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CArbon-14 Source Term

CAST

Intermediate report on the analysis of Zircaloy samples C-14 content (D3.6)

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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.

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

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Intermediate report on the analysis of Zircaloy samples C-14 content

Executive Summary

D3.6 forms part of CAST task 3.3 “Characterisation of C-14 released from irradiated Zirconium fuel clad wastes”. This report summarises the progress at ITU to the end of March 2015. Cladding materials have been selected and cut from a high burn-up LWR reactor (~100GWd/tU) with a Zircaloy 4 cladding (with outer lining). There are cladding cross-sections from the upper plenum and the maximum power positions of the fuel rod. Cladding samples will be leached in solutions of NaOH (pH12-12.5) at 30°C to simulate the cement-based pore waters of concepts for intermediate- level waste repositories.

Testing will be for a minimum of 3 months in an autoclave without intermediate sampling. Testing will be started when the analytical facilities are in operation.

The heating mantle requires the installation of a thermocouple before the introduction of the autoclave in the hot cell. The samples require cleaning.

The construction of the C-14 analytical glove box and the installation of the total C content analysis device in a hot cell are continuing. These are expected to be operating by the end of 2015. Testing & analytical procedures will be harmonised with INE to help consistency.

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1 Materials

1.1 *Zircaloy Composition and Burn-up (BU)*

The cladding test material was initially thought to be Zircaloy 4, but is, documented as a duplex Zircaloy cladding probably as Zircaloy -4 cladding with a thin external Zr-2.5Nb cladding. The cladding comes from a high burn-up LWR fuel. Table 1 below gives typical specifications for both the external (Zr-2.5Nb) and the internal (Zry-4) alloys of the duplex cladding. These values can be used for the maximum impurity levels of C,N,O. If a measured value is available for a similar fuel cladding this could be used. The mean burn-up is 100.5 GW/tU. Local BU and irradiation data will be available for the LWR fuel cladding.

Table 1 : Specification for composition of Ziracloy-4 and Zr-2.5 Nb cladding alloys (incl. impurities).

Zircaloy 4		**Zr-2.5Nb**	
Element	**Content (wt%)**	**Element**	**Content (wt%)**
Zr (Hf)	97.56-98.27 **(Hf**<0.02**)**	**Zr**	rest
Sn	1.20-1.70	**Nb**	2.5-2.8
Fe	0.18-0.24	**Sn**	-
Cr	0.07-0.13	**Cr**	-
Ni	<0.007	**Fe**	-
C	<0.027	**Ni**	-
N	<0.008	**O (ppm)**	900-1200
H	<0.0025	**Max. impurity levels/ppm**	Al 75, B 0.5, Cd 0.5, C 270, Co 20, Cu 50, Mn50, Ti 50, W 100,Cr 200; Hf 150, H 24, P 130; Mg 20, Mo 50, N 60, Si 120; Na 10; Ta 200; V 50 Cr 200.
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		

1.2 *Sample preparation*

Samples have been cut as 5mm long rings or half-rings (1-0.5g).

a) Some samples have been cut at fuel height: they will need fuel removing but they will present higher burn-up and C-14 content,

b) Further samples have been cut from above fuel height which are clean but then have a lower irradiation and C-14 content. The samples containing fuel will have the fuel removed by pressing out, followed by HNO_3 dissolution for removal of the remaining fuel. The cladding rings may also be treated to see if it is possible to remove the oxide layers and try to determine the C-14 content in both metal and oxide. A list of samples is given in Table 1 below.

Zircaloy 4 cladding from PWR irradiated fuel (BU 100GWd/tU)
Top plenum (segt. 8): 5 x 10mm rings (to be cleaned)
Fuel (segt. 7): 1 x 5mm ring (metallography)
Fuel (segt. 7): 4 x 5mm ring (to be cut and defuelled)

Table 1: list of samples cut from the stainless steel and Zircaloy-4 claddings

One sample will be mounted for metallography, another will be used for total C content determination. It is also intended to capture the CO_2 in the exhaust flow on a charcoal filter capsule for transfer to the analysis glove box and determination of the C-14 fraction of the total C content. This will complement INE's C-14 content determination by dissolution of Zircaloy cladding. The remaining samples will go for leach testing in the autoclave. Any extra samples will be retained for future repeat testing.

2 Autoclave for leach tests

ITU will use an autoclave with a lining made of PEEK. This autoclave will be used in the framework of both, WP2 and WP3. Introduction of the autoclave is intended for 3rd Quarter 2015, in parallel with advances in the analytical glove box construction. An additional heating jacket was purchased (Feb. 2014) for enabling temperatures to go to 250°C and 150 bar pressure. The autoclave testing parameters will be 30°C and 1-2 bar pressure (the slight pressure can aid the gas sample extraction). The autoclave and the heating mantle are seen in Figure 1. The temperature stability of the heating mantle was found to be too slow in its reaction; for this reason it has been decided to run the reaction at either ambient temperature or in the case of elevated temperatures to use an older autoclave jacket in the hot cell that has already been successfully used at elevated temperatures (~60°C). This hot cell will need adaptations for detachable connectors to the gas and liquid sampling lines of the autoclave. This will enable gas (and possibly liquid) sample extraction directly to the analytical glove box that is being constructed (see below). A small cylindrical volume has also been purchased for connection to the autoclave and which can act as an alternative gas and liquid sampling system (sample mouse). Ceramic (Al_2O_3) sample holders also need to be made by the workshops for installation in the autoclave. It is intended that the first autoclave test will be approaching completion as the commissioning of the glove box & its analytical techniques are ready. In a recent ITU –INE meeting (April 2015), preparation of the samples was discussed. This requires the sample to be cleaned of fuel and fission products from the upper fuel-free samples by aqueous or dilute acid cleaning (eg.1M HNO_3 or 16% H_2SO_4). For the fuel-containing samples, this requires cracking of the cladding samples to remove their fuel and, if possible, to cut up into small parts to optimise the surface area. In this case, estimates of the content in the surface oxide layer (as performed by RWMC [1] by separate dissolution of the external oxide layer beforehand) will not be possible. This may be considered in later tests. The first autoclave tests will be expected to start in the final quarter 2015 as the glove box commissioning is nearing completion.

The leaching solution will be NaOH solution, pH 12 at one test temperature: 30°C. The leach tests will be of 3 months duration. Separate gas and liquid samples will be taken at the end, with no intermediate samples.

The choice of simple NaOH solution was made at the last annual progress meeting as the possibility of calcite precipitation in more prototypical solutions of $Ca(OH)_2$ would lead to more variation in the individual testing conditions and determination of the total C-14 released into solution that would hinder comparisons between tests.

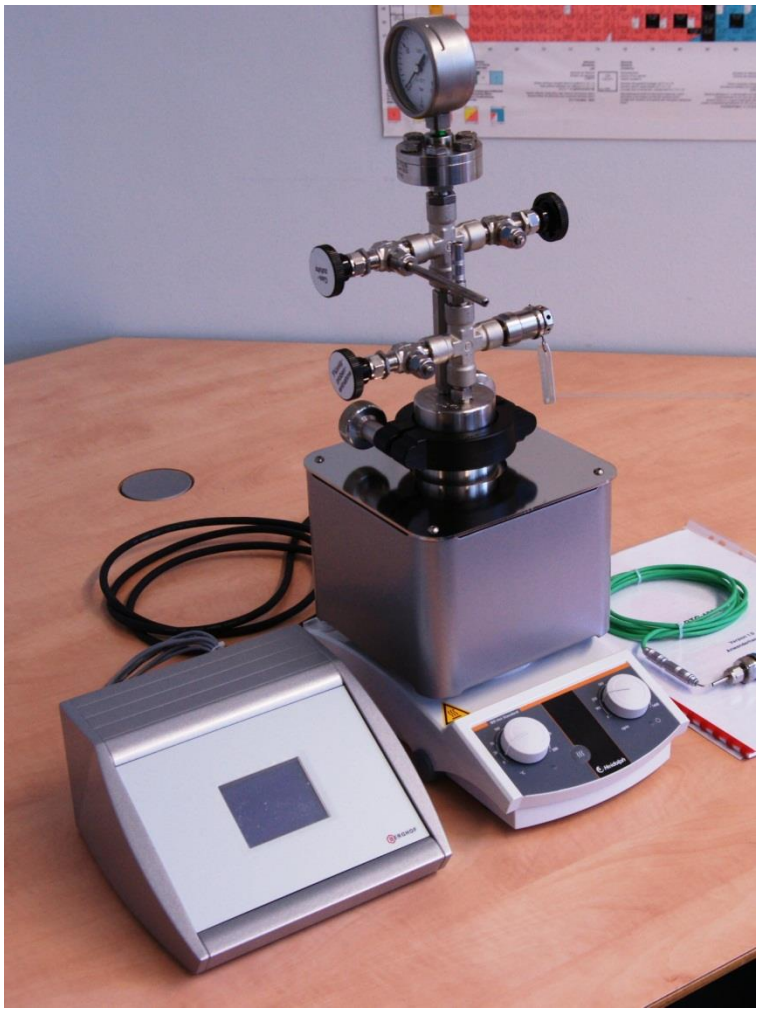

Figure 1: Autoclave with heating mantle and hot plate for assuring a constant temperature during the leach tests

3 Analysis

3.1 *Glove box preparation*

A glove box will be required to collect and analyse the carbon-containing gases and liquids from the autoclave. The gases will be transferred under a high purity N_2 gas purge of the autoclave to the glove box the gas purge lines will be passed over wash bottles for H^3 (5% H_2SO_4) and for I removal (4% $AgNO_3$) before being passed through an alkaline solution (2M NaOH) with scintillator (Carbosorb-absorber + Permaflor-scintillator- Perkin Elmer) for collection and subsequent LSC counting for C-14 determination in CO_2. There are also 2 switches in the gas line: a) one to enable the gas purge to pass over a furnace with CuO catalyst at 300-350°C to convert CO to CO_2 before collection & LSC counting and so determine the total C-14 content in CO & CO_2 forms; b) a second to route the gas purge through a second furnace at 750°C with CuO/ Pt on Al catalyst to convert CH_4/CO to CO_2 before capturing in the alkaline scintillation cocktail for counting & determination of total C-14 in CH_4/CO/CO_2 forms. In addition there is still the possibility of residual contamination from other radio-active fission products from the hot cells. In this case it may be necessary in addition to capture the CO_2 content on a molecular sieve in an ampoule (CARBOSPHERE® carbon molecular sieve (60/80 Mesh) [2] before performing the C-14 analysis. The ampoule will then be switched to a second high purity N_2 gas line which can purge the CO_2 captured on the sieve and collect it in a liquid scintillation cocktail ready for counting by LSC.

The liquid phase in the autoclave will be pumped from the autoclave directly into a bottle in the Hot Cell for direct transfer to an analytical glove box where the liquid will be heated under acidified (8M H_2SO_4) and wet oxidation (5% $K_2S_2O_8$ + 4% $AgNO_3$ catalyst) conditions to drive off the inorganic and organic fractions respectively and a pure N_2 gas flow passed through an alkaline collection bottle with scintillation chemicals and then through a oxidation furnace for conversion of CO/CH_4 to CO_2 and then through a second set of

alkaline collection bottles. Then the 2 sets of liquid aliquot would be ready for scintillation counting.

The C-14 analyses will be performed by existing beta (scintillation) counting equipment (Perkin Elmer Wallac Guardian liquid Scintillation Counter 1414 with Wimspectral software 2.0) already set up in a specific spectroscopy laboratory in ITU.

The analytical technique will be as close as possible to that used by KIT-INE. It is intended that ITU and INE will collaborate on the technical construction of the analytical glove box, firstly as to provide as similar and as optimum an analytical technique as possible (given INE's experience in this field) but also to enable the best possible comparison between the results from the two Hot Laboratories and reduce the detection level to the lowest possible. The draft design of the glove box and the necessary chemical glassware and ampoules have been submitted to the workshop. The design has been modified and accepted by the drawing office and a schedule was drawn up in early September 2014. The schedule foresees the main construction will be finished by June 2015 with further refinement in the following quarter. Some cold testing will be necessary of the glove box before it can be used on radioactive test aliquots.

In a joint INE-ITU meeting in early April 2015 the purchase of the same glassware (e.g. wash-bottles, 3-neck vessel and reflux columns and glass connectors) as used by INE was agreed. It will be bought from the KIT glass-blowing workshop for installation in the ITU glove box.

The analytical chemicals for LSC absorption & scintillation and the carbon molecular sieve (Carbosorb-Perkin Elmer) as well as the certified standards of C-14 (eg NIST traceable standards: stainless steel (NIST standard: # 493-12-2), high purity N_2 gas) will also be ordered at the same time. The remaining items of equipment to be purchased are an analytical balance and a vacuum pump with adjustable valve to ensure a constant, controlled gas flow under negative pressure. This will ensure an efficient transfer of the $^{14}CO_2$, including that from the oxidation of other ^{14}C-containing gases, to the absorbant solution

(NaOH) for measurement and avoid any unnecessary contamination of the glove box. A schematic diagram of the analytical glove box layout is shown in Figure 2 below.

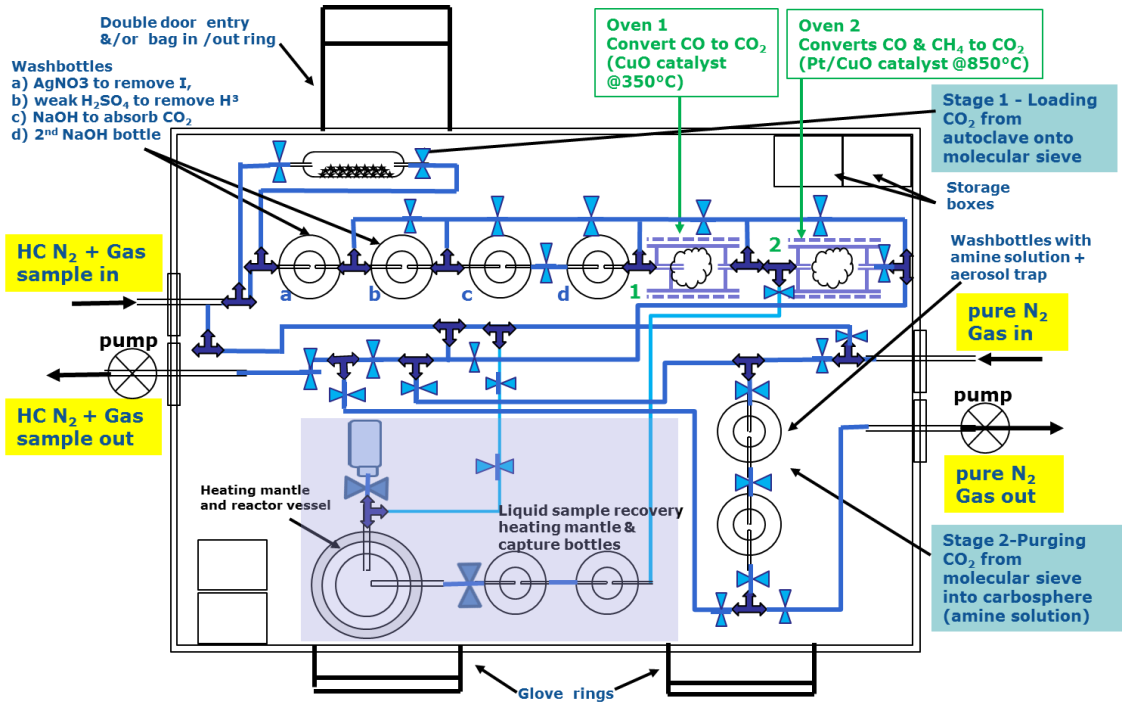

Figure 2 : Schematic layout of the C-14 glove box arrangement based on the design of the KIT-INE glove box for C-14 analytical glove box

3.2 *Device for total C and C-14 content determination*

ITU has located a suitable total (inorganic) C determination device suitable for metallurgical samples and adaptable to C-14 determination in the irradiated cladding samples. ITU has discussed the adaptations necessary with the manufacturer for the installation in a hot cell. The technical specifications and justifications were written and issued in a tender process. A Bruker ICARUS H4 total inorganic C determination device was selected and the contract signed by Dec. 2014. The planning is for 6 months construction and 2 months cold commissioning, followed by installation in a hot cell by September 2015. First tests could be possible for end 2015, with initial samples in the following months (early 2016). The device performs complete Zircaloy sample oxidation to convert the total inorganic C (in effect the total C content as there is no organic content in the samples) to CO_2. The CO_2

concentration is then measured directly by IR absorption for known sample weight. This yields the total C concentration. The induction heating furnace will be sited in the hot cell, while the analytical section will be located in an airtight unit attached next to the hot cell. The purge gas carrying the CO_2 from the oxidised sample will be passed over the measurement IR spectroscopy for on-line and accumulated CO_2 content, before passing back to the hot cells. It is intended to install a unit for a molecular sieve capsule, which can then absorb this CO_2 content. This can then be taken from this unit for transfer to the analytical glove box for purging with N_2 into an alkaline scintillation cocktail for C-14 measurement. The possibility of being able to determine the total N content in the cladding (by hot extractive analysis) is also being examined. A schematic diagram of the device and airtight instrumentation cabinet of the total inorganic carbon determination device is shown in Figure 3. The instrument cabinet will enable the determination and also the collection of C (and C-14) samples on a molecular sieve.

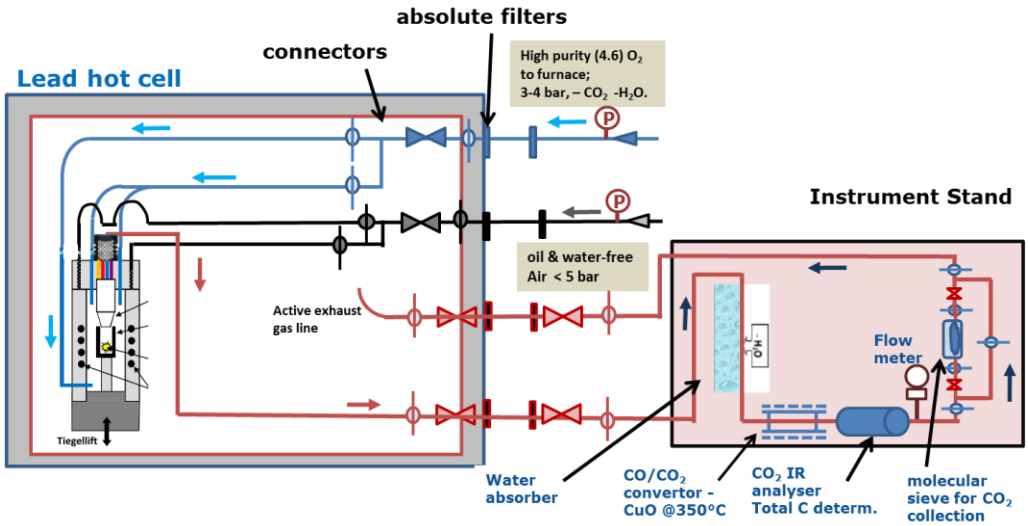

Figure 3: Schematic diagram of the total inorganic carbon determination (ICARUS – Bruker) that is to be installed in a lead hot cell for determination of the total C and C-14 by oxidation.

References

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