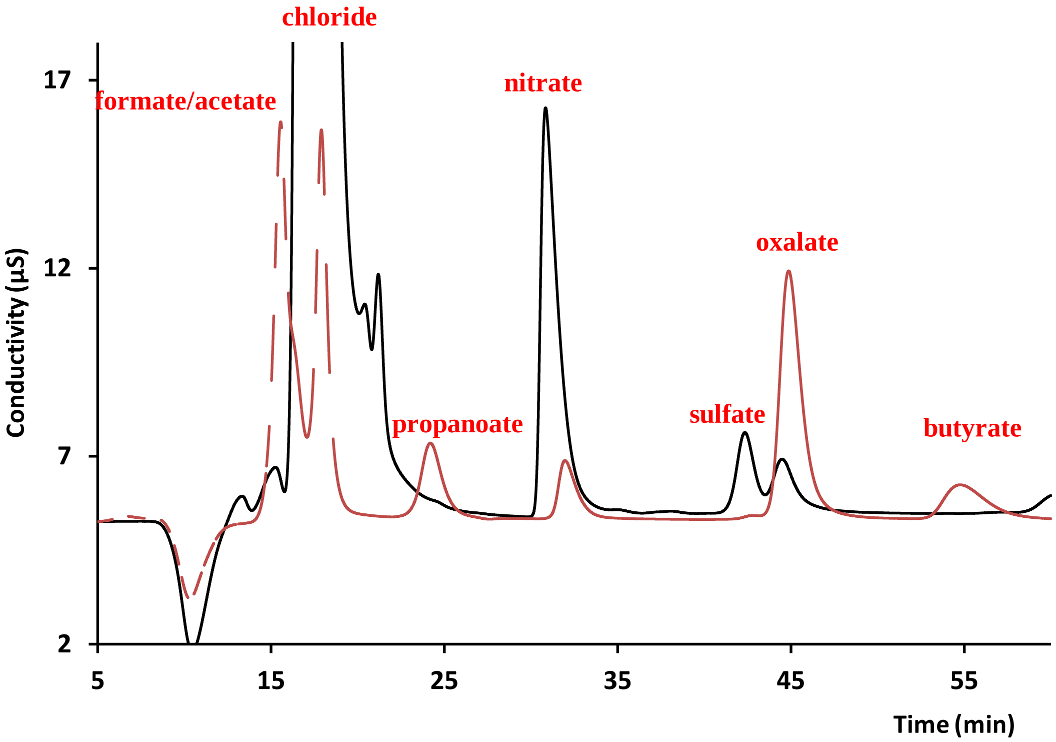


Figure 7: Chromatograms of the decontaminated leaching solutions (solid line) and the mixture of standard carboxylic acids (dotted line). Mobile phase: Na_2CO_3 (7.5 mM) and NaOH (0.75 mM) (Injected volume 250 µL).

The fraction collection was performed every five minutes to ensure a full coverage of the carboxylic acids contained in the leaching solution.

To determine C-14 activity, two peaks were selected: oxalate and butyrate with a total collected volume equal to 3 mL. The quantification of carbon-14 was then performed by LSC. Formate/acetate and propanoate were not analysed because the retention time window for formate/acetate coincide with that of antimony, and for propanoate the retention time overlap with that of chloride and unknown compound(s). Therefore to overcome this uncertainty, the collection is performed in the window of oxalate and butyrate time retention.

5.4 *Quantification of C-14 carboxylic acids in the leaching solution*

The quantification of carbon-14 organic compounds can be performed by LSC by using a typical Tri-Carb counter (Figure 8) having a detection limit around 0.02 Bq/mL. 2 mL of Ultima Gold LLT Liquid scintillation cocktail was added to the collected fractions by using 5 mL standard vials. The total counting time was 2 hours and the C-14 counting efficiency was equal to 72%. Table 7 summarizes the activity obtained for the 2 collected carboxylic acids expressed as CPM.

Figure 8: Tri-Carb analyzer used for C-14 carboxylic acids analysis in the collected fractions

Table 7: Activities in the carboxylic acids collected fractions expressed as CPM and Bq/mL. Values in parenthesis correspond to the uncertainties.

	blank	Oxalate fraction	Butyrate fraction
CPM	3 (16%)	7 (9%)	5 (11%)
Bq/mL		0.03	0.02

The activities measured in the carboxylic acids collected fractions were extremely low and very close to the background noise. These results confirm that the C-14 carboxylic acids concentrations are close to the detection limit of LSC. Therefore, a more sensitive technique such as the accelerator mass spectrometry (AMS) is necessary.

5.5 *Towards AMS analyses*

To remind, the strategy developed by SUBATECH/ARMINES is (1) to decontaminate the leaching solutions by inorganic ion exchanger to remove the major radionuclides (^{137}Cs, ^{60}Co, ^{125}Sb and ^{106}Ru/^{106}Rh, (2) to separate the organic carboxylic acids by ion chromatography and to collect, and (3) to measure the collected fraction by liquid scintillation counting (LSC). The application of this strategy on leaching solution after 14 days of contact with irradiated M5 hulls was applied and 2 fractions (oxalate and butyrate retention time windows) were collected for which the results were below the detection limit of the LSC (0.02 Bq/mL). In addition, the peak at about 45 min (Figure 7) corresponding to oxalate carboxylic acid appears and this result is coherent with the data obtained by CEA/LRMO on the same leaching solution without any decontamination. This also indicates that the method of decontamination does not degrade the carboxylic acids released in solution.

Therefore, the final step of the strategy is to analyse the collected fraction by a more sensitive method. In collaboration with CEA/LSE & LRMO, a contact has been established with LMC14 laboratory to realize the measurements by AMS. Several meetings were organized between July and September 2016 to discuss:

1 / The ratio limit of ^{14}C/^{12}C acceptable by the AMS,
2 / The sample conditioning,
3 / The decontamination degree of samples.

The outcome of the discussion on the points is as follow:

1 / The highest acceptable ^{14}C/^{12}C ratio at LMC14 laboratory is 10^{-12} in 1 mg of C in total. Applied on the results obtained by CEA/LASE with 6.1 ± 0.4 Bq/g (or 3.7×10^{-2} ng/g) in total ^{14}C with a contribution of 16 mg/L of ^{12}C, the ratio ^{14}C/^{12}C is 2.3×10^{-6} in total ^{14}C, which is 6 orders of magnitude higher than the acceptable ratio. Similarly, for collected fractions at SUBATECH, the activity corresponding to the oxalate fraction is 0.03 Bq/mL (or 1.8×10^{-4} ng/mL) in ^{14}C, and 0.07 mg/L of ^{12}C, thus the ratio

$^{14}C/^{12}C$ is 2.5×10^{-6}, which is also 6 orders of magnitude higher than the acceptable ratio. Therefore, dilution with carbon-12 is necessary to increase the ratio by diluting the solution with a solution of NaOH. A test sample to validate AMS measurement will be performed by CEA/LASE at LMC14 laboratory in November 2016 with a blank solution of NaOH with 10 mg/L of ^{12}C and a synthetic solution of ^{14}C 200×10^{-6} Bq with 10 mg/L of ^{12}C in NaOH solution. The objective of the blank NaOH solution is to estimate the background level of ^{14}C.

2 / The sample should be a solution, and only the inorganic fraction of dissolved carbon could be analysed at LMC14 laboratory. The reason is the treatment process which can only extract the inorganic form of ^{14}C by acidification of the solution is available. Therefore another step of the analytical strategy needs to be added for SUBATECH to find a suitable method to oxidize the organic fraction of ^{14}C dissolved in the collected fractions into organic form and trapped in solution which could be treated thereafter by acidification at LMC14 laboratory. SUBATECH is now looking for a method.

3 / The decontamination strategy developed by SUBATECH allows the measurement of samples by AMS at LMC14 laboratory. Gamma measurements on the collected fractions will be also provided for verification.

Figure 9 presents the detailed steps of the analytical strategy developed by SUBATECH and the prospective of work for solution sample analyses by AMS.

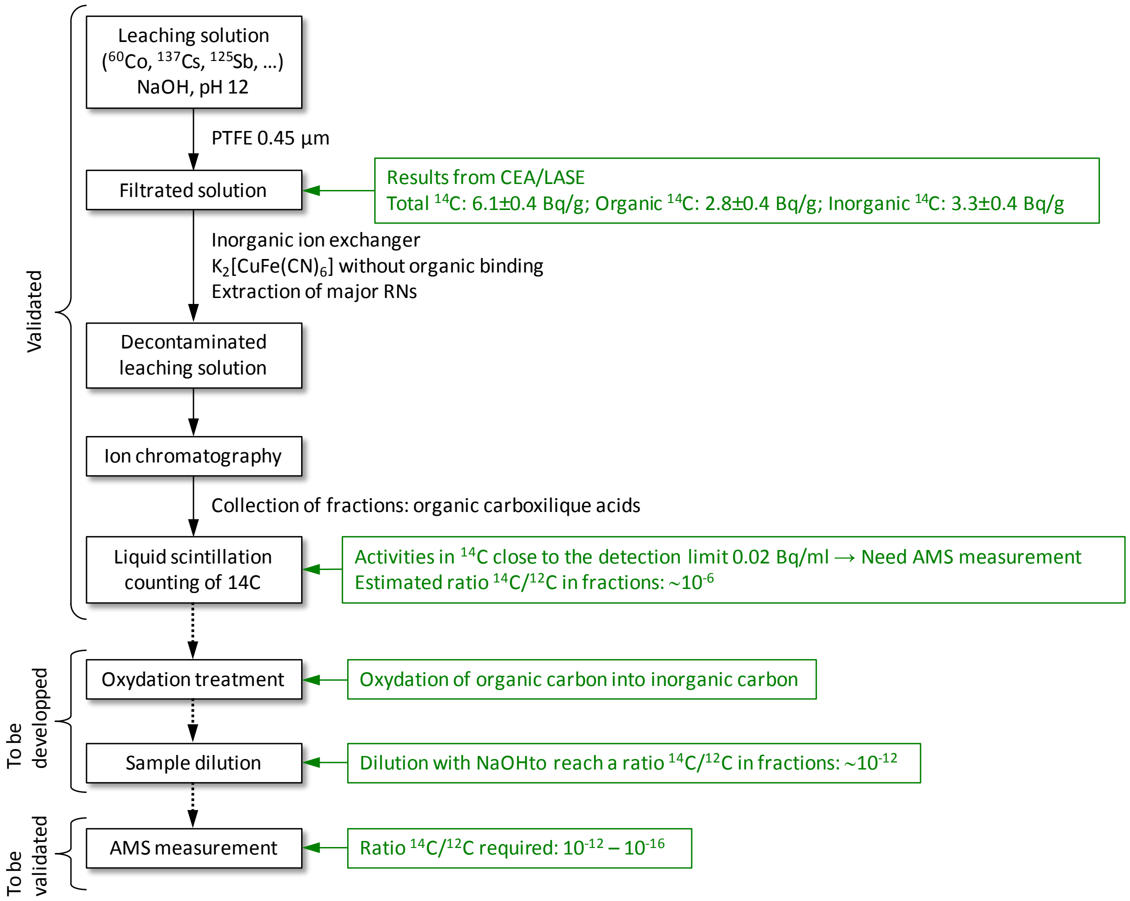


Figure 9: Flowchart of the analytical strategy and the reasons conducting to analyse the organic carboxylic acids collected by AMS

6 Analyses of ^{14}C in gaseous phase by RWMC

RWMC contributes to the determination of C-14 inventory and its partition in gaseous and liquid phase by two methods: (1) recovery of C-14 after digestion of pretreated irradiated Zircaloy-2 claddings in BWR in HF/HNO_3 to obtain the initial inventory of C-14; and (2) recovery of C-14 during leaching experiments of irradiated Zircaloy-2 claddings in BWR in NaOH pH 12.5 to determine the inorganic/organic partition of C-14 in liquid phase and the fraction of C-14 in liquid/gas phases. The analytical procedures have been described previously in [Herm et al., 2014; Takahashi et al., 2014; Yamashita et al., 2014].

6.1 *Inventory measurement of pre-treated Zircaloy-2 specimen by digestion (method 1)*

Figure 10 present the flowchart of the analytical procedure using a Zircaloy-2 specimen, the outline of an inventory measuring apparatus is shown in Figure 11. The digestion process by a mixed acid of nitric acid and fluoric acid generates two types of samples: gas and liquid samples. The gas emitted at the time of the sample digestion was drawn in the recovery line which consists of an iodine trap, a cold trap, and an alkaline trap, and collected C-14. The liquor of digestion was recovered and gamma nuclides activities were measured by the germanium semiconductor detector. Carrier and oxidizer and catalyst were supplied to the remaining solutions, wet oxidation of the remains organic matter was carried out, and C-14 was collected.

6.2 *Inventory measurement of leached Zircaloy-2 specimen (method 2)*

Figure 12 shows a flowchart of the analysis procedure performed in the leaching test, Figure 13 presents the outline of apparatus for gaseous total C-14 analysis, and Figure 14 shows the hulls conditioning in glass vial.

Total C-14 analysis and inorganic/organic C-14 analysis were conducted using part of the immersion solution, and the amount of C-14 contained in the liquid phase and the ratio of organic and inorganic forms were measured. Finally, the presence of C-14 remaining in the inner glass container was checked by conducting combustion analysis of the inner container at 900 °C.

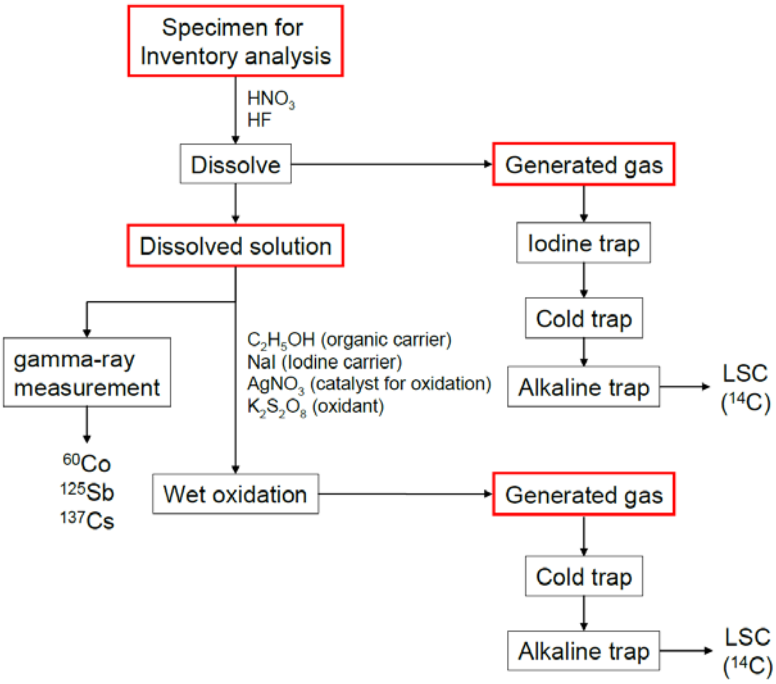


Figure 10: C-14 inventory analysis flow applied of Zircaloy-2 specimens by digestion (method 1)

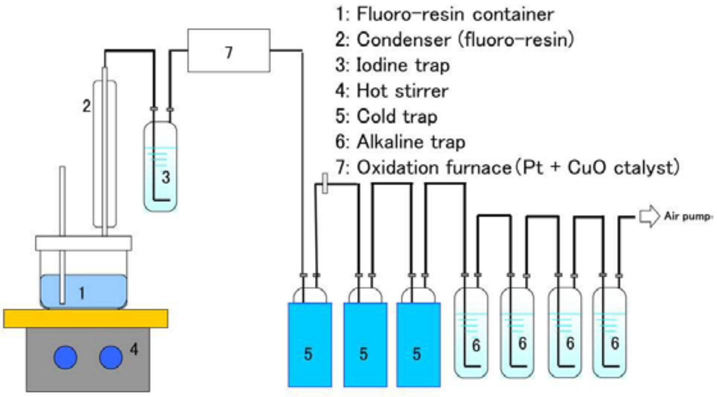


Figure 11: Outline of inventory measuring apparatus for quantification of C-14 of Zircaloy-2 specimens

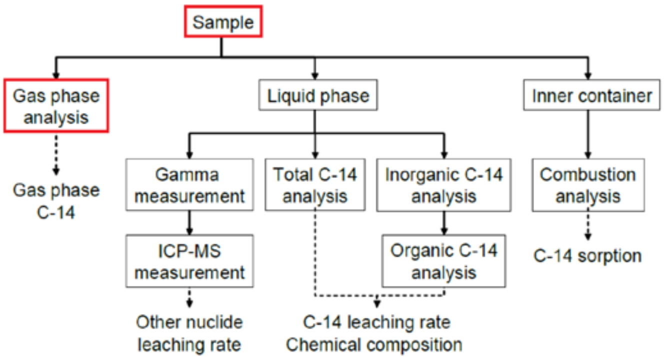


Figure 12: Flowchart of analysis procedure for leaching test (method 2)

6.3 *C-14 analyses in gas phase*

6.3.1 Analysis of total C-14 in gas samples

Figure 13 shows the procedure of gaseous total C-14 analysis. The glove bag was filled up with air containing 0.25vol% of CO_2 before-hand. Outer and inner containers (Figure 14) were opened inside the glove bag, and C-14 contained in the gaseous phase released from the inner and outer containers was then collected in the alkali traps (1.0 mol dm^{-3} NaOH solution) after passing through an oxidization furnace. C-14 collected in the alkaline traps was then liberated to the gaseous phase by the addition of concentrated sulfuric acid, recollected in Carbosorb®, and measured using a liquid scintillation counter (LSC). From cold and tracer test results, the C-14 recovery rate of this method was about 87.2%.

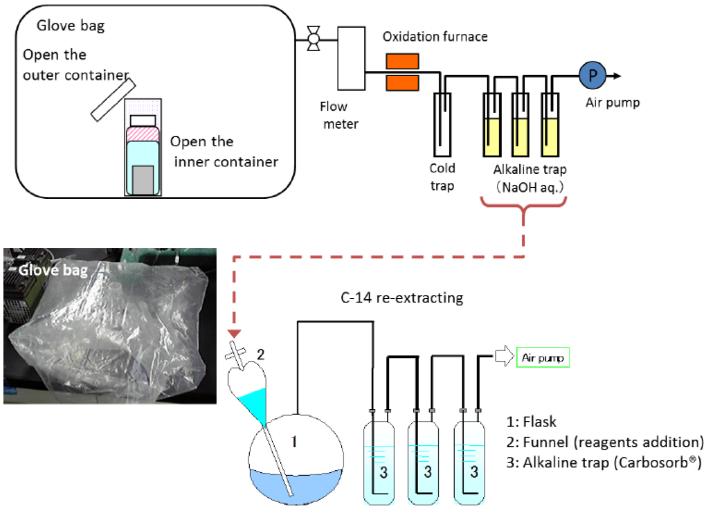


Figure 13: Outline of apparatus for gaseous total C-14 analysis

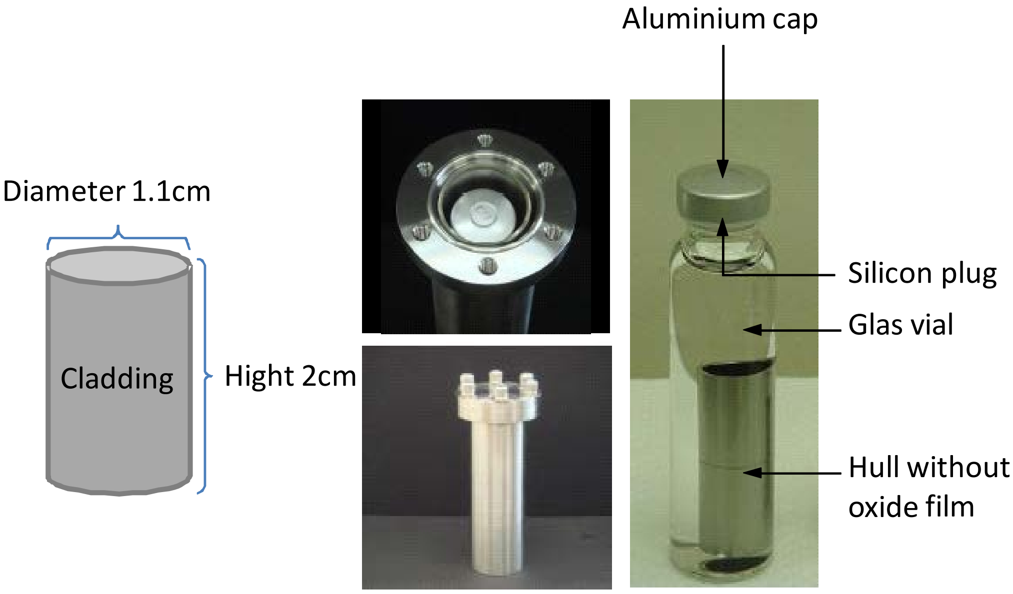


Figure 14: Sample conditioning in glass vial

6.3.2 Trial for analysis of organic/inorganic C-14 in gas samples

Some cold tests were carried out using equipment as shown in Figure 15 for the purpose of separation of CO_2 and other carbon compounds such as CO, CH_4 and other hydrocarbons included in the gaseous phase. As a first step, only CO_2 and CH_4 were used for the cold test investigating whether CO_2 could be separated from other carbon compounds. Collection of CO_2 is carried out by the alkaline trap I installed before the oxidation furnace and collection of CH_4 is carried out by the alkaline trap II installed after the oxidation furnace. The results showed the possibility of separation of CO_2 from other carbon compounds. However this separation method has not been applied to a hot test because the C-14 quantity partitioned into the gaseous phase seemed to be smaller than the minimum-limit-of-detection of this method (0.05 Bq).

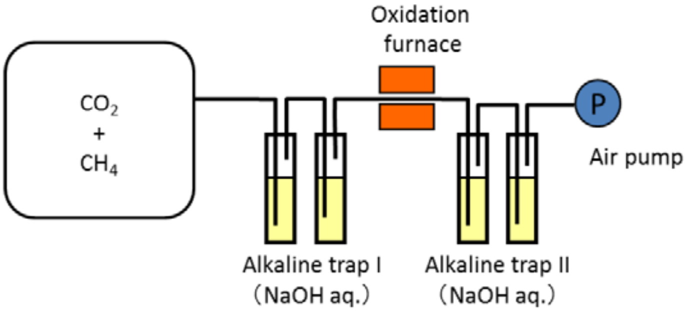


Figure 15: Outline of the equipment for separating CO_2 and CH_4

6.3.3 Results of C-14 analysis

The quantification of total inventory in C-14 in the hulls and of C-14 released in gas phase, and the partition of inorganic/organic C-14 in liquid phase were determined for seven Zircaloy-2 samples, six of which were pretreated and without the oxide layer and one was with the oxide layer. Table 8 summarizes the experimental conditions.

Table 8: Experimental leaching conditions of Zircaloy-2 hulls in NaOH solution at pH 12.5

Sample No	Fuel cladding type	Leaching time, years	m/V (g/mL)
1	Zry2 hulls, without oxide	0.5	0.29
2	Zry2 hulls, without oxide	0.75	0.29
3	Zry2 hulls, without oxide	1	0.29
4	Zry2 hulls, without oxide	2	0.29
5	Zry2 hulls, without oxide	3	0.29
6	Zry2 hulls, without oxide	5.5	0.39
7	Zry2 hulls, with external oxide	6.5	0.20

Figure 16 shows the distribution of C-14 in liquid and gas phases obtained for the leaching experiments. The results for the samples without the oxide layer show a release of C-14 to gas and solution phases with a significant fraction released as gas (53-55%) during the first year. As the experiments continue, the fraction of C-14 released as gas decreases relative to the release to solution with a maximum release fraction to gas of up to 5-6% after 3-5.5 years. For sample with external oxide, which has the longest duration of leaching, the release fraction of C-14 in gas phase is 16%. In solution phase, C-14 is dissolved under inorganic and organic forms with an increasing fraction of organic form with time: the ratio inorganic/organic passes from 2/3 to 1/3.

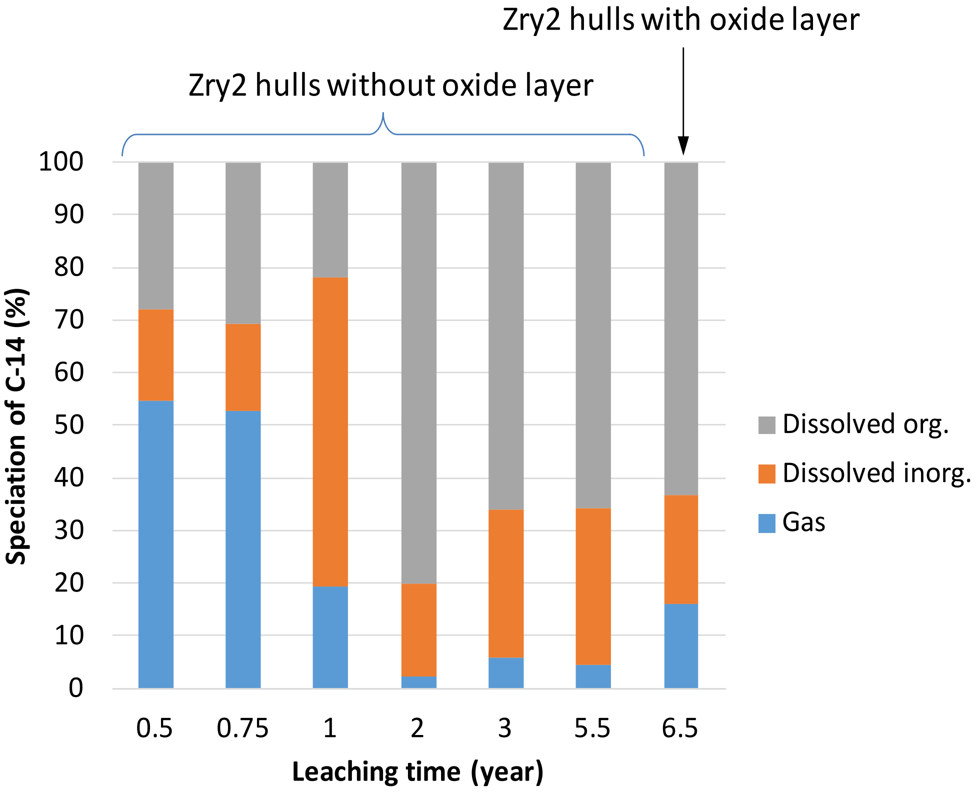


Figure 16: Speciation of C-14 in gas and liquid phases

Figure 17 shows the leaching ratio of C-14 in liquid and gas phases compared to the total inventory of C-14 in the hull samples after digestion. The leaching ratio is defined as: Ratio = Leached C-14 / Initial inventory. One can see the leached C-14 in Figure 17 in which the leaching ratios were returned to the leached C-14 before conversion (Note, the C-14 in gas for

1 and 2 year are the detection limit values). Except 1 year, the total leached C-14 increases with time. The difference between the leaching ratio and leached C-14 is due to the difference of the initial inventory. Because a sample of 5.5 years (sample #6) has a weight of 7.7 gram (inventory 200000Bq), but others are 5.8 gram or around (inventory 100000Bq). These have the same tube shape but different thickness due to polishing strength. The results show also a non-negligible contribution of the oxide layer (sample #7) for the total inventory of C-14. The majority of C-14 stems from the oxide layer formed during the operational use of claddings in reactor, here BWR type. In absence of oxide layer, the leaching ratio increases with leaching time indicating the possible diffusion of C-14 from bulk (hull sample) to solution. A recent work performed by [Xu, 2015] reveals by Kinetic Monte Carlo simulation that C-14 formed in Zr-metal or ZrO_2-monoclinic structure remains stable in the interstitial sites within the solid, with an extreme low diffusion coefficient of C in Zr with 10^{-34} cm²/s and in ZrO_2 with 10^{-22} cm²/s. From the experimental results obtained here and compared with the theoretical simulation, diffusion through grain boundaries may be a diffusion mechanism of C-14 towards the solution and gas phases.

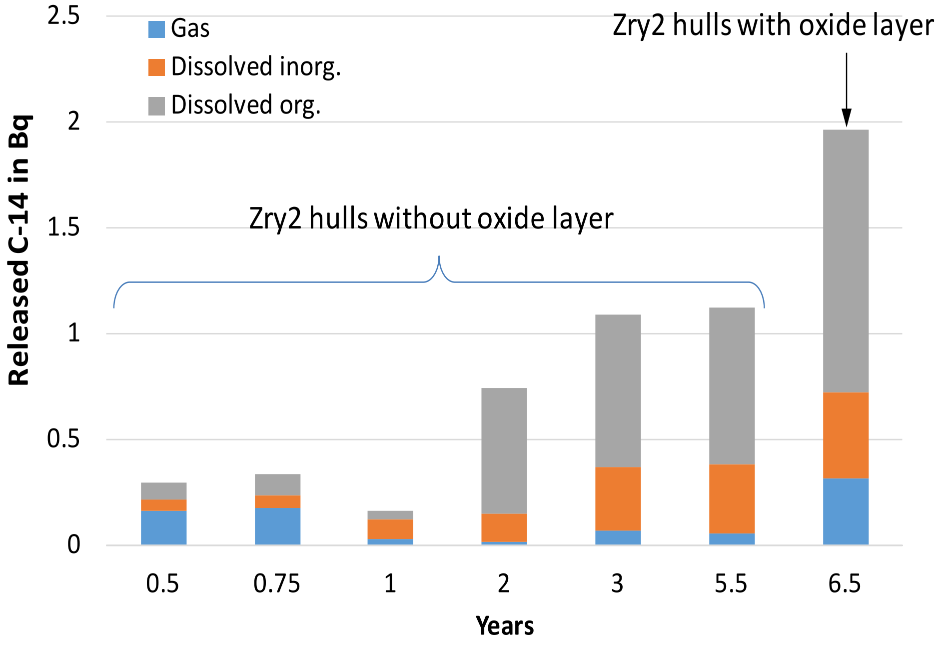


Figure 17: Leaching ratio of C-14 as function of leaching time

7 General conclusion

This reports concerns the analytical strategy developed by SUBATECH/ARMINES and RWMC on the measurement of C-14 in liquid and gaseous phases, respectively.

SUBATECH/ARMINES developed and optimized a method of decontamination (based on inorganic ion exchanger) in aqueous media to analyse and separate organic carbon-14. Fractions of organic C-14 are collected by ion chromatography and measured by liquid scintillation counting. This method is reliable and applied on leaching solution for irradiated zircaloy cladding in collaboration with CEA. However, due to the extreme low quantity of organic C-14 in collected fractions (below the detection limit of LSC), additional development is needed to measure and quantify, for example with accelerator mass spectrometry AMS.

RWMC analysed the organic and inorganic carbon fractions in the Zircaloy-2 solid samples by digestion method, and in the leaching solutions based on their analytical procedure described in the deliverable D3.3. The main results show (1) an important release fraction of C-14 in gas phase during the first year of leaching experiments which decreases with time, and (2) an increasing release fraction of C-14 in liquid phase with time with a ratio inorganic/organic C-14 passing from 2/3 (< 1 year) to 1/3 (at 5.5 years).

8 Acknowledgments

The authors acknowledge C. Mérignac for ion chromatography analyses, SMART laboratory (Le Service de Mesure et d'Analyse de la Radioactivité et des éléments Traces) for the radiochemical analyses by gamma spectrometry and by alpha/beta counting, J. Molina (Areva STMI), and METI for supporting the RWMC work.

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

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