

# Carbon-14 Source Term

CAST



## Final Report from JRC-Karlsruhe: Determination of $^{14}\text{C}$ Content in and Release from Zircaloy cladding (D3.14)

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

For more information, please visit the CAST website at:

<http://www.projectcast.eu>



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## Executive Summary

Within the CAST project, the JRC Karlsruhe (formerly JRC Institute for Transuranium Elements) developed a new device for the determination of total carbon using a gas extraction method. For the zircaloy investigations in WP3, an accuracy of 10 to <1% can be expected for carbon contents in the 5 to 500 ppm range, respectively. Further equipment to perform leaching tests and <sup>14</sup>C determination by liquid scintillation counting (LSC) has been prepared. Their deployment has been hindered due to technical difficulties and finally due to an upgrade of the cells to meet new legislation. This report summarises the achievements made so far.

This report has been compiled and edited by J. Somers following the retirement of the project leader David Bottomley in February 2017.

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## JRC TECHNICAL REPORTS

# Final Report from JRC Karlsruhe: Determination of $^{14}\text{C}$ Content in and Release from Zircaloy Cladding (D3.14)

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**Title** CAST D3.14: Determination of 14C content and Release from Zircaloy Cladding**Abstract**

Within the CAST project, the JRC Karlsruhe (formerly JRC Institute for Transuranium Elements) developed a new device for the determination of total carbon using a gas extraction method. For the zircaloy investigations in WP3, an accuracy of 10 to <1% can be expected for carbon contents in the 5 to 500 ppm range, respectively. Further equipment to perform leaching tests and 14C determination by liquid scintillation counting (LSC) has been prepared. Their deployment has been hindered due to technical difficulties and finally due to an upgrade of the cells to meet new legislation. This report summarises the achievements made so far. This report has been compiled and edited by J. Somers following the retirement of the project leader David Bottomley in February 2017.

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## 1. Introduction

The main objective of these investigations is the release and speciation of <sup>14</sup>C during corrosion of irradiated zircaloy under disposal conditions. Even though one might expect very low release rates under such conditions, considerable uncertainties exist, and assessment is hindered as <sup>14</sup>C is a difficult to measure nuclide. The potential speciation of <sup>14</sup>C is particularly important, especially the relative proportions of organic <sup>14</sup>C vs. inorganic <sup>14</sup>C that might be released. Thus the degree of speciation can also affect the safety assessment of the waste repository too. WP3 of the CAST project concentrates on the identification and quantification of <sup>14</sup>C species formed during corrosion of irradiated zircaloy under conditions expected in cement based repositories. Overall, the project aims at reducing uncertainties and setting “bounds” on the release rates. Improved measurements, or even bounded uncertainties lead to reduction in conservatism, and more realistic safety assessments

A major effort in CAST WP3 is the development of methods to extract (or leach under cementitious conditions) <sup>14</sup>C from irradiated zircaloy (the major light water reactor (LWR) cladding material), as well as the amelioration of methods to assay accurately <sup>14</sup>C. Typical release rates must be known to avoid overly cautious assessments in the licensing of the geological repositories. Migration, or potential migration, of <sup>14</sup>C is of substantial interest in such safety assessments. In the case of <sup>14</sup>C, this aspect is of unprecedented importance as its transport can occur in a number of ways, i.e. in gaseous form (CO, CO<sub>2</sub>, CH<sub>4</sub>,...) as well as in liquid form (hydrocarbons or carboxylic acids, etc.). The total <sup>14</sup>C released and its rate of release represent important parameters, but the universalisation of the data implicitly requires a deep knowledge of the <sup>14</sup>C speciation, i.e. the fractional release rates of the chemical species involved.

The JRC Karlsruhe (formerly JRC ITU) contributes to the determination of the influence of pH on the corrosion rate (see review by Swanton 2014). Though highly alkaline conditions would be expected in cementitious conditions, lower pH values could also prevail (e.g. if decomposition of organic materials would neutralise the alkalinity). WP3 partners cover a range of pH with JRC focussing on pH 12. Thus the contribution of the JRC is

- the determination of <sup>14</sup>C in zircaloy irradiated in a light water reactor, with samples to be taken from the fuel zone of the pin,
- the determination of the release rate of <sup>14</sup>C therefrom under aqueous conditions (pH = 12 (NaOH)).

For this work JRC Karlsruhe selected zircaloy cladding from PWR fuel pins, which were readily available. In reality, however, zircaloy will be present in spent fuel waste streams in two forms, namely:

- untreated as removed from the reactor and sent directly for disposal, or
- as hulls resulting from aqueous recycling of irradiated fuel pins

The results of these investigations have a direct bearing on the latter (i.e. recycling hulls), as the tests simulate accurately the treatment of the hulls during reprocessing using the PUREX process, i.e. fuel dissolution in 7M HNO<sub>3</sub>. On account of the acid wash used in WP3 (essential for the determination methodology), the results might not exactly emulate the conditions encountered for disposal of LWR zircaloy fuel pins directly into a geological repository. This report summarises the progress and achievements made by JRC Karlsruhe.

Waste management is a key component of the JRC direct actions in support of the Member States.

## 2. Materials and methods

### 2.1 Materials

The zircaloy chosen for the JRC Karlsruhe measurements was a duplex zircaloy cladding stemming from a fuel pin irradiated in a commercial nuclear power plant to a relatively high burn-up. Samples were taken from the mid height position, essentially to maximise the <sup>14</sup>C content. A summary of the sample characteristics is provided in Table 2.1. The samples for the tests in the CAST project were cut in the form of 3-5 mm rings, or half rings with masses in the 0.5 – 1 gram range. The major part of the fuel could be removed by mechanically levering it out, but to eliminate all residues, two washes (each 15 minutes) in 8M HNO<sub>3</sub> were performed. The samples were then washed in distilled water in an ultrasonic bath (15 minutes) and then dried in air. The oxide layer should have remained unaffected under these conditions. The inside of the cladding had a bluish hue as is shown in Figure 2.1. No information on the chemical composition of such cladding material prior to irradiation is known. In Table 2.2 below typical specifications for Zry4 are provided.



**Figure 2.1 Visual inspection of the Zry cladding sample**

**Table 2.1 Summary of characteristics of the Zircaloy fuel cladding**

Cladding	Zry-4
Fuel	UO <sub>2</sub>
Sample position	Mid plane
Oxide thickness	30 μm
Sample size	3-5 mm rings or half rings
Fuel removal	Mechanical, followed by washing in 8 M HNO <sub>3</sub>

**Table 2.2: Typical specifications for the composition of Zircaloy-4 cladding**

Zircaloy 4	
Element	Content (wt%)
Zr (Hf)	97.56-98.27 (Hf<0.02)
Sn	1.20-1.70
Fe	0.18-0.24
Cr	0.07-0.13
Ni	<0.007
C	<0.027
N	<0.008
H	<0.0025
O	1400 ppm max
Others (ppm)	Al 75, B 0.5, Cd 0.5, Co 20, Cu 50, Mn 50, Ti 50, W 100, Si 200, U 3.5

The quoted specifications above were given additional credence by chemical analysis of a Zry-4 sample available at JRC Karlsruhe. This sample was dissolved for ICP MS analysis of the metallic components, while C, N and O contents were measured by gas extraction methods. The results are shown in Table 2.3 and Table 2.4. The Sn (1.2%), Fe (0.2%) and Cr(0.1%) are all in line with the above specifications, where ranges were given. The values for C, N and O are also in line with nominal cladding specifications. It is also important to note, that, as they are the main precursors for <sup>14</sup>C generation, their content is no more than a factor of 2 less than that prescribed in the specification, which gives some uncertainly limits

for nuclear physics estimates of <sup>14</sup>C generation during irradiation. There were some perceived inefficiencies in the above carbon measurements made at JRC Karlsruhe and they were repeated in a contractual measurement by Bruker, a commercial supplier of such instrumentation. The data are given in Table 2.5 below. The overall agreement for nitrogen is good. For carbon, these tests (in as far as they can be seen as representative at all) indicate that the carbon content can be a factor of 20 lower than in the specifications. In the absence of manufacturer data, no further conclusions can be drawn on the virgin zircaloy cladding used in the CAST tests.

**Table 2.3 Chemical composition of a nominal Zry-4 cladding determined by ICPMS**

Element	Content (µg/g)	Uncertainty
Hf	61.5	7.4
B	<140	
P	<32	
Sn	12396	1488
Ni	38	38
Fe	2240	2240
Cr	1174	141

**Table 2.4 Non metallic impurities determined by total combustion methods**

Element	Content (µg/g)	Uncertainty (absolute)
O	0.117	0.019
C	<0.05	
N	0.0044	0.00102

**Table 2.5 Re-measurement (Bruker) of non-metallic impurities determined by total combustion methods**

Element	1 <sup>st</sup> test JRC Karlsruhe		2 <sup>nd</sup> test Bruker	
	Content (µg/g)	Uncertainty (absolute)	Content (µg/g)	Uncertainty (absolute)
C	<0.0500		0.0009	0.0003
N	0.0044	0.0010	0.0031	0.0005

### 3. Methods and Experimental Conditions

#### *3.1 Collection of carbon from the samples using the gas extraction method*

Total carbon measurement in carbide and nitride fuels has been made at JRC Karlsruhe for more than 40 years and was driven by the advanced nitride and carbide fuel for fast reactor programmes. In this manner, JRC Karlsruhe has built up a strong capability and knowledge base for carbon determination using so called gas extraction method, which is often referred to as a total combustion method.

To our knowledge, no such gas extraction facility has been installed in a hot cell environment, for carbon determination, though many laboratories have such devices installed for H determination in cladding materials. For the CAST project, JRC Karlsruhe has purchased a device from Bruker known as ICARUS (see Figure 3.1). The device is centred on a compact high frequency induction furnace, in which the sample is incinerated in a flowing oxygen atmosphere to generate CO<sub>2</sub>, which is then detected using a solid state infrared detector system (see Figure 3.2 – JRC Karlsruhe device is not equipped for Sulphur detection). About 1 gram of high purity copper is added to the crucible for each measurement as an accelerator (achieved by the relatively low melting temperature of Cu). This addition means that the sample melts quickly and that a large pulse is detected rather than a broad peak. Due to the integration over time, the former signal yields more accurate data. Supplier specifications cover operation in the 1-60000 ppm range for sample masses in the 0.5-1.0 gram range. Calibration is performed against certified standards. The device measures total carbon. The detector system is not capable of distinguishing between <sup>14</sup>C and <sup>12</sup>C.

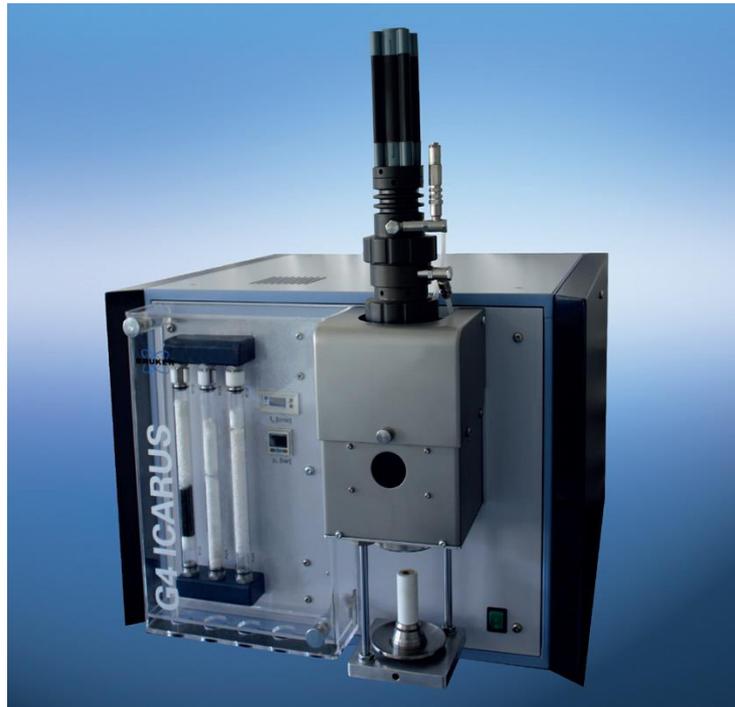


Figure 3.1 ICARUS device in its standard configuration

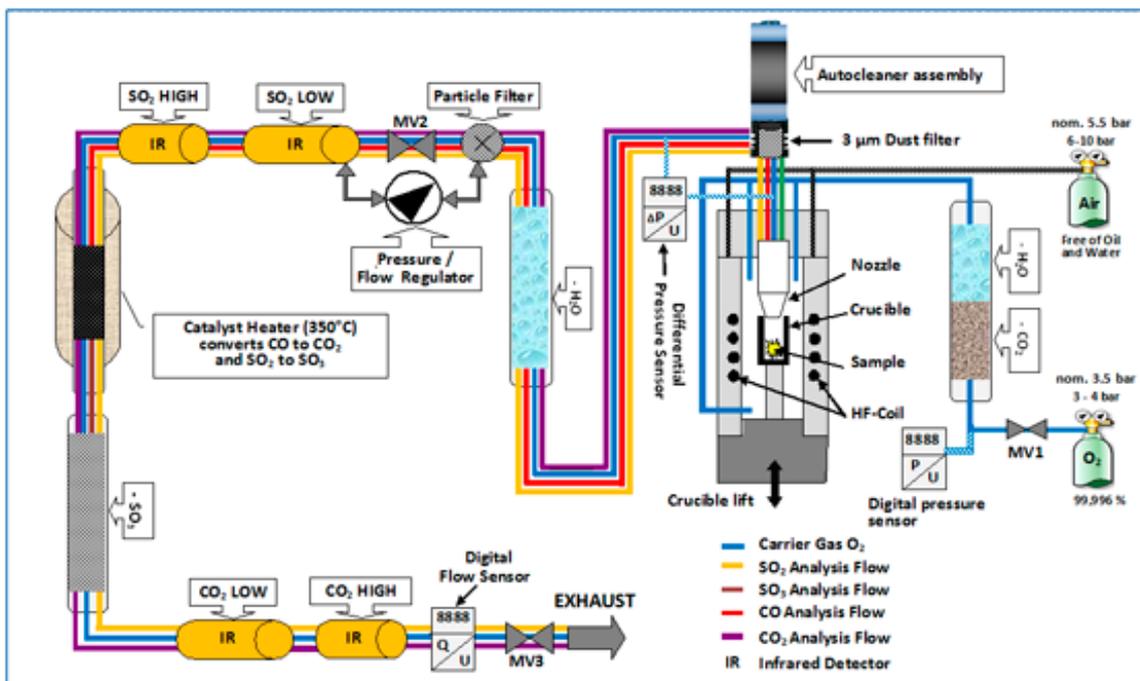
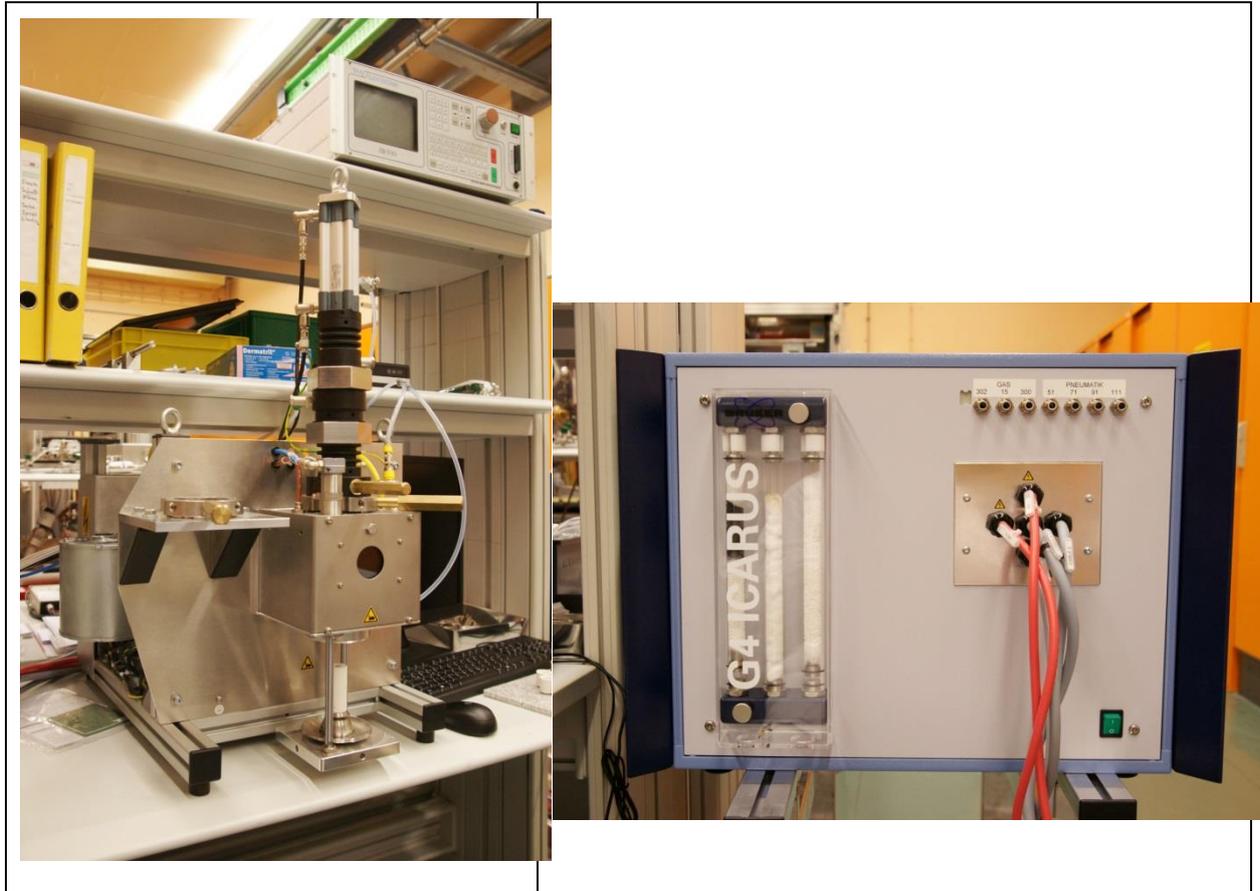


Figure 3.2 ICARUS device operating principle

The device needed major adaptation to render it suitable for hot cell application, so that the major electronic components had to be separated from the core furnace to be incorporated in the hot cell. This has been achieved and the separated device is shown in Figure 3.3. The overall layout and integration of the device for hot cell work is shown in Figure 3. 4. Briefly, only the section containing the furnace is inserted in the hot cell. To do so a lengthy procedure is needed and is achieved in the following steps.

- The hot cell must be thoroughly cleaned using its telemanipulators so that manual intervention is possible (i.e. dose rates must be reduced to a minimum)
- An intervention cell is docked onto the back of the hot cell
- Physical access to the cell is then achieved, whereby staff operating in fully ventilated suits, open the door and lift the equipment inside.
- Connecting all cables for power and sensors to the standard connector bank in the cell
- Connecting the gas lines from the ICARUS furnace via double filters to the outside, from whence the gas passes through the detector system, before being returned into the cell via a second set of double filters.

Within this configuration, total carbon is measured directly by the instrument. All carbon generated is collected on a molecular sieve, located in the hot cell. For <sup>14</sup>C determination, this molecular sieve must be transferred to the <sup>14</sup>C preparation glove box, which is described later.



**Figure 3.3 ICARUS device separated into 2 components**

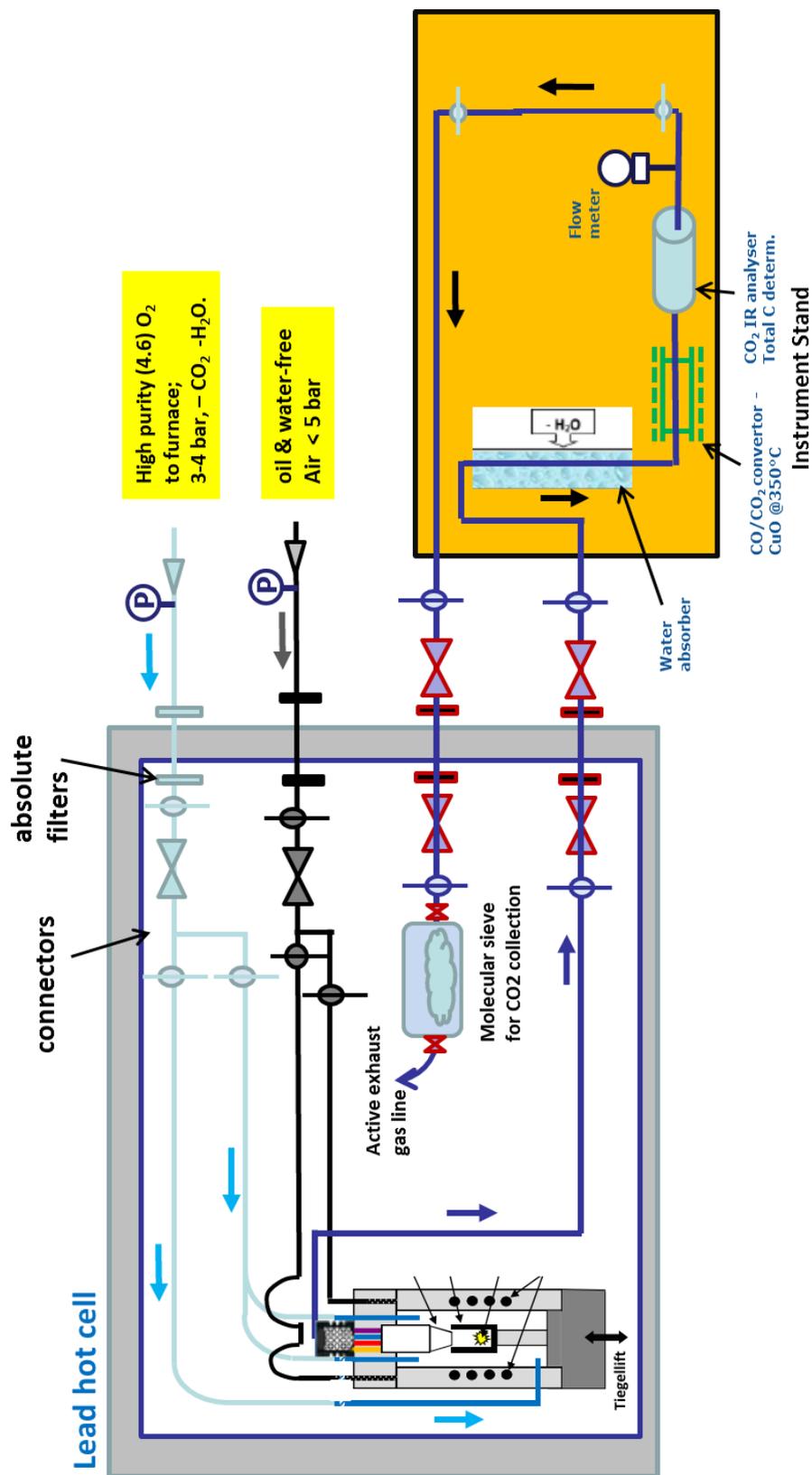


Figure 3.4: Concept for integration of ICARUS device in a Hot Cell

On delivery the performance of the device has been determined against a set of materials containing known quantities of carbon. The results are summarised in Table 3.1 below. The calibration is made with a set of standards. In all cases preheated crucibles have to be used to ensure no residues of carbon are within the sample crucible itself. The set of follow up measurements made with the same standards show exceptionally good agreement.

**Table 3.1: Measured Carbon content in a set of qualification materials**

Sample	Calibration			Repeat measurements			
	Mass (g)	[C] ppm	SD* ppm	Mass (g)	[C] ppm	SD ppm	No. of analyses
Blank (Cu)	1						
CRM 088-2	1	6	2	1	5.51	0.51	5
ZRM 191-2	1	43	2	0.5	43.98	1.90	5
				1.0	43.45	0.38	5
ZRM 284-2	1	201	5	0	202.48	1.11	5
				1.0	200.77	1.68	5
IRSID 114-1	0.5	440	20	0.5	442.91	1.63	5
Zry4				0.4	77.52	3.63	8

\* Data provided by the supplier of the standards

### *3.2 Leaching of <sup>14</sup>C from samples in autoclaves*

While the ICARUS device provides a convenient method to collect total carbon from a sample, the same can be achieved using an autoclave, when the sample is digested aqueously. For the CAST project, however, an autoclave is an essential tool to collect <sup>14</sup>C from a leach test, whereby the sample is exposed to an aqueous solution with a chemical composition similar to that expected in a geological repository.

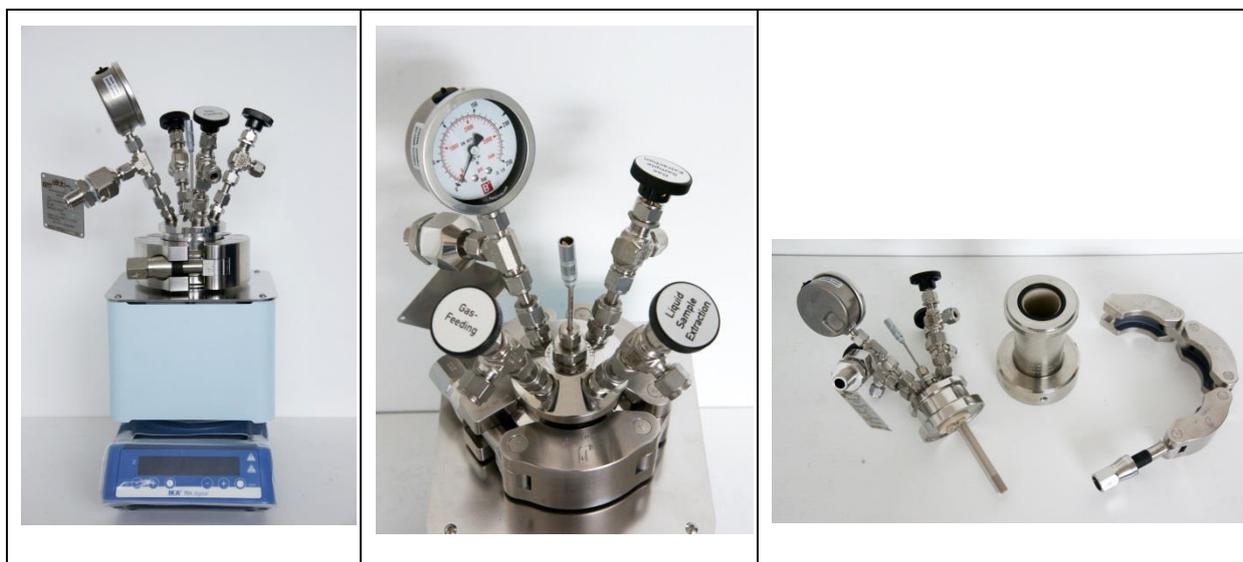
The autoclave can be implanted in the JRC-Karlsruhe hot cells via the connecting tunnel underneath the cells. The dimensions of this tunnel are large enough to permit transfer to the cell. Assembly has to be made by telemanipulators, with a restriction that individual components should weigh less than 5 kg.

The major operational problem encountered in a JRC Karlsruhe hot cell is that of poor cleanliness against which measured described later were planned. JRC Karlsruhe hot cells are old (some approaching 50 years) and extremely dirty, so that careful handling and packaging of all of the experimental components is essential, especially as the final <sup>14</sup>C determination is made by Liquid Scintillation Counting (LSC). Successful application of this technique requires that the final <sup>14</sup>C sample is free of radioactive isotopes that could interfere with the LSC measurement.

Two autoclaves were prepared at JRC Karlsruhe to permit two experiments to run in parallel, a contingency plan to mitigate the consequences of ever increasing delays within the project. The autoclave with its internal components is shown in Figure 3.5. The device can withstand severe conditions (150 bar and 200°C), but for the purpose of the CAST programme was to be operated at 1-2 bars excess pressure (Argon) and without heating (i.e. hot cell temperature of about 30°C). The internal liner is made of PEEK, a material highly resistant to strong irradiation fields. The samples themselves are placed on pre fired ceramic holders. The second autoclave is shown in Figure 3.6 and has similar characteristics.



**Figure 3.5: Berghof autoclave (left) with its gas sampling vessel, and a view of its internal components (right)**



**Figure 3.6: Second Autoclave with heating mantel**

A key aspect of the CAST is the collection of the <sup>14</sup>C sample, which can be in both liquid and gaseous forms. Liquid samples can be removed by direct sampling therefrom, taking due care that the sampling vessels do not pick up contamination from the surrounding hot cells.

The gas sample is more problematic and is achieved using a gas sampling vessel (a transport vessel to collect gas, see Figure 3.5). At the end of the experiment, the valve connecting the gas sampling vessel to the autoclave is closed and the gas sampling vessel unit can be detached using the quick fit connector system and transferred into the hot cell support tunnel. From there, it can be removed from the hot cells using the main auxiliary support glovebox at the end of the service tunnel. Again, contamination from the cells poses a major issue (especially in view of 3 month leaching times), and must be avoided. To achieve this goal the sampling vessel is packed in 3 layers of polyethylene sacks, the last being installed on the sampling vessel just as the sampling vessel is connected. This outer layer is removed in the hot cell, before its transfer to the tunnel. The next sack is removed in the support hot cell, and the sampling vessel is bagged out using a double bag system to be installed in the glove box for the actual <sup>14</sup>C determination.

The handling procedures are very similar to those used at KIT-INE [Herm et al 2015; Herm 2015], with the well-known caveat that JRC Karlsruhe hot cells are older and more highly contaminated than those in KIT INE, necessitating yet more care and vigilance in sample handling and manipulation.

### 3.3 Glovebox for sample preparation and LSC determination

In all, three types of sample must be foreseen for treatment to collect effectively the <sup>14</sup>C in a manner that it can be used for LSC determination of the <sup>14</sup>C content. The procedures are near identical to those followed at KIT INE [Herm et al 2015; Herm 2015].

- Liquid samples from the autoclaves: The <sup>14</sup>C in the liquid sample is released in several steps
  - By dropping the solution, taken from the autoclave, into a solution of 8M H<sub>2</sub>SO<sub>4</sub>, which is simultaneously purged by a N<sub>2</sub> flow (typically 250 ml per minute at a slight (0.2 mbar) under pressure), whereupon inorganic CO/CO<sub>2</sub> is released.
  - Further addition of a strong oxidising agent (potassium peroxodisulphate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) with AgNO<sub>3</sub> as catalyst) combined with simultaneous heating (95°C) to oxidise all organic carbon into CO/CO<sub>2</sub>.
- Gas samples from the autoclaves are taken “as is”. In contrast to KIT-INE where very clean sampling could be achieved and the gas sampling vessel was attached to the outside of the glovebox, the “dirtier” conditions of the JRC hot cells restrict handling options so that the gas sampling vessel had to be inserted in the glove box and linked to the wash stations therein.
- Molecular sieve samples from the total C determination using the ICARUS device, which need to be purged of their CO<sub>2</sub> by an N<sub>2</sub> flow with or without gentle heating.

The steps followed are drawn entirely by a scheme developed and well documented by KIT-INE [Herm et al 2015; Herm 2015]. A new glove box has been constructed at JRC Karlsruhe according to the technical design in Figure 3.7 with the finished product shown in Figure 3.8.

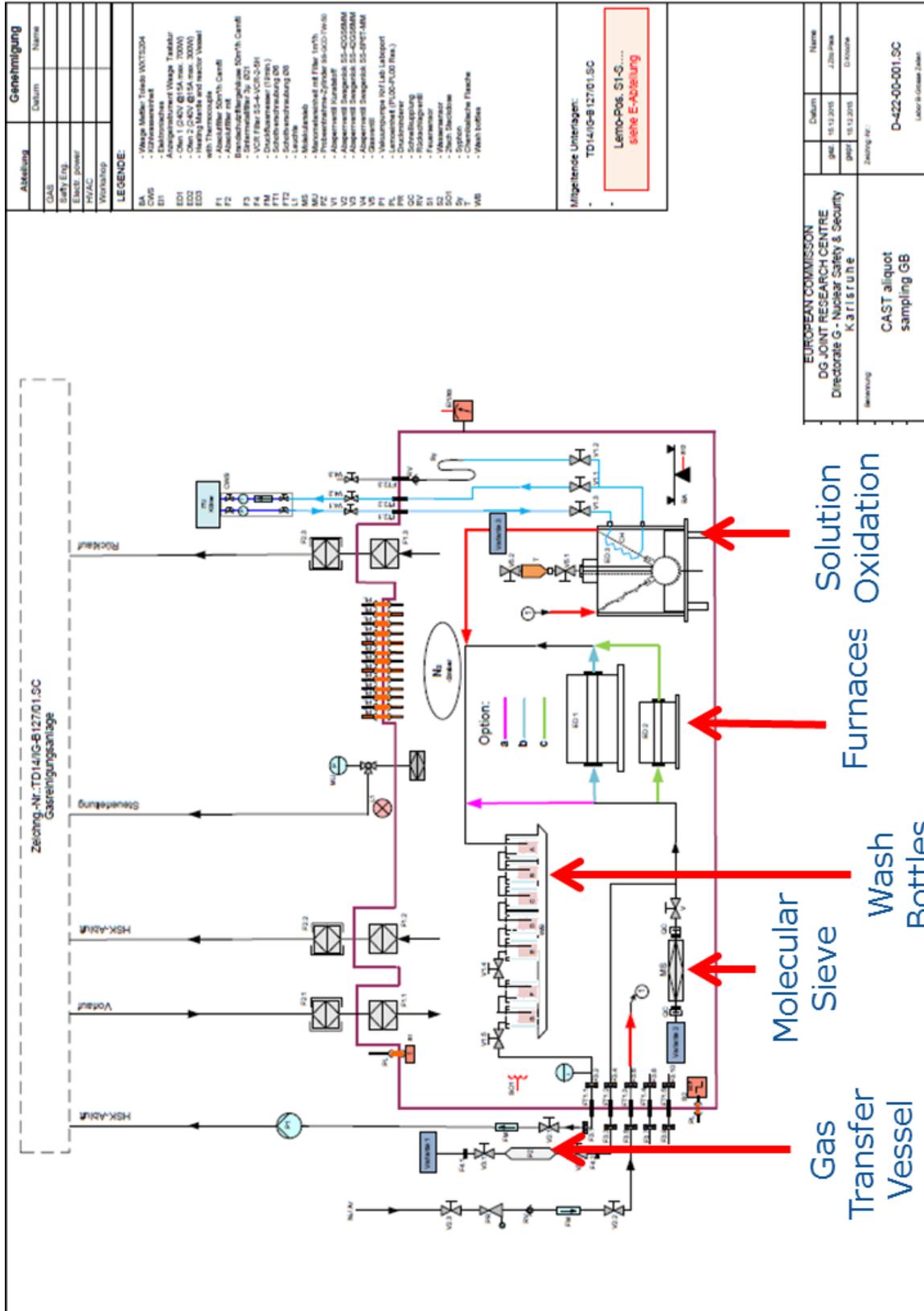
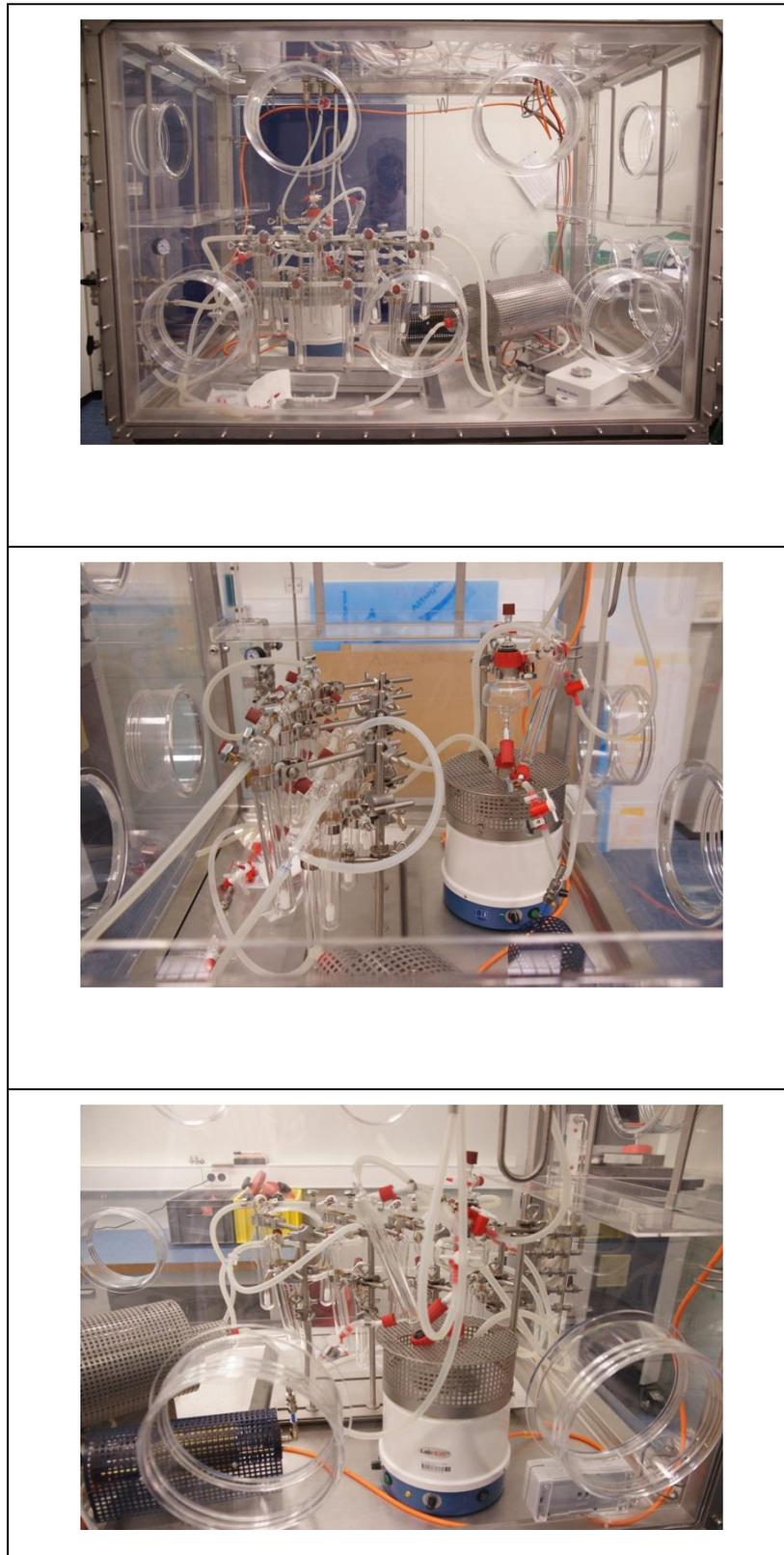


Figure 3.7: Technical design for the  $^{14}\text{C}$  preparation glove box



**Figure 3.8: Views of the Completed Glove box for  $^{14}\text{C}$  sample preparation.**

The above construction might appear complicated, but at its heart is centred on the following steps. The gas containing CO/CO<sub>2</sub> mixtures is passed through a variety of wash bottles or furnaces:

- 1<sup>st</sup> set of Wash bottles
  - Wash Bottle 1: 0.1 M AgNO<sub>3</sub> to trap <sup>129</sup>I
  - Wash Bottle 2: 5% H<sub>2</sub>SO<sub>4</sub> to trap <sup>3</sup>H<sup>1</sup>
  - Wash bottle 3: 2M NaOH to trap CO<sub>2</sub>
  - Wash bottle 4: 2M NaOH to trap CO<sub>2</sub>
- Furnace 1: at 400°C with a CuO catalyst to convert CO to CO<sub>2</sub>, which with a by-pass can be bled to second set of wash bottles. (This option was envisaged to quantify CO/CO<sub>2</sub> ratios in the samples, but dilutes what are already low quantities of <sup>14</sup>C)
- Furnace 2: at 750°C fitted with a CuO / Pt/Al catalyst to convert CH<sub>4</sub> or CO to CO<sub>2</sub>
- 2<sup>nd</sup> set of wash bottles
  - Wash Bottle 5: 5% H<sub>2</sub>SO<sub>4</sub> to trap <sup>3</sup>H
  - Wash Bottle 6: 5% H<sub>2</sub>SO<sub>4</sub> to trap <sup>3</sup>H
  - Wash bottle 3: 2M NaOH to trap CO<sub>2</sub>
  - Wash bottle 4: 2M NaOH to trap CO<sub>2</sub>

This rather intriguing separation design (copied in its entirety from KIT INE) opens the possibility to determine <sup>14</sup>C as

- Inorganic in the solution from the autoclave
- Inorganic in the gas phase from the autoclave (also with the potential to distinguish CO and CO<sub>2</sub> via two furnaces)
- Organic in the solution from the autoclave
- Organic in the gas phase from the autoclave.

Being ever cautious of the possibility of deleterious cross pollution and contamination of the samples with isotopes detrimental to liquid scintillation counting, an additional precaution was taken and an independent molecular sieve trap is available in the glove box to collect CO<sub>2</sub> without going over the NaOH traps. The molecular sieve chosen is from CARBOSPHERE® carbon molecular sieve (60/80 Mesh). In this way, the ampoule could be switched to an

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<sup>1</sup> <sup>3</sup>H has to be removed before the beat counting by LSC

independent high purity N<sub>2</sub> gas line to purge the CO<sub>2</sub> captured on the sieve and collect it directly in the liquid scintillation cocktail ready for counting by LSC.

At the end of the process, there are 4 solutions bearing NaOH, from which aliquots (2cc) can be taken and added to 18 cc of the organic fluoride solution used for liquid scintillation counting (LSC). Samples are bagged out and measured in an independent device ((Perkin Elmer Wallac Guardian liquid Scintillation Counter 1414 with Wimspectral software 2.0)).

## 4. Results

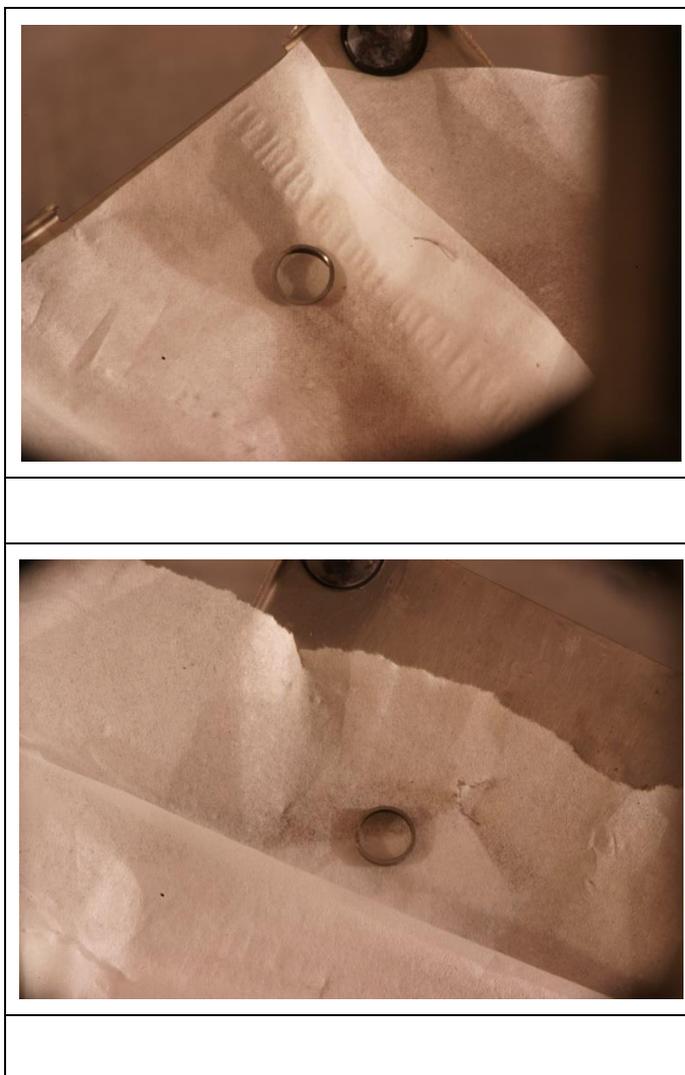
### 4.1 Characterisation of the zircaloy samples

A total of 8 rings were prepared from the fuel rod cladding. They were selected from a position about 3000 mm from the bottom end plug. Their dimensions and dose rates are summarised in Table 4.1. After the manual defueling using a die, the dose rate of the cladding lay in the 200 mSv/h range, while after washing twice in 8 M HNO<sub>3</sub> for 15 minutes, it was decreased considerably to about 80 mSv/hr. The dose rates of sample 2 and 2/3 are lower than the others, most likely due to their lower mass. Images of these two samples are shown in Figure 4.1.

**Table 4.1 Dose rate of zircaloy samples before and after washing in HNO<sub>3</sub>\***

Sample	Mass (grams)	Dose rate before	Dose rate after
2	0,2658		33
2/3	0,2714		42
3	0,3798	220	105
4	0,3909	175	73,5
5	0,3142	191	93,3
6	0,3725	201	109
7	0,4383	166	81
8	0,3682	176	84

\* Dose rates in red were measured directly in the cell, and have a contribution of about 18 mSv/h due to the cell background dose rate. The measurements in blue were also executed in the cell, but within a lead container, which reduced the background contribution to about 4 mSv/h.



**Figure 4.1 Images of the rings No 2 and 2/3 after washing in 8M HNO<sub>3</sub>**

The dose rate of sample 2 was low enough to extract the sample from the cell via the service transfer system and its associated glovebox. The sample itself (dose rate 33 mSv/hr) was mounted in multipurpose holder in such a manner that it is held firmly and centrally against the bottom of a cylindrical aluminium can. The can was mounted on a bench with the bottom of the can facing a gamma detector, equipped with a Genie 2000. Calibration is achieved using a Eu-152 source located in a separate measurement at the same distance from the gamma detector. The activities of isotopes detected are provided in Table 4.2. The usual

activation products of the zircaloy cladding are present. The dominant activity comes from fuel (Cs and Am), which shows that the wash was not entirely effective or that a certain pick up of fuel particles from the cells occurred during the handling of the sample.

**Table 4.2 Activity of Zry ring after nitric acid washes**

Isotope	Activity (kBq)	uncertainty
Co 60	219	6
Nb 94	214	8
Zr 95	81	5
Cd 109	4365	456
Sb 125	957	30
Cs 134	894	20
Cs 137	48506	2913
Eu154	936	21
Am241	240	24

## 4.2 Sources of error

Currently, the ICARUS device is ready to be placed in the hot cell. No measurements on irradiated steel samples have been performed yet. Several campaigns on non-irradiated zircaloy samples have been performed and the results are given in Tables 2.4 and 2.5. In terms of repeatability, the gas extraction method performs well. Such devices lend themselves to optimisation, i.e. when the carbon content is low, the accuracy decreases, but can (within limits) be offset by increasing the sample mass. The operation in a hot cell environment brings additional challenges, which can also influence the accuracy of such measurements. The cleanliness of the crucible is of utmost importance, as any “foreign” carbon can severely impair the results. The cells themselves at JRC Karlsruhe are operated under N<sub>2</sub> which is purged of particulate matter by the double filters of the cell itself. Further precaution includes treatment of the crucibles in oxygen beforehand and their storage inside the cell in sealed containers to ensure no contact with carbon sources therein.

The results of Table 4.2 clearly indicate the problems of performing sensitive measurements in old and highly polluted hot cells. Great caution must be exercised if the samples are to be maintained free of deleterious cross pollution by fuel and fission products, whose presence in the steps involving the separation of <sup>14</sup>C from the solutions and the gases from a leaching study could render the sensitive liquid scintillation counting analysis totally useless.

Finally, it was decided to apply an acid wash to the zircaloy samples to remove fuel from the samples. While this is fully acceptable with respect to zircaloy hulls from reprocessing, it could markedly affect the availability of <sup>14</sup>C at the surfaces of the sample. Thus, the reliability of the results with respect to deep geological disposal of standard once through LWR fuel could be impaired. Here, there is a need for innovation to improve the procedure or develop new methods less sensitive to cross pollution than LSC. Cavity ring down spectroscopy (CRDS) [Giusfredi et al., 2010] is a tool being developed for environmental monitoring of <sup>14</sup>C (as CO<sub>2</sub>) which might bring a step change in <sup>14</sup>C analysis, matching the accuracy of accelerator mass spectrometry (AMS) but at a fraction of the cost, and eventually as a mobile measurement station.

## 5. Conclusions

Considerable effort has been made and progress achieved at the JRC Karlsruhe during the course of the CAST project, as testified above. Nevertheless, the work was stricken by numerous delays and it has not been possible to complete all experiments within the project duration. The glovebox is ready to be installed at the hot cell building. The autoclaves are ready too. An upgrade at the insistence of the JRC Karlsruhe's licensing authorities was made in 2017/2018, rendering insufficient space to install the autoclaves. Thus, final experimental activity had to be suspended until 2018. On completion, by the end of 2018, an unplanned additional report with the outstanding results will be provided to all partners (and uploaded onto the CAST project's publications website), outside of the project and beyond its formal end. Publication of the final results is also planned.

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## Abstract

Within the CAST project, the JRC Karlsruhe (formerly JRC Institute for Transuranium Elements) developed a new device for the determination of total carbon using a gas extraction method. For the zircaloy investigations in WP3, an accuracy of 10 to <1% can be expected for carbon contents in the 5 to 500 ppm range, respectively. Further equipment to perform leaching tests and <sup>14</sup>C determination by liquid scintillation counting (LSC) has been prepared. Their deployment has been hindered due to technical difficulties and finally due to an upgrade of the cells to meet new legislation. This report summarises the achievements made so far.

This report has been compiled and edited by J. Somers following the retirement of the project leader David Bottomley in February 2017.



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