CArbon-14 Source Term
CAST

Description of the analytical procedure for gaseous and dissolved C-14 species quantification (D3.3)

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CAST – Project Overview

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

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

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

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

CAST		
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Document title
Description of the analytical procedure for gaseous and dissolved C-14 species quantification

Executive Summary

The present report describes sample preparations and analytical procedures for quantification of C-14 species of irradiated Zircaloy, which have been developed and will be applied by KIT-INE, RWMC and JRC-ITU.

KIT-INE will analyse the C-14 inventory and speciation of irradiated Zircaloy-4 cladding, sampled from a PWR fuel rod segment, whereas the C-14 inventory and speciation of irradiated Zircaloy-2 cladding from a BWR fuel rod will be analysed by RWMC. Both types of cladding samples are used in dissolution / leaching experiments conducted in the research centres. Gaseous and liquid aliquots of the dissolution / leaching experiments are sampled and treated in specifically designed set-ups for C-14 extraction. JRC-ITU will provide clean, non-contaminated gas and liquid samples from heavily-contaminated hot cells and perform valid measurements of C-14 contents at near-background levels. Detailed descriptions of the procedures and conditions for C-14 extraction, separation of various C-14 fractions and consecutive radiochemical analysis methods are presented in this report.

Contents

1 Introduction

Due to its half-life of about 5730 a and assumed mobility, C-14 is one of the crucial radionuclides with respect to estimated doses arising from release to the environment in a canister failure scenario for spent nuclear fuel. In long-term safety assessments of spent nuclear fuel disposal facilities following scenario is taken into consideration: upon contact with water, C-14 bearing species are released from the fuel rods into aqueous solution and gas phase as inorganic or organic compounds. C-14 species will also be released from Zircaloy in packaged intermediate-level wastes from the reprocessing of spent nuclear fuel. Solubility, sorption behaviour and distribution between solution and gas of C-14 depends strongly on its chemical form.

Only very few previous studies dealing with C-14 quantification and/or speciation from irradiated materials from nuclear reactors are available. Neeb et al. (1980) and Bleier et al. (1984) determined the inventory and distribution of C-14 and H-3 in boiling water reactor (BWR) and pressurized water reactor (PWR) irradiated fuel rod specimen. Bleier et al. (1988) investigated the chemical status of C-14 after leaching of cladding material from spent PWR and BWR fuel rods in a salt solution. Yamaguchi et al. (1999) determined the inventory and chemical form of C-14 in irradiated Zircaloy hull waste from spent nuclear fuel reprocessing. Zhang (1993) performed leaching experiments with spent pebbles of a pebble-bed reactor and Stroes-Gascoyne et al. (1994) determined the inventory of C-14 in CANDU fuel released from gap and grain boundaries to aqueous solutions. Very recently a study published by Schumann et al. (2014) determining the C-14 content in activated steel components from a neutron spallation source and a nuclear power plant (NPP). There are several studies on C-14 quantification and/or speciation in spent ion exchange resins or NPP process water, an overview is given in Magnusson (2007).

KIT-INE, RWMC and JRC-ITU developed methods that allow the separation and quantification of inorganic and organic/CO C-14 species in gaseous and aqueous samples taken from dissolution experiments with irradiated claddings of a PWR fuel rod segment and a BWR fuel rod, respectively. The sample preparations and analytical procedures are described in the following chapters.

2 Sample preparations and analytical procedures for quantification of C-14 species of irradiated PWR Zry-4 (activities by KIT-INE)

2.1 Preparation and pretreatment of Zry-4 specimens

At KIT-INE, the C-14 inventory and speciation of irradiated Zircaloy-4 (Zry-4) is analysed. The selected Zry-4 cladding was sampled from the fuel rod segment SBS1108–N0204, which was irradiated at the PWR Gösgen in Switzerland. Relevant characteristic parameters of the Zry-4 specimen are given in Table 1. After a cooling time of about 23 years after discharge from the reactor, the fuel rod segment was transferred to JRC-ITU in 2012 to perform the puncturing tests and non-destructive testing (NDT) (Papaioannou et al. (2012), Wegen et al. (2012)). The plenum part of the fuel rod segment including the stainless steel spring was cut and both, the Zry-4 cladding and the spring were transferred to KIT-INE (Figure 1). Dimensions of the cladding are given in Figure 2. As this part only comprised the plenum spring, almost no contamination with UO_2 fuel is expected.

Table 1 Features of Zry-4 specimen studied by KIT-INE

Fuel Type	Reactor Type	Material	Nitrogen conc. (nominal)	Burnup (GWd/t)	Cycles	Outer oxide film thickness (average, µm)
UO_2	PWR	Zry-4	65 ppm (Neeb, 1997)	50.4	4	<15

Figure 1Irradiated Zry-4 plenum specimen used for the dissolution experiments

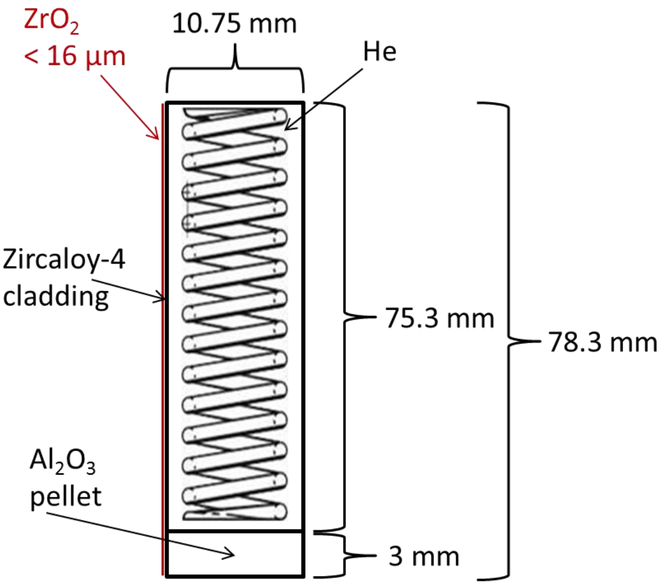

Figure 2Scheme of the Zry-4 cladding with the stainless steel plenum spring inside

Sample preparation is conducted in the KIT-INE shielded box line and a preparation scheme is shown in Figure 3. Samples are dry cut (~1 cm samples) under inert gas atmosphere using a low speed saw shown in Figure 4 (Isomet 11-1180, Buehler Ltd.). After the cutting a wash cycle will be performed prior to the dissolution experiments to remove fines/dust which is potentially adhering to the sample. This wash cycle will be performed using ultrapure water (Milli-Q, 18.2 Ω, Millipore, Merck) and an ultrasonic bath. Finally a surface analysis is carried out using an optical microscope (DigiMicro 2.0, Drahtlose Nachrichtentechnik, dnt) available inside the shielded box to determine the geometric surface area of the sample.

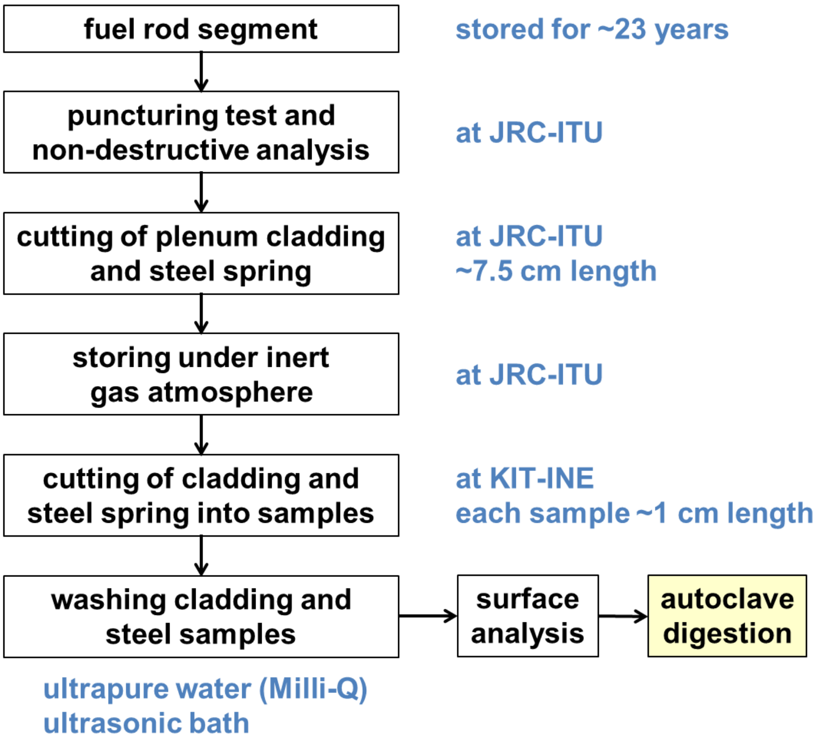

Figure 3Sample preparation scheme of Zry-4 specimens

Figure 4Low speed saw for cutting of Zry-4 specimens under Ar atmosphere in the shielded box-line of KIT-INE.

2.2 Experimental procedures for quantification of C-14 of Zry-4 specimens

2.2.1 Overview of the experimental program for quantification of gaseous and dissolved C-14 species of Zry-4 specimens

For determining the inventory/chemical form of C-14, dissolution experiments with the Zry-4 cladding are going to be performed in autoclaves under reducing conditions at ambient temperature in the KIT-INE shielded box line using a dilute H_2SO_4/HF mixture. An overview on the experimental program including extraction and analytical techniques is outlined in Figure 5.

A method that allows the separation and quantification of inorganic and organic C-14 species in gaseous and aqueous samples taken from the dissolution experiments is currently set-up in a specifically manufactured glove box. This C-14 separation and quantification method is based on a method developed for determining C-14 in spent ion exchange resins and process water from nuclear reactors Magnusson and Stenstroem (2005), Magnusson (2007) and Magnusson et al. (2008). The analytical C-14 separation procedure, shown in Figure 6, involves several steps (i.e. acid stripping and wet oxidation) during which the inorganic and organic carbon fractions are extracted and converted into CO_2 which is then absorbed in washing bottles containing 2 M NaOH. A catalytic furnace between the two sets of washing bottles (first set with bottles #2 and #3, second set with bottles #4 and #5, Figure 7) ensures oxidation of reduced compounds like CO or CH_4 methane.

The method does not distinguish between $^{14}CH_4$ and ^{14}CO. Both species are oxidised in the catalytic furnace and absorbed in the first washing bottle after the furnace. The method distinguishes between $^{14}CO_2$ released by acidification of inorganic compounds (i.e. carbonates, bicarbonates) and $^{14}CO_2$ released by wet oxidation of hydrocarbons (alcohols, carboxylic acids…). For gaseous samples the method also distinguishes between $^{14}CO_2$ released from inorganic compounds during the digestions experiments and i.e. $^{14}CH_4$/^{14}CO which passes the "inorganic" washing bottles unaffectedly and is then oxidised in the catalytic furnace to $^{14}CO_2$ and absorbed in the first washing bottle after the furnace.

The content of C-14 (weak β^- emitter) in the NaOH solutions is finally determined by liquid scintillation counting (LSC).

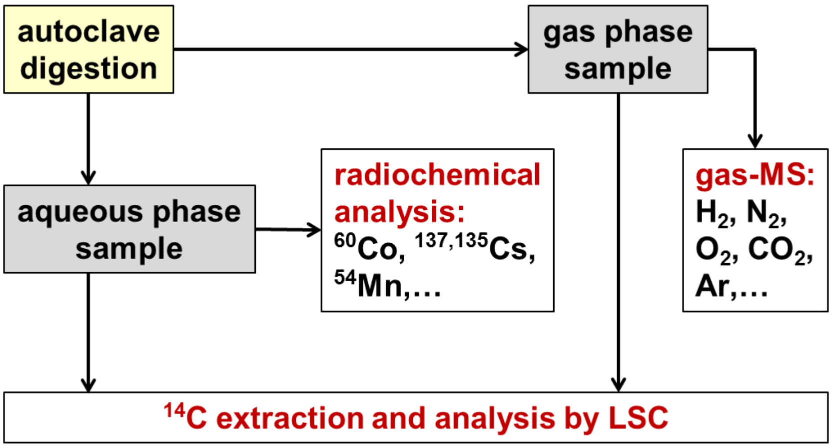

Figure 5 Scheme of the experimental procedure for quantification of C-14 species of Zry-4 specimens

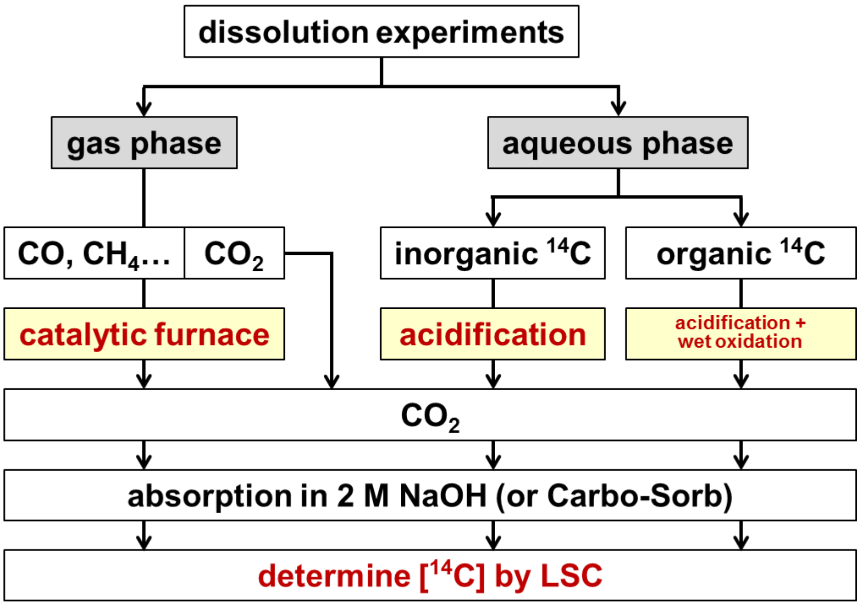

Figure 6 Scheme of C-14 extraction procedure for gaseous and dissolved aliquots of experiments with Zry-4 specimens

2.2.2 C-14 extraction and analytical methods for gaseous and dissolved aliquots of experiments with Zry-4 specimens

The experimental design outlined in Figure 7consists either of a 500 mL three-neck flask with connections (Rodaviss, Duran) for gas-inlet, 120 mL dropping funnel and cooler for aqueous samples or a gas collecting cylinder with two valves (Figure 8, SS-4CS-TW-50, Swagelok) for gaseous samples, connected to the CO_2 gas absorption system.

The CO_2 gas absorption system consists of in total five customized washing bottles equipped with a fritted glass tip of porosity 1 (see Figure 9) filled with 50 mL 2 M NaOH respectively (TitriPUR, Merck), except bottle #1, which is the H-3 trap and contains 50 mL 5% H_2SO_4 (p.a., Merck). The washing bottles #3 and #5 are used as safety bottles.

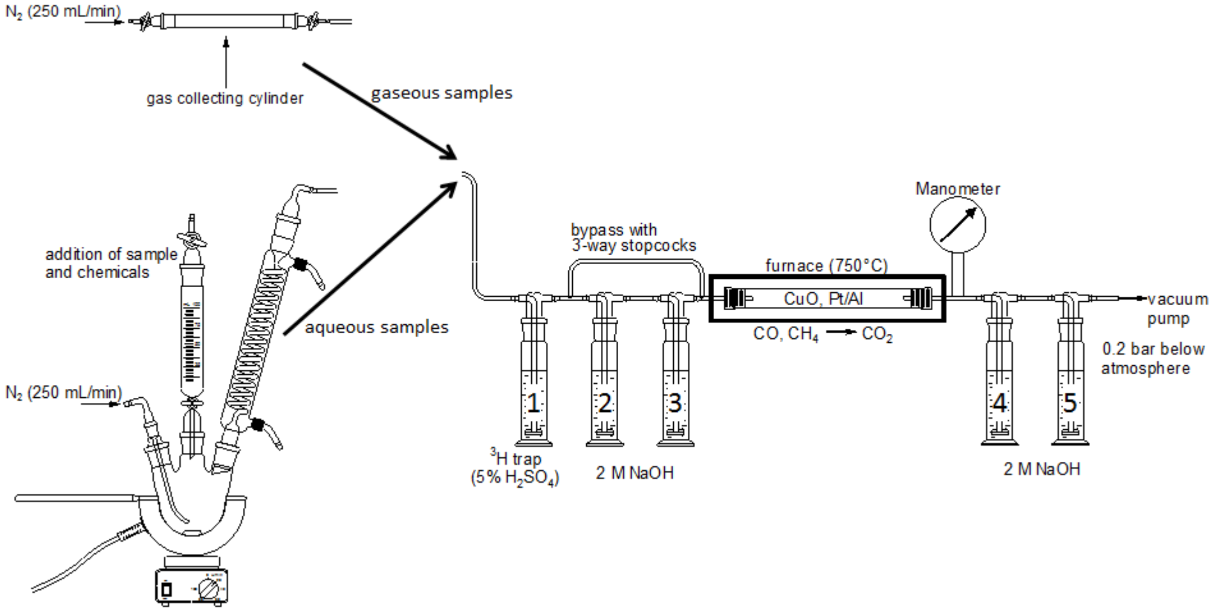

Figure 7 Experimental design for C-14 extraction of gaseous and dissolved aliquots of experiments with Zry-4 specimens

The catalytic furnace consist of a tube furnace (MTF 12/25/250, Carbolite) operated at 750°C, holding a quartz glass tube of ~50 cm length with an outer diameter (OD) of around 2.5 cm. The glass tube is filled with the catalyst mixture over the length of about 20 cm. The mixture is composed of 1 wt.% platinum on alumina pellets (3.2 mm, Sigma-Aldrich) and CuO/Cu$_2$O wire (0.65 mm×6 mm, p.a., Merck). The mixing ratio is about 30 wt.% Pt on Al and 70 wt.% copper oxide wire. The mixture is held in place inside the quartz glass tube by quartz glass wool.

The system is interconnected by silicon tubing (8.5 mm ID, 11.5 mm OD) with two PP/PTFE three-way stopcocks (Nalgene) placed before and after washing bottles #2 and #3. Nitrogen (99.99%, Alphagaz 2, Air Liquide), supplied by a gas bottle connected through a buffer volume, is used as carrier gas. Flow rate (~250 mL/min) through the system is controlled by a flow meter (Model P, Aalborg Instruments & Controls). In order to prevent the loss of any gases in the case of a leakage, the system is operated under subatmospheric pressure (0.2 bar below atmosphere) by means of a diaphragm vacuum pump with fine-adjustment valve and manometer (max. 16 L/min, N816.3 KT.18, KNF).

Figure 8 Two valves gas collecting cylinder for gaseous aliquots of experiments with Zry-4 specimens

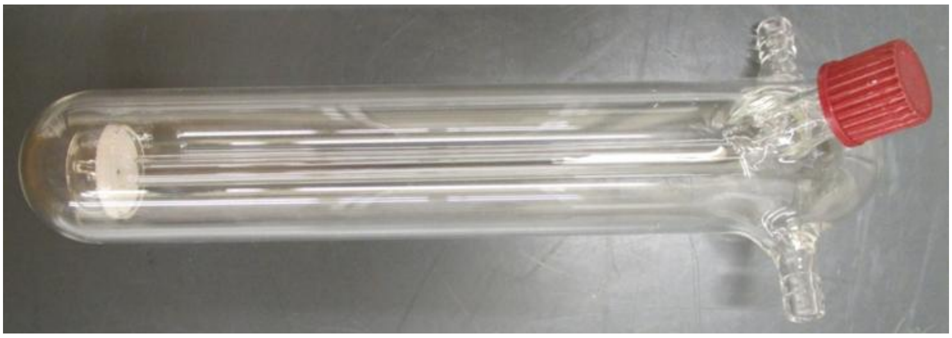

Figure 9 Customized washing bottle equipped with a fritted glass tip of porosity 1

Aqueous sample treatment procedure: Aqueous aliquots, which are sampled from the dissolution experiments, are introduced in the dropping funnel (100 mL) and the system is evacuated to 0.2 bar below atmosphere. Subsequently the nitrogen carrier gas flow rate is set to 250 mL/min. The sample solution is added slowly to the three-neck flask containing a volume of 50 mL 8 M H_2SO_4. The solution is purged and stirred for two hours, during which the inorganic fraction is released as CO_2 and absorbed in the washing bottle #2 (Figure 7). Reduced carbon compounds like CO, released during the acid stripping are oxidized in the catalytic furnace and absorbed in washing bottle #4. Prior to the wet oxidation step, washing bottles #2 and #3 are disconnected from the system using the three-way stopcocks. The remaining carbon compounds in the sample solution (organic fraction) is oxidized by a strong oxidant ($K_2S_2O_8$, p.a., Merck), catalyst ($AgNO_3$, VWR Chemicals), heat and magnetic stirring. Consecutively 50 mL 5% potassium peroxodisulfate solution and 5 mL 4% $AgNO_3$ solution are added immediately to the sample container through the dropping funnel under simultaneous heating (~95°C). After one hour the same amounts of potassium peroxodisulfate and silver nitrate are added to the flask and the mixture is purged, heated and stirred for another hour. After in total four hours samples are collected from all washing bottles (Figure 7) for LSC measurements (details see below).

Gaseous sample treatment procedure: The gas collecting cylinder with two valves is connected to the first washing bottle of the CO_2 gas absorption system and the nitrogen gas bottle as shown in Figure 7. The pressure in the system is lowered to about 0.2 bar below atmosphere and the N_2 gas flow rate is set to 250 mL/min. The content of the gas collecting cylinder is flushed into the CO_2 gas absorption system, where carbon dioxide released from inorganic carbon compounds during the dissolution experiments is absorbed in washing bottle #2. Reduced carbon compounds like CO or CH_4 will be oxidized in the catalytic furnace to CO_2 and absorbed in washing bottle #4 after passing through bottles #2 and #3 unaffectedly. After in total one hour samples are collected from the washing bottles for LSC measurements as described below.

Liquid scintillation counting: For liquid scintillation counting an ultra-low level counter (Quantulus 1220, Wallac Oy, PerkinElmer) is used. Three millilitre samples are collected from the washing bottles containing 2 M NaOH and mixed with 18 mL scintillation cocktail (Hionic Fluor, PerkinElmer) for LSC measurements (30 min per sample after allowing to stand for 24 hours). Up to 4 mL sample + 17 mL cocktail is possible. Quench correction curves, shown in Figure 10 were obtained by the addition of nitromethane (0–65 µL). In order to get the maximum sensitivity to C-14 and the vials (20 mL, PE, Zinsser Analytic) used for measuring the best energy window setting was determined. The average counting efficiency is ~92%.

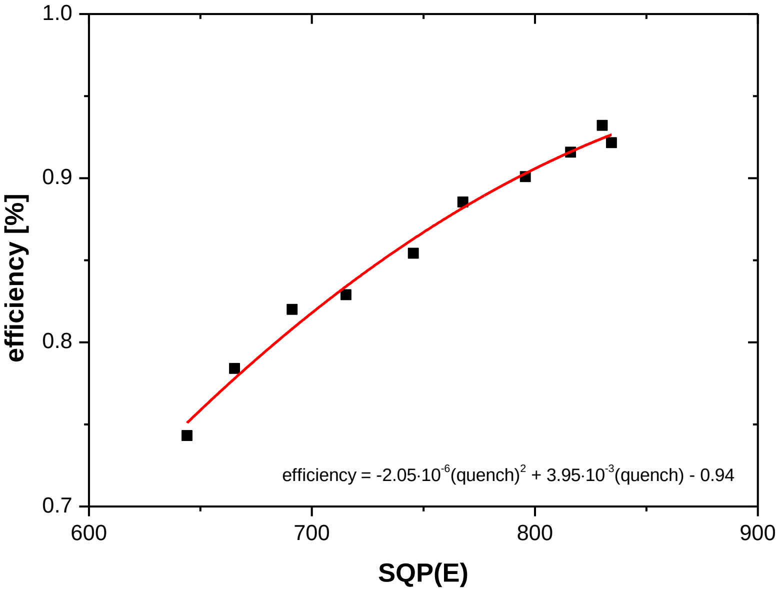

Figure 10 Quench correction curve obtained for 3 mL 2 M NaOH + 18 mL Hionic Fluor

Gas sampling and gas mass spectrometry: For collecting gas samples an evacuated gas collecting cylinder with a volume of 50 mL is connected at the back of the shielded box (left picture, Figure 11). Via tubing inside the box the cylinder is connected to the autoclave (right picture, Figure 11). Prior to the sampling the tubing is evacuated and flushed with argon 5 times à five minutes each time. After evacuating the tubing for a last time, the valves of the autoclave and the gas collecting cylinder are opened and the gas phase is sampled.

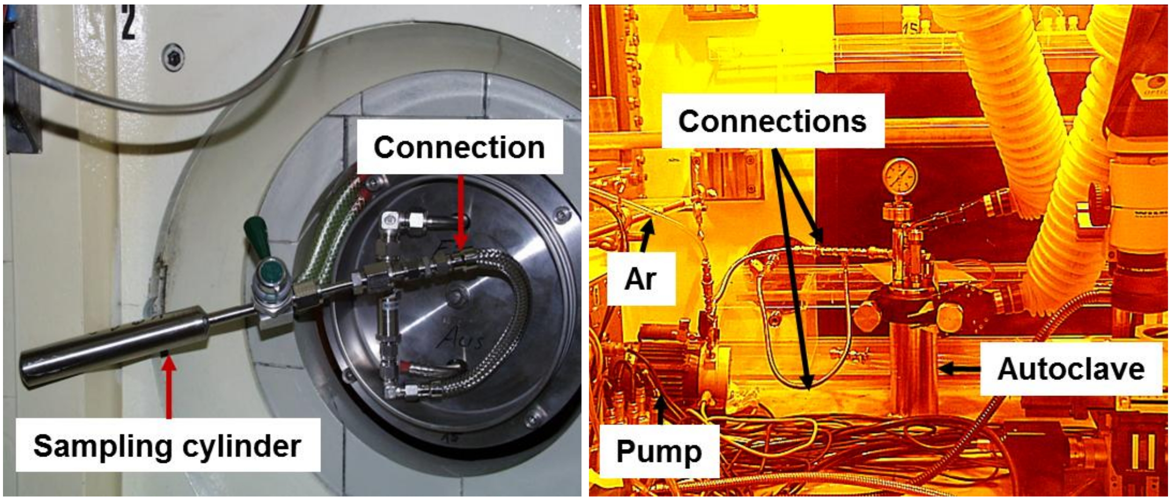

Figure 11Gas sampling at the KIT-INE shielded box line

The gas samples are analysed for H_2, N_2, O_2, CO_2, Ar, CH_4, etc. by means of a quadrupole gas mass spectrometer (gas-MS, GAM400, InProcess Instruments). The gas-MS is equipped with a secondary electron multiplier (SEM) detector and a batch inlet system, optimized for low gas consumption (see Figure 12). Within the gas dosage and inlet system, the total gas pressure was monitored at four successive positions. It applied three different expansion volumes to charge relatively low gas contents in the desired pressure range. Ten scans of each gas sample are measured, using the SEM detector and the mean value is taken. Calibration of the gas-MS analysis is performed in the same pressure range as the respective range for analysis of the sample aliquots.

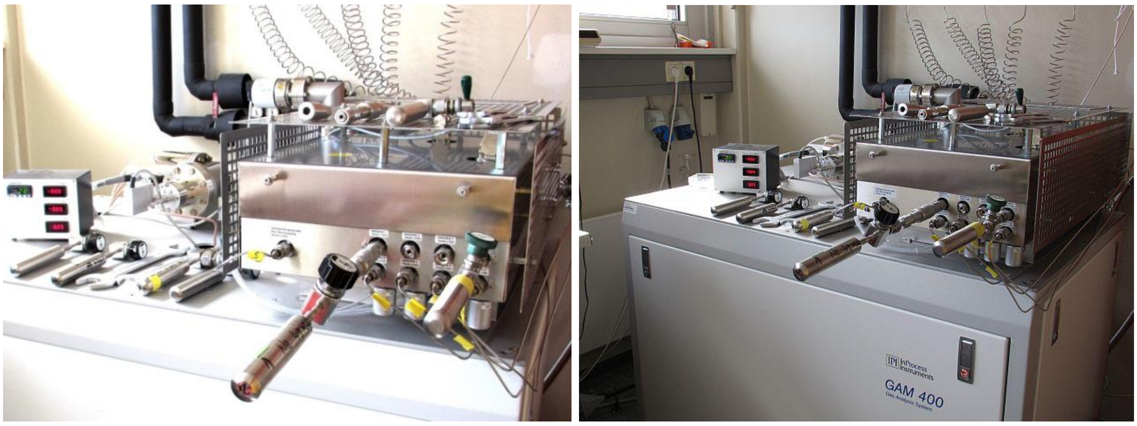

Figure 12 Image of GAM400 quadrupole gas-MS and the batch inlet system

2.2.3 Test of experimental set-up and calibration of analytical methods for quantification of gaseous and dissolved C-14 species of Zry-4 specimens

Recovery tests were performed with C-14 labelled sodium carbonate (Na_2CO_3, 200 kBq, Eckert & Ziegler) and sodium acetate (CH_3CO_2Na, 1.85 MBq, PerkinElmer) reference material with 100–1000 Bq for the inorganic and organic reference material respectively. Also different ratios of activity between sodium carbonate and acetate were investigated. The recovery tests indicate that the chemical yield of the separation method is > 88% for both the inorganic as well as the organic ^{14}C fraction (Table 2). The efficiency of the catalytic furnace was tested using a mixture of 10% methane and 90% argon (Air Liquide) with a yield of ~99% for the conversion of CH_4 to CO_2.

Table 2 Results of recovery tests performed with C-14 labelled Na–carbonate and Na–acetate

^{14}C added		**recovery of [Bq]**		**recovery of [%]**	
form	activity [Bq]	$^{14}C_{inorg.}$	$^{14}C_{org.}$	$^{14}C_{inorg.}$	$^{14}C_{org.}$
Na_2CO_3	932.10	801.8	–	86.00	–
Na_2CO_3	983.90	855.0	–	86.90	–
Na_2CO_3	987.30	964.4	–	97.70	–
CH_3CO_2Na	1142.2	–	1086.3	–	95.1
CH_3CO_2Na	1121.8	–	1036.2	–	92.4
Na_2CO_3 + CH_3CO_2Na	955.10 + 1082.4	961.2	984.70	100.6	91.0
Na_2CO_3 + CH_3CO_2Na	71.500 + 84.000	74.70	67.500	104.5	80.4
CH_3CO_2Na	882.00	–	756.00	–	85.7
Na_2CO_3 + CH_3CO_2Na	74.300 + 88.300	70.60	79.700	95.10	90.3
Na_2CO_3 + CH_3CO_2Na	74.800 + 87.800	60.01	69.400	80.20	79.1
Mean ± SD				**93.0 ± 8.8**	**87.7 ± 6.1**

3 Sample preparations and analytical procedures for quantification of C-14 species of irradiated BWR Zry-2 (activities by RWMC)

3.1 Pretreatment of Zry-2 specimens

Irradiated Zry-2 claddings from a BWR were used for the tests at RWMC. The features of the specimens are shown in Table 3. The claddings were cut to heights of 2 cm for the leaching tests. The pretreatment procedure is shown in Figure 13. First, bonding fuel elements were removed by mechanical drilling. After that, reprocessing steps were imitated and fuel dissolution processing was carried out with 4 N boiling nitric acid for 4 hours. After fuel dissolution processing, the specimens were cleaned ultrasonically with pure water. Underwater polishing with a diamond file was carried out in the order of #150 and #800 grits to remove oxide films on the inside and outside surfaces and expose the base material. A picture of specimen before polishing is shown in Figure 14.

Table 3Features of Zry-2 specimens before pretreatment

Fuel Type	Reactor Type	Materials	Nitrogen conc.	Burnup (GWd/t)	Cycles	Outer oxide film thickness (average, μm)
STEP3	BWR	Zry-2	Not opened	39.7	3	4.7

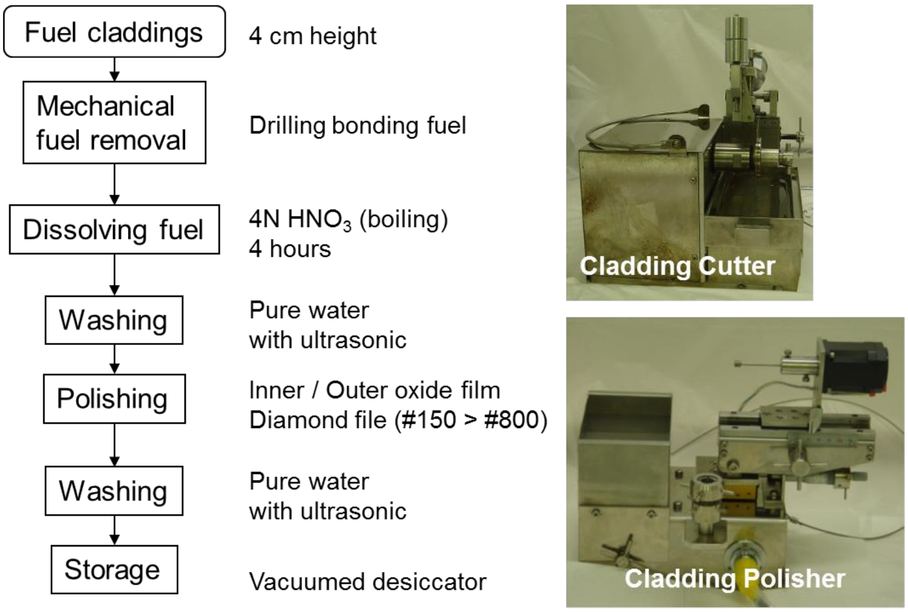

Figure 13Pretreatment for Zry-2 specimens

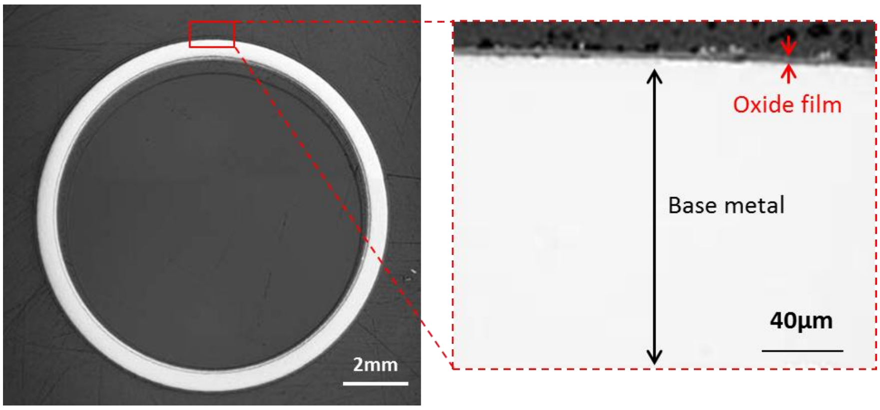

Figure 14Picture of Zry-2 specimen before polishing

3.2 Inventory measurement of pretreated Zry-2 specimen

Inventory analysis was conducted according to the flow chart given in Figure 15 using a Zry-2 specimen that was subjected to the pretreatment described above. The outline of an inventory measuring apparatus and conditions of apparatus are shown in Figure 16 and Table 4 respectively. This apparatus consists of a fluoro-resin container for dissolving process, an iodine trap, condenser with Pt and CuO catalyst, three cold traps, three or four alkaline traps and an air pump. The gas emitted in the fluoro-resin container is introduced into each trap by an air pump.

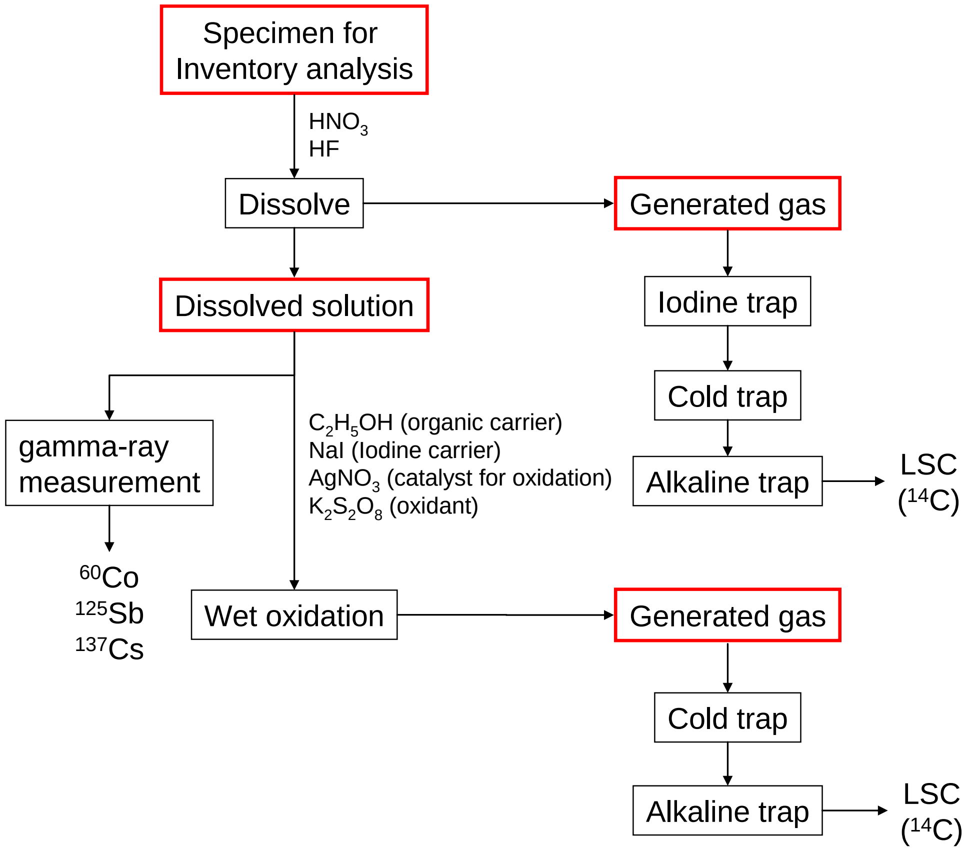

Figure 15 C-14 inventory analysis flow applied for Zry-2 specimens

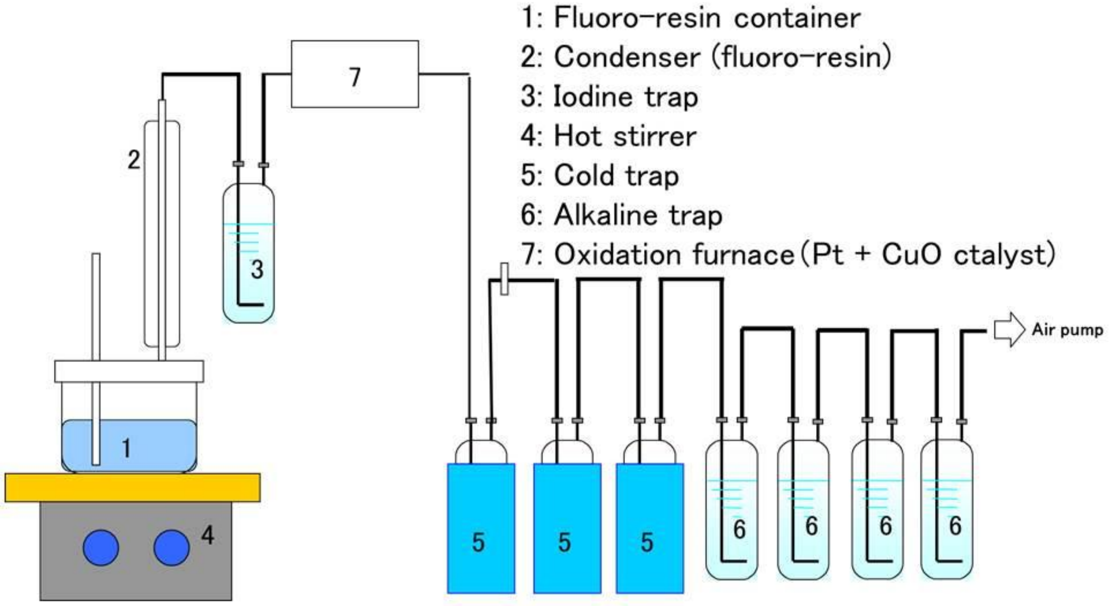

Figure 16Outline of inventory measuring apparatus for quantification of C-14 of Zry-2 specimens

Table 4 Conditions of inventory measuring apparatus for quantification of C-14 of a pretreated Zry-2 specimen

Iodine trap	0.1 mol dm^{-3} $AgNO_3$ solution
Cold trap	Cool by dry ice or ice
Alkaline trap	Carb-sorb or 1.0 mol dm^{-3} NaOH solution
Oxidation furnace	Pt + CuO catalyst 800 degree-C

3.3 Inventory measurement of Zry-2 specimen recovered from leaching experiment

Inventory analysis of a Zry-2 specimen recovered from a leaching experiment in NaOH solution (pH 12.5) was conducted according to the analysis flow chart shown in Figure 15 (Takahashi et al., 2013; Yamashita et al., 2013). Analytical conditions for this C-14 inventory analysis are given in Table 5. For inventory analysis, the apparatus shown in Figure 16 was used.

The mixed acid of nitric acid and fluoric acid was used for the dissolution of a sample. The amount of addition was adjusted checking a dissolution situation. The gas emitted at the time of the sample dissolution was drawn in the recovery line which consists of an iodine trap, a cold trap, and an alkaline trap, and collected C-14. Some solutions were isolated preparatively and gamma nuclides concentration was 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.

Table 5 Conditions of inventory measuring apparatus for quantification of C-14 of a recovered from leaching experiment

Dissolving process	Acid*		HNO_3, HF
	Temperature		80 - 100 degree-C
	Time		30 min after dissolving
Wet oxidation process	Carrier	Carbon	C_2H_5OH, 2.0 x 10^{-5} mol
		Iodine	NaI, 1.0 x 10^{-4} mol
	Oxidizer		$K_2S_2O_8$, 9.5 x 10^{-4} mol
	Catalyst		$AgNO_3$, 7.7 x 10^{-4} mol
	Temperature		60 - 80 degree-C
	Time		60 min

* continue to add until a sample dissolves

According to some cold and tracer tests, C-14 recovery rate was about 94.8%, and the decontamination factor of I-129 was estimated about 1.8x104. Almost all C-14 was released in the dissolving process, and the C-14 content in the gas from the wet oxidation was about 2%.

3.4 Analysis of release fractions of C-14 and other radionuclides

Figure 17 shows a flowchart of the analysis procedure performed in the leaching test. The method was based on the one reported by Takahashi et al. (2013). The outer and inner containers were opened inside the glove box or glove bag, and C-14 contained in the gaseous phase in the inner and outer containers were collected in the alkali traps (1.0 mol dm^{-3} NaOH solution) through an oxidization furnace. C-14 collected in the alkali traps was moved to the gaseous phase by the addition of concentrated sulfuric acid, was re-collected in Carbosorb®, and was measured by using a liquid scintillation counter (LSC). Part of the collected liquid phase was used to measure the gamma-emitting radionuclides with a germanium semiconductor detector, and another part of the liquid phase was used to measure nonradioactive elements by inductively coupled plasma mass spectroscopy. As target nonradioactive elements, Zr, which is the main constituent of the cladding, and the additional elements Sn, Ni, and Cr were chosen. 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.

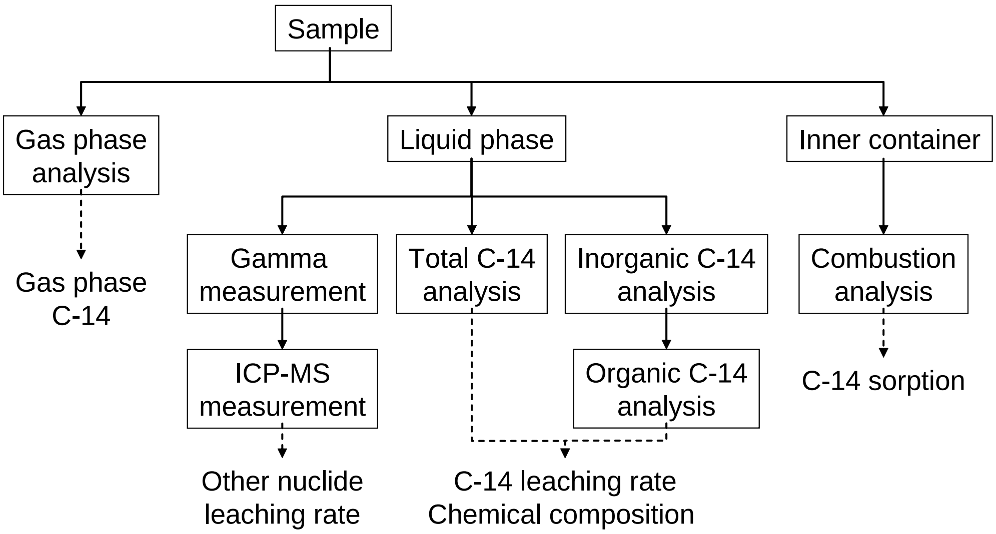

Figure 17Flowchart of analysis procedure for leaching test

The release fraction, R, of the radioactive nuclides released was calculated by

$$R = (A_G + A_L + A_C) / I$$

where A_G (Bq) is the activity of the gas phase, A_L (Bq) is the activity of the liquid phase, A_C (Bq) is the activity of nuclides remaining in the inner container, and I (Bq) is the radioactivity inventory of nuclides in Zry.

3.4.1 Leached C-14 analysis: Gaseous phase

Analysis of total C-14 in gas samples: Figure 18 shows the procedure of gaseous total C-14 analysis. The glove bag was filled up with the air which contains 0.25vol% of CO2 beforehand. Outer and inner containers were opened inside the glove bag, and C-14 contained in the gaseous phase in the inner and outer containers were collected in the alkali traps (1.0 mol dm-3 NaOH solution) through an oxidization furnace. C-14 collected in the alkaline traps was moved to the gaseous phase by the addition of concentrated sulfuric acid, was re-collected in Carbosorb®, and was measured by using a liquid scintillation counter (LSC). According to some cold and tracer tests, C-14 recovery rate of this method was about 87.2%.

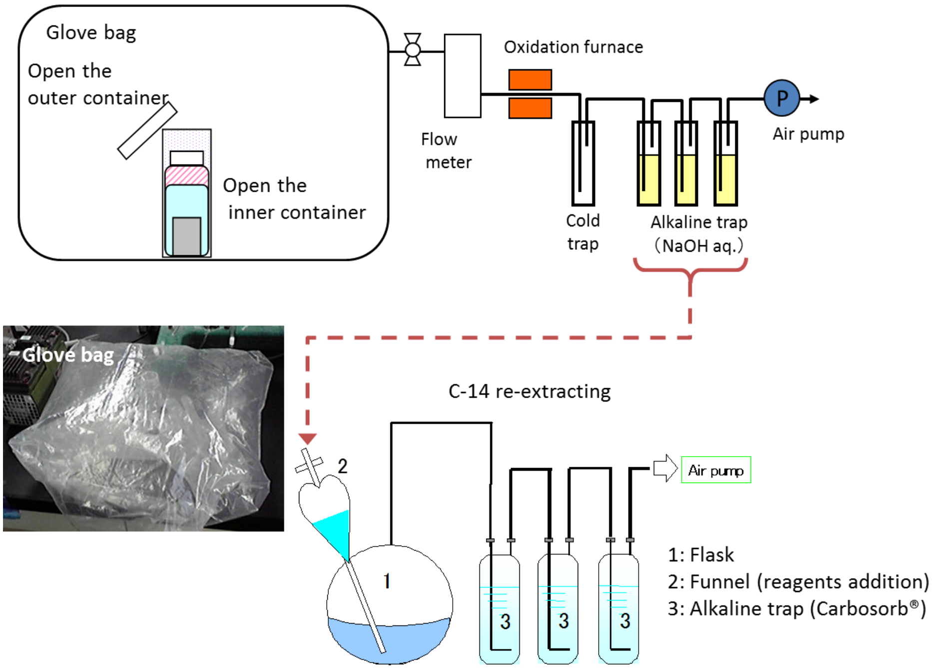

Figure 18 Outline of apparatus for gaseous total C-14 analysis

Trial for analysis of organic/inorganic C-14 in gas samples: Some cold tests were carried out using equipment as shown in Figure 19 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).

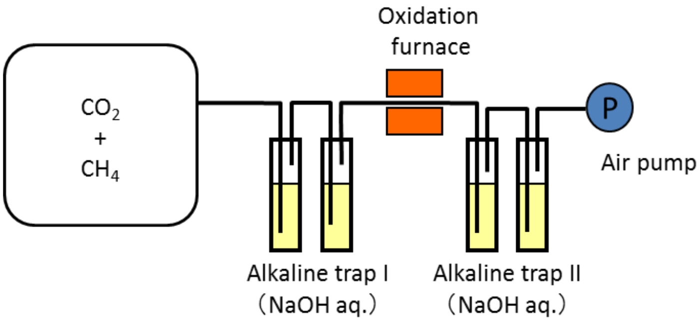

Figure 19 Outline of the equipment for separating CO2 and CH4

C-14 speciation in gas samples: Development of the analytical method of C-14 chemical species of gaseous form has not been carried out.

3.4.2 Leached C-14 analysis: Liquid phase

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.

Analysis of total C-14 in liquid samples: Total C-14 analysis of leachate was conducted by the apparatus shown in Figure 20. The condition of analysis was shown in Table 6.
Carriers were added in the reaction container. The leachate and catalyst were supplied to the reaction container. Inorganic C-14 were made to shift to the gaseous phase by adding sulfuric acid and acidifying solution, and collected by the alkaline trap. By supplying oxidizer and heating, organic C-14 were decomposed and collected by the alkaline trap. Alkaline trap was measured by LSC.

According to some cold and tracer tests, this method can recover about 100% of C-14 and the decontamination factors of Tc, I, Sb were over 4500.

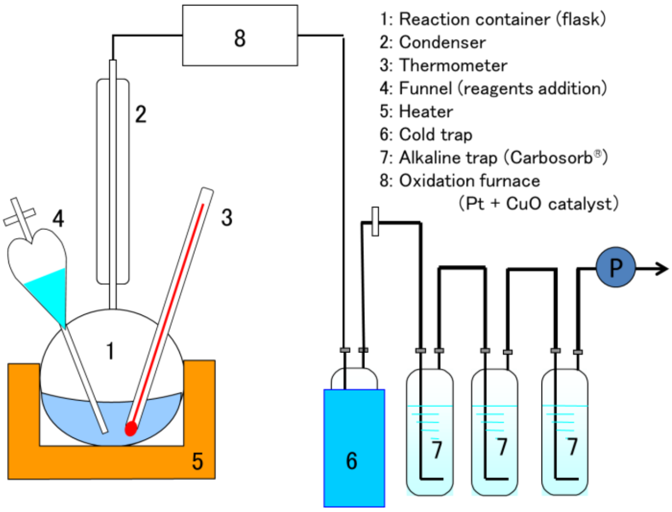

Figure 20Apparatus of C-14 analysis in liquid samples

Table 6 Conditions of liquid phase measurements

Carrier	Inorganic	Na_2CO_3, $1.0x10^{-3}$ mol as C
	Organic	C_2H_5OH, $4.0x10^{-5}$ mol as C
	Iodine	NaI, $1.0x10^{-4}$ mol
Reagent	Oxidizer	$K_2S_2O_8$, $9.5x10^{-4}$ mol
	Catalyst	$AgNO_3$, $7.7x10^{-4}$ mol
	Acid	H_2SO_4, $3.1x10^{-2}$ mol
Treatment temperature		80 degree-C
Treatment time		60 min
Cold trap		Cool by ice
Alkaline trap		Carbosorb®
Oxidation furnace		Pt + CuO catalyst 800 degree-C

<u>Analysis of organic / inorganic C-14 in liquid samples:</u> Organic/inorganic analysis of leachate was conducted using the same apparatus as total C-14 analysis. In the organic/inorganic analysis, alkaline traps are replaced with new one before supplying an oxidizer. Thereby, an inorganic form and an organic form are separable.

C-14 speciation technique under investigation and consideration: The speciation technique of organic C-14 chemical species is under investigation and consideration now, and is not applied to a hot test yet. One technique under consideration is to combine HPLC (High Performance Liquid Chromatography) and LSC (Liquid Scintillation Counter). The outline of analytical method is shown in Figure 21 and a device conditions are presented inTable 7, respectively. When the retention value of a peak of the organic compound in a sample is in agreement with that for the chemical species of a standard reagent, the organic compound is identified as the chemical species of the standard reagent. However, the results of the hot tests shows that C-14 chromatogram is not obtained by the influence of Sb-125 contained in Zircaloy immersion liquid. For this reason, the exclusion method of Sb-125, control method of carbon form change accompanying it, and improvement of a minimum-limit-of-detection are subjects.

Another issue of the analytical techniques using HPLC was pointed out by Takahashi et al. (2013). When the distribution coefficient of cementitious material was calculated from C-14 chromatogram of the leachate of irradiated graphite, it was not consistent with the value acquired with C-14 labelled compound. From this result, they remarked that the C-14 chemical species identification using techniques other than HPLC is also important.

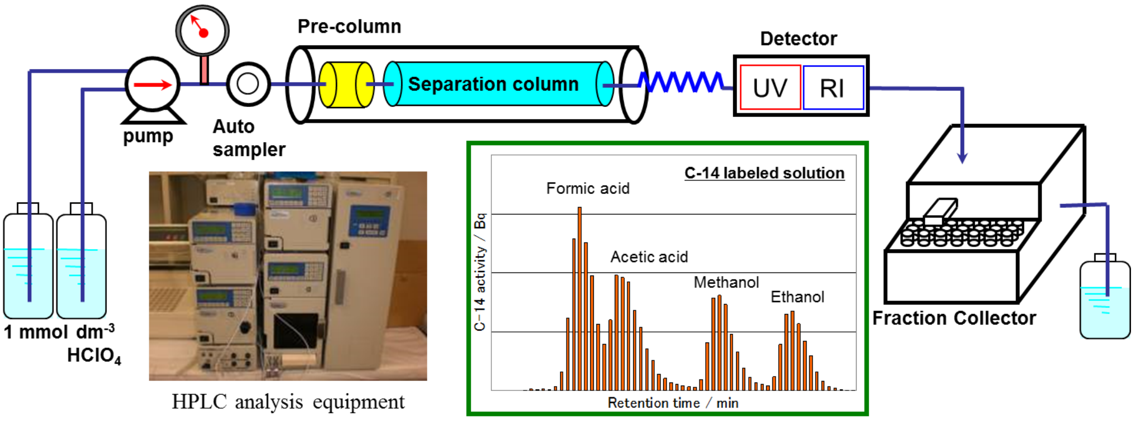

Figure 21 Outline of HPLC analytical method

Table 7 HPLC conditions

Separation column	Shodex KC-811
Pre-column	Shodex KC-LG
Eluent	1 mmol dm^{-3} $HClO_4$
Flow rate	0.8 cm^3 min^{-1}
Temperature	40 degree-C
Detector	UV (210 nm) RI (0.25x10^{-6} RIU / 10 mV)
Injection volume	0.1 - 0.5 cm^3

UV: Ultraviolet-visible spectroscopy
RI: Differential refractive index detector

Although the method of applying AMS (Accelerator Mass Spectroscopy) instead of LSC is also under investigation, the institution which can accept a hot sample is not found for the moment in Japan.

Moreover, it is under investigation also about the technique using LCMS (Liquid Chromatography Mass Spectroscopy) or GCMS (Gas Chromatography Mass Spectroscopy). It is likely that these techniques can be applied to chemical species analysis of C-12. However, the amount of leached C-14 is very small, and application of the technique is difficult.

3.4.3 Calculation of equivalent corrosion rate

When comparing the immersion test result of an irradiated cladding with the corrosion test result of a non-irradiated cladding, it is assumed as follows:

(1) C-14 is homogeneously distributed over the specimen

(2) C-14 is released from the inner and outer surface of the specimen

(3) The thickness of a sample is assumed to be 800μm and 540μm for BWR and PWR, respectively.

The equivalent corrosion rate was calculated by the following formula:

$$R_C = \frac{R_A}{T} \times t\,,$$

where RC (μm year^{-1}) is the equivalent corrosion rate, RA is C-14 leaching fraction, T is test time (year), t is thickness of specimen(μm).

4 Experimental work performed at JRC-ITU

4.1 Materials

The test material is standard Zry-4 from a high burn-up LWR fuel. There is no further information for the claddings other than the manufacturer's specifications (Table 8). For impurity levels (eg C, N, O), if necessary, ITU will use a standard specification value of Zircaloy-4 if no other value is available (e.g. 80 ppm N for Zry-4). Alternatively a best estimate could be taken such as 75% of the upper limit - e.g. 60 ppm N for Zry-4. If a measured value is available for a similar fuel cladding this could be used. For stainless steel clad, cladding from a fast reactor fuel project NIMPHE 2 will be used. These were 25%Pu-U nitride and carbide fuels that were irradiated in the Phenix reactor. Metallography of the cladding of the selected NIMPHE 2 carbide fuel of approximately 55 GWd/t_{HM} burn-up is available.

Table 8 Specification values for main elements in Zircaloy-4 (ATI-Wah-Chang production specifications*)

Element	**Content (wt%)**
Zr (Hf)	97.56-98.27 (Hf<0.01)
Sn	1.20-1.70
Fe +Cr	0.28-0.37
Fe	0.18-0.24
Ni	<0.007
C	<0.027
N	<0.008
H	<0.0025
O	not given

*[www.alleghenytechnologies.com/wahchang]

Total burn-up (probably local BU) and irradiation data will be available for the high burn-up NIMPHE 2 fuel and Zircaloy-4 cladding. C-14 content could be estimated at this stage as it is very unlikely that measurements are available. Samples will be cut as 5mm long rings:

a) Some samples will be cut at fuel height: they will need fuel removing but they will present higher burn-up/C-14 content.

b) Further samples will be cut from above fuel height which are clean but then have a lower irradiation and C-14 content.
One sample will be mounted for metallography, another will be used for total carbon content determination (not only C-14 content). The remainder will go for leach testing in the autoclave. Any excess samples will be retained for future repeat testing.

4.2 Analyses

Further to performing leaching test (see § 5.2 in the D3.2 report), gas samples will be transferred to the glove box outside the hot cell for treatment (^{3}H & I_2 removal) where it will pass over a CuO oven at 350°C for CO/CO_2 conversion (see Figure 22). The oven will only convert, CO to CO_2. The total CO_2 content is measured by infra-red absorption. Therefore, only the total C-14 release as gaseous CO_2 will be determined, and not the different components.

Then liquid scintillation counting (LSC) analysis will be performed after absorption in solution (e.g. Carbosorb + Permafluor E+, PerkinElmer) to determine the C-14 content of the inorganic C gases released. Liquid samples will be transferred to a clean bottle before closing and removing to an analysis glove box for removal of other isotopes (eg. ^{3}H by passing through mild acid or through a cold (~0°C) tube and I_2 by passing through a $AgNO_3$ solution) and then capturing for LSC of C-14.

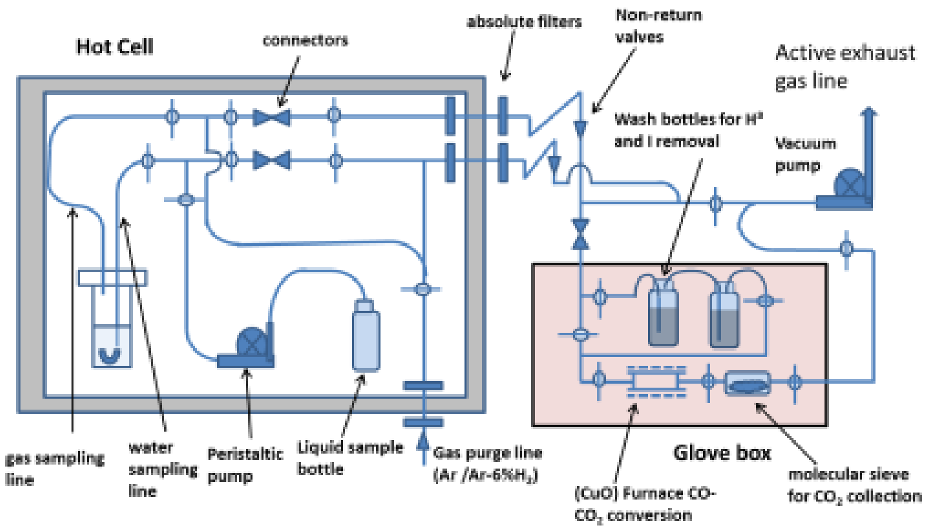

Figure 22Schematic diagram of the hot cell testing and sampling glove box for subsequent analysis by liquid scintillation counting

The details of the transfer between hot cell autoclave and glove box with filter traps and absorbants/ampoules before transferring to LSC measurement device still need to be worked out. The analytical details may be refined in view of the experience of other participants.

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