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# CArbon-14 Source Term

# CAST

## WP2 Annual Progress Report - Year 3, October 2015 – September 2016 (D2.6)

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| **PU** | Public | **X** |
| **RE** | Restricted to the partners of the CAST project | |
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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 re-lease 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*

*WP2 Annual Progress Report - Year 3 (D2.6)*

| **CAST** | | |
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## Executive Summary

CAST Work Package 2 (WP2) addresses the release and speciation of $^{14}C$ from activated steel during corrosion under conditions of a cement based deep geologic repository. Twelve organisations participate in WP2.

WP2 is subdivided into four tasks. In Task 2.1 a literature review is to be made; Task 2.2 aims at the development of analytical methods to measure the speciation of $^{14}C$ at low concentrations; in Task 2.3 leaching experiments will be performed with subsequent measurement of $^{14}C$ speciation and, finally, in Task 2.4 a summary and synthesis on the outcome of the experiments will be given. In the third project year, the participants were mainly engaged in Task 2.3.

The development of analytical methods and protocols to measure the release of $^{14}C$ from the activated steel samples and the speciation in the aqueous and gaseous phase was done by PSI and Armines in close cooperation with the partners from WP3 and support from other participants of WP2. The main work in Task 2.2 could be concluded after the second project year. The results of the method development are documented in D2.3, issued in the first half of the third project year, whereas a second report (D2.4) is still in review. Analytical methods to identify and quantify low molecular weight organic molecules as carrier of $^{14}C$ comprise High-Performance Ion Exchange Chromatography and Gas Chromatography, both coupled to Mass Spectrometry and are proposed for aqueous and gaseous samples, respectively. In most cases, a highly sensitive detection technique as Accelerator Mass Spectrometry will be needed to detect $^{14}C$ at the expected extremely low concentrations. A

technology has been developed for that and the experimental groups make effort to get access to this technique if necessary.

The preparation of the corrosion experiments to measure the release and speciation of $^{14}C$ in Task 2.3 has been concluded in the past reporting period. The installation and testing of the equipment in Hotcells or shielded gloveboxes as well as the preparation and characterisation of activated samples could be finalised in nearly all experimental groups. The required approval of the setup and the procedures could be obtained from the radiation protection commissioner. Consequently, the corrosion and leaching experiments could be started in all experimental programmes with the exception of JRC where the optimisation of the equipment is still in progress.

During the third project year, a common Technical Meeting with WP3 was held during the General Assembly Meeting on 13 October 2015 in Bucharest. A further Technical Meeting was organised by Ciemat on 01 – 02 June 2016 in Madrid. One deliverable was due in the second project year: this annual report, which will be issued in the next reporting period. The report on selected analytical procedures at PSI (D2.3), due in the end of the second project year, was issued in early 2016 and the corresponding report from Armines (D2.4) is still in preparation to be issued as soon as possible. No milestones have been defined in the third project year.

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# 1 Introduction

CAST Work Package 2 (WP2) addresses the release and speciation of $^{14}C$ from activated steel during corrosion under conditions of a cement based deep geologic repository. In many programmes, activated steel represents the major source of $^{14}C$.

Twelve organisations participate in WP2: Amec Foster Wheeler (UK), Armines (FR), Ciemat, ENRESA (ES), JRC (EU), KIT (DE), Nagra (CH; WP leadership), NRG (NL), PSI (CH), RWMC (JP), SCK·CEN (BE) and VTT (FI).

WP2 is subdivided into four tasks:

Task 2.1 provides a literature review on corrosion mechanisms and rates, the release of $^{14}C$ and its speciation.

Within Task 2.2 analytical methods are developed to measure the $^{14}C$ speciation at extremely low concentrations of $^{14}C$ in the liquid and gaseous phase. As this topic emerges in WP3 (Zircaloy) in a similar manner, the partners involved in these particular Tasks in WP2 and 3 cooperate closely.

Task 2.3 deals with the corrosion experiments using different materials and a range of experimental conditions. Subsequently, the speciation of $^{14}C$ is measured in the aqueous and gaseous samples.

In Task 2.4 an interpretation of the results and a synthesis with focus on the inventory, the release and the speciation of $^{14}C$ is documented in a final report.

This Annual Progress Report describes the activities and main results of the third project year (October 2015 to September 2016). The report is edited by Nagra and contains contributions from all participants.

# 2 Amec Foster Wheeler contribution to CAST WP2 Third Annual Report

As part of WP2, Amec Foster Wheeler are working in collaboration with NRG at Petten, to measure the releases of carbon-14 to the gas and solution phases from samples of irradiated stainless steel on leaching under anaerobic conditions at high pH. These experiments are being performed in the G1 chemical hot cell in NRG's Hot Cell Laboratories (HCL) at Petten (see Section 8). Amec Foster Wheeler through its sub-contractor RadioCarbon Dating Limited (RCD) is contributing the expertise in selective capture and quantitative analysis of gas phase carbon-14 to these experiments. Details of the experimental methodology employed by RCD were presented in the Second Annual Report [MIBUS *et al.* 2015b].

During Year 3 of the CAST project, work under a separate project from CAST concerned with the manufacture, installation and commissioning of all of the equipment required to perform the experiments planned by Amec Foster Wheeler and NRG under CAST, was completed successfully. This included the performance of a blank experiment designed to fully test the equipment and procedures before final installation and commissioning of the equipment in the G1 chemical hot cell. Details of the blank experiment from that work, including the gas phase results, are presented in in the NRG progress report (see Section 8).

The three CAST experiments started at NRG with addition of the NaOH solution leachant on consecutive days between 31 May and 2 June 2016. Sampling of the gas and solution phases was performed after 1, 3 and 6 week's duration. Samples of gas-phase carbon-14, selectively captured as $CO_2$, CO and hydrocarbon fractions absorbed onto soda lime columns at each duration (9 columns in total), were transported by courier to RCD in Oxfordshire, UK, in late July 2016 and are currently (30 August 2016) undergoing analysis.

Sampling after 3 months duration is planned at the end of August 2016.

Amec Foster Wheeler will contribute the gas-phase sampling results and interpretation of the data to the Final Report D2.8 on carbon-14 release and speciation from stainless steel under alkaline reducing conditions, which will be delivered by NRG to Nagra in April 2016.

# 3 Armines contribution to CAST WP2 Third Annual Report

## 3.1 *Introduction*

SUBATECH/ARMINES is in charge of the development of an analytical strategy for measuring the speciation of carbon-14 species formed during the corrosion of irradiated steels and Zircaloys under conditions relevant to cement-based repositories in aqueous solution.

During the third year of CAST project, tests on leaching solution treatment have been pursued and applied on real leaching samples provided by CEA-Marcoule on irradiated zircaloy hulls. Detailed methods and results will be available in deliverable D2.4 “Selected analytical procedures at Armines/Subatech” [BARHRI *et al.*, in prep. a] and in deliverable D3.9 “Quantification of $^{14}$C in liquid and gas phases” [BAHRI *et al.*, in prep. b].

This work was undertaken as part of WP2 and WP3 and has also been reported in the third annual progress report from WP3 [NECIB *et al.*, 2016].

## 3.2 *Analytical strategy: principle*

The proposed strategy aims to detect and quantify low molecular weight organic compounds released with extremely low concentrations, in presence with other radionuclides such as activated products, fission products and actinides. Characterisation of carboxylic acids with low carbon chain length is of importance since they are preferentially released compounds from Zircaloy and steels [SASOH, 2008; TAKAHASHI *et al.*, 2014; HEIKOLA, 2014]. Such characterisations will be performed thanks to the combination of Ion Chromatography (IC) and Liquid Scintillation Counting (LSC). Ion Chromatography technique will be used for the separation and the fractionation of the carboxylic acids present in the leachates. This technique is not enough sensitive to quantify the very low concentrations of small carboxylic acids expected in the leaching solution. Therefore, collected carboxylic acids fractions will be transferred to the LSC device for the quantification of carbon-14 activity. LSC is a sensitive analytical technique (detection limit DL 0.02 Bq/mL). For the extremely low activity level of leached $^{14}$C in the collected fractions, below the detection limit, the quantification of $^{14}$C in the collected fractions will be considered with a technique of ultralow detection limit such as the accelerator mass spectrometry (AMS) with an external laboratory. 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.

A second major objective developed at SUBATECH/ARMINES is to implement one simple and adapted method for the extraction of the main water soluble radionuclides besides $^{14}$C in the leaching solution using ion exchange resins. The resin treatment stage has several goals:

- Reduction of the total activity in leachates to avoid further dilution of the leaching solutions due to activity acceptance limits of the laboratories and to make easier the leachates handling;
- Limit the analytical devices contamination, especially for AMS analyses where institutions equipped with AMS cannot accept hot samples;
- Removal of the beta emitter radionuclides which interfere with the measurement of $^{14}$C activity by LSC. Indeed, some soluble radionuclides are negatively charged in the hydroxides or oxo-anions forms and thus may appear in the collected fractions preventing an accurate quantification of $^{14}$C using LSC.

The developed extraction method based on ion exchange resin meets two essential criteria: (1) minimisation of the number of treatment stages inducing a loss of $^{14}$C and (2) no alteration of $^{14}$C target molecules. Figure 3.1 shows the overview of this strategy.

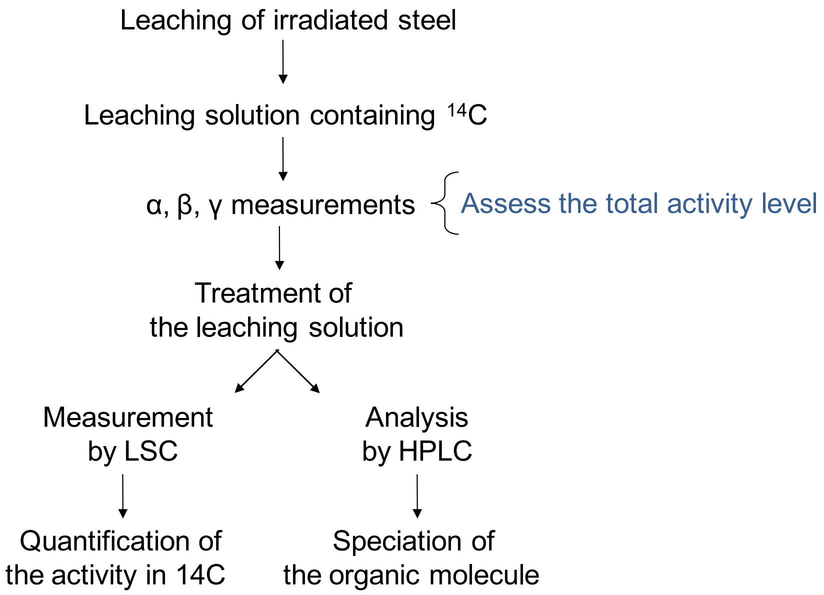


**Figure 3.1: Analytical strategy for the speciation of carbon-14 in solution. No studies for gaseous and volatile forms will be carried out.**

## 3.3 *Leaching solution treatments*

### 3.3.1 Removal of caesium

The caesium removal can be ensured using a resin such as inorganic ion exchanger like potassium hexacyanocobalt(II) ferrate(II), potassium hexacyanonickel(II) ferrate(II) and potassium hexacyanocopper(II) ferrate(II). These resins are good candidates for a rapid and quantitative fixation of caesium, stable over the entire pH range, efficient for any pH value ranging from acidic to alkaline, radiation resistant and have weak interaction with nonmetallic ions [COLLINS *et al.*, 1995; MIMURA *et al.*, 1997; KAMENIK *et al.*, 2012].

In this work, commercial potassium hexacyanocopper(II) ferrate(II) $K_2[CuFe(CN)_6]$ was tested for radionuclides extraction tests. An organic binding polymer based on polyacrylonitrile PAN is added to the active component to improve its mechanical and granulometric properties (Figure 3.2). Nevertheless, the free residual cyano groups of the polymer support are reactive toward carboxylic groups and lead to a significant loss of the target carboxylic acids in the leaching solution.

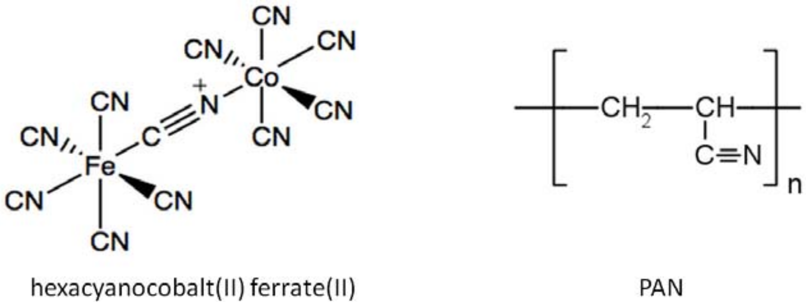


**Figure 3.2: Structure of potassium hexacyanocobalt(II) ferrate(II) resin and the organic binding polymer based on polyacrylonitrile PAN**

$K_2[CuFe(CN)_6]$ without binding polymer supplied by Areva STMI (Sociétés des Techniques en Milieu Ionisant) is considered in the experiments. The sorption measurements were made with batch equilibration tests containing 100 Bq of $^{137}Cs$. The remaining activity in the solution after resin contact is measured thanks to liquid scintillation counting. The same experiment is reproduced with $^{14}C$ labelled short chain mono- and di-carboxylic acids to verify the absence of interaction with the resin. Table 3.1 summarises the recovery of $^{137}Cs$

and $^{14}$C labelled carboxylic acid after contact. The obtained results validate the quantitative removal of caesium and the selectivity of the used resin.

**Table 3.1: Recovery of $^{137}$Cs and $^{14}$C labelled carboxylic acids after 1 hour contact with KCFC resin, initial activity was 100 Bq**

| Radionuclides | % Recovery |
|---|---|
| $^{137}$Cs | 1% |
| $^{14}$C formate | 100% |
| $^{14}$C propanoate | 99.5% |
| $^{14}$C butyrate | 100% |
| $^{14}$C oxalate | 96% |

### 3.3.2 Removal of cobalt, nickel, iron, chromium and manganese

Chelex 100 resin has a strong retention of multivalent transition metals, usually used for removing of trace metal contaminants in natural waters, stable over the entire pH range, the weak interaction with organic anions species, radiation resistant and used for extraction and pre-concentration of radionuclides [PAI, 1988; PAI *et al.*, 1988; ALLIOT *et al.*, 2013; PAKALNS, 1980]. Chelex 100 holds iminodiacetate ions acting as chelating groups for polyvalent metal ions. Figure 3.3 shows the structure of Chelex 100 resin at two different pH values.

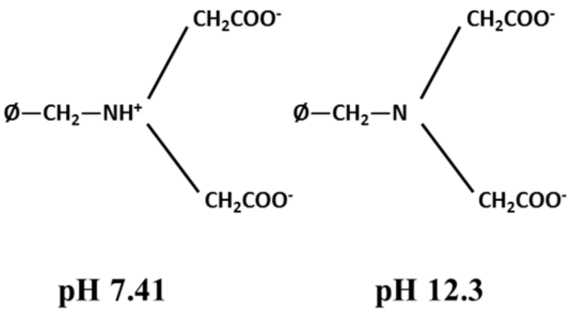


**Figure 3.3: Structure of Chelex 100 resin**

Under 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. Unlike KCFC, Chelex 100 efficiency is strongly pH dependent, the equilibrium pH value of the batch is a parameter that affects strongly the fixation of polyvalent transition metals [PAI *et al.*, 1988]. In this work, the pH value of the leaching solution, initially equal to 12, requires to be adjusted at neutral range to ensure free metal cations avoiding hydroxide complexes that cannot enter the bore structure of the resin [PAI, 1988]. At this acidification stage, carboxylic acids remain ionised as the pH is higher than their pKa (mostly smaller than 5).

Chelex 100 (Analytical Grade Chelex 100 Resin, 50-100 mesh, supplied by Biorad) batch tests were made; solutions containing radionuclides ($^{60}$Co, $^{63}$Ni and $^{14}$C) are put into contact with Chelex 100 under agitation for at least 24 hours. After centrifugation, the supernatant is recovered and the remaining activity of each tested radionuclide is quantified by liquid scintillation counting. The measurements summarised in Table 3.2 confirm the efficiency of removal of $^{60}$Co and $^{63}$Ni with Chelex 100 and the absence of interaction with $^{14}$C labelled carboxylic acids.

**Table 3.2: Recovery of $^{60}$Co, $^{63}$Ni and $^{14}$C labelled carboxylic acids after 24 hours contact with Chelex 100 resin, initial activity was 100 Bq**

| Radionuclides | % Recovery |
|---|---|
| $^{60}$Co | 5% |
| $^{63}$Ni | 3% |
| $^{14}$C formate | 100% |
| $^{14}$C propanoate | 93% |
| $^{14}$C butyrate | 98% |
| $^{14}$C oxalate | 98% |

## 3.4 Application of the analytical strategy on leaching solution of irradiated zircaloy hulls

Up to date, this analytical strategy was applied on leaching solution of irradiated Zircaloy. As a similar solution composition is expected in the steel experiments, the application of the approach will be shortly presented here. During the technical meeting in Madrid (1-2 June, 2016), NRG was interested to apply the decontamination process on their leaching steel solution to determine the speciation in organic matter. Discussions started on the feasibility of the application of the method, and on the management of sample shipment.

Leaching tests are carried out at CEA Marcoule using zirconium-niobium M5 alloys supplied by AREVA for use in WP3. Details on the experimental conditions and characteristics of the used Zircaloy cladding are presented in the D3.2 report [CARON *et al.*, 2014]. Details on the experimental conditions and results of decontamination and solution analysis are given in the D3.9 report [BAHRI *et al.*, draft]. Leaching experiments are carried out in alkaline solution pH 12 at room temperature (25°C) and anoxic atmosphere.

### 3.4.1 Decontamination using $K_2[CuFe(CN)_6]$ without binder polymer

After 14 days of leaching experiments, CEA-Marcoule sent the solution after filtration by PTFE membrane filter. The solution has been decontaminated by the resin $K_2[CuFe(CN)_6]$ without binder polymer due to its short time to reach equilibrium (one hour) and for its capacity for decontamination of several radionuclides encountered in the leaching solution. For an optimal sorption on resin, the leaching solution, with an initial pH of 12, was acidified by adding HCl. After contact with $K_2[CuFe(CN)_6]$, actinides were efficiently removed with a significant decrease of the total alpha activity. Likewise, total beta activity is considerably lowered to reach 50 Bq/mL. For gamma emitters initially present in the leaching solution, most noteworthy is the remaining activity due to $^{125}$Sb and $^{106}$Ru/$^{106}$Rh which were substantially decreased compared to their activities before contact with $K_2[CuFe(CN)_6]$.

After decontamination of the leaching solution, ion chromatography IC technique was used for the separation and the fractionation of the anionic carboxylic acids present in the leachates.

### 3.4.2 Ion chromatography of the decontaminated leaching solution

Decontaminated leaching solution has been injected into the chromatographic device with the following characteristics: eluent/mobile phase $Na_2CO_3$ (7.5 mM) and NaOH (0.75 mM), suppressed conductivity detection, separation column Metrosep Asupp 16 250-2.0, injected volume 250 µl, pump flow maintained at 0.15 mL/min to maximise the separation peaks. To analyse the $^{14}C$ related to 1 mL of the leaching solution, fractionation of the decontaminated leachates is repeated four times and the carboxylic acids are collected separately based on the retention time of the carboxylic acids standards. Figure 3.4 shows the chromatograms of the decontaminated leaching solution and the mixture of carboxylic acids standards. For the analysis of $^{14}C$ activity in the collected fractions, two peaks are selected: oxalate and butyrate with a total collected volume equal to 3 mL. The quantification of carbon-14 is therefore performed using LSC.

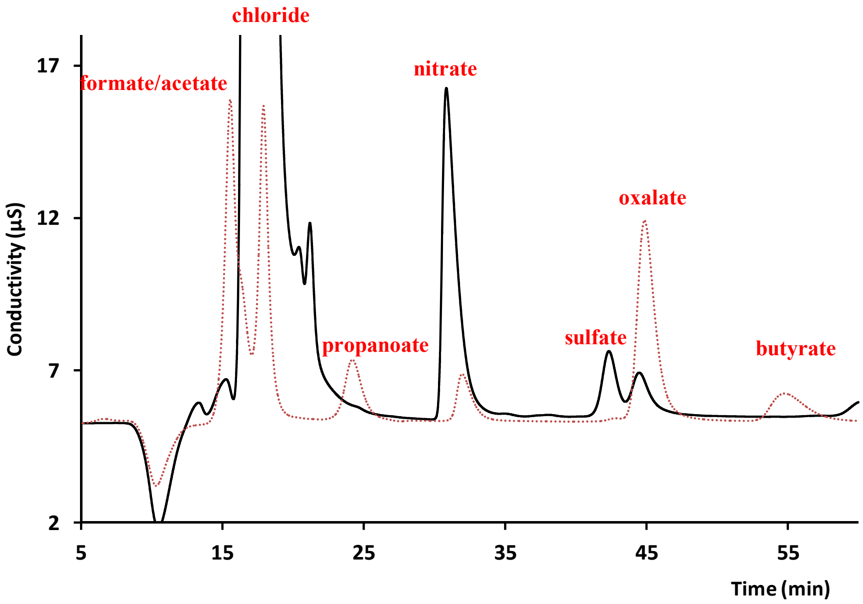


**Figure 3.4: Chromatograms of the decontaminated leaching solutions (solid line) and the mixture of carboxylic acids (dotted line). Mobile phase: $Na_2CO_3$ (7.5 mM) and NaOH (0.75 mM). Injected volume 250 µL**

### 3.4.3 Quantification of $^{14}C$ carboxylic acids in the decontaminated leaching solution by LSC

The quantification of carbon-14 containing organic compounds was performed by using a typical Tri-Carb counter for the three fractions collected with a detection limit of 0.02 Bq/mL and an efficiency of detection of 72% in Ultima Gold LLT Liquid scintillation cocktail. Table 3.4 summarises the activity obtained for two collected carboxylic acids expressed as counts per minute (CPM).

**Table 3.4: Activities in the carboxylic acids collected fractions**

| $^{14}C$ carboxylic acids | CPM | Bq/mL |
|---|---|---|
| Blank | 3 | |
| F4 - Oxalate | 7 → 4 | 0.03 |
| F5 - Butyrate | 5 → 2 | 0.02 |

The activities measured in the carboxylic acids collected fractions are extremely low and below the detection limit of the device. These results confirm that the $^{14}C$ carboxylic acid concentration is too low to be measured by LSC and it is necessary to use an ultra-sensitive detection method like accelerator mass spectrometry AMS to quantify the $^{14}C$ related to the carboxylic acids in the collected fractions.

### 3.5 *Summary*

In this work Subatech proposes an analytical strategy for the analysis of the $^{14}C$ carboxylic acids released from irradiated Zircaloy (WP3) and steels (WP2). 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 $^{14}C$ in the IC collected fractions. A method for extraction of the main aqueous 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 characterised by its selectivity for the identified radionuclides and the absence of interaction with target $^{14}C$ carboxylic acids. The experimental protocol combining IC and LSC further to filtration and resin treatment stages of the leaching solution from Zircaloy leaching shows that the $^{14}C$ carboxylic acid activities are below the quantification limits of LSC, *i.e.* 0.02 Bq/mL. Alternative methods such as the use of AMS will be considered. The next step would be the application of this method on leaching solution of irradiated steel, but discussion with NRG needs to continue.

# 4 Ciemat contribution to CAST WP2 Third Annual Report

## 4.1 *Introduction*

During the third year of the CAST project the following tasks have been carried out:

- preparation of the samples of activated stainless steel from reactor upper internals of José Cabrera NPP,
- set-up of the equipment acquired for speciation studies: Gas Chromatograph coupled to a Mass Spectrometer (GC-MS) and Ion Chromatography System (IC) and,
- design, development and implementation of the leaching experiments.

## 4.2 *Sample Preparation*

As it was mentioned in [MIBUS *et al.* 2015b] (section 4.2) the "Procedure for cutting irradiated metallic pieces which will be used for performing leaching assays" PT-URBMA-22-04 was modified in October 2015 (21/10/2015) and was approved, both by the Head of the Department for the Prevention of Occupational Risks and by the Head of the Department of Security and Licensing of Facilities of CIEMAT, in November 2015.

The Head of the Radiological Protection Department indicated (December 2015) that before cutting the sample, the piece had to be decontaminated. Once all requirements were fulfilled, the decontamination and cutting process were performed in June 2016.

The decontamination of the piece was carried out by dipping it in a solution with a sequestering agent (2%) in an ultrasonic cleaner (35 KHz) for 15 minutes.

The cutting of the piece was performed according to the procedure described in [MIBUS *et al.* 2015b] (sectoin 4.2). Four pieces were obtained as shown in Figure 4.1 - Right. The size of the 4 pieces was approximately 36 x 14 x 6 mm. Contact dose rates ranged between 25 and 60 microSv/h.

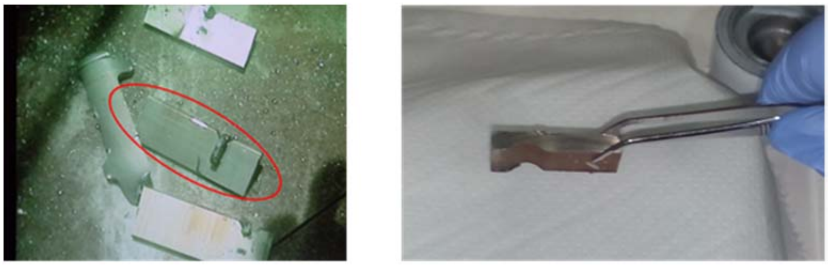


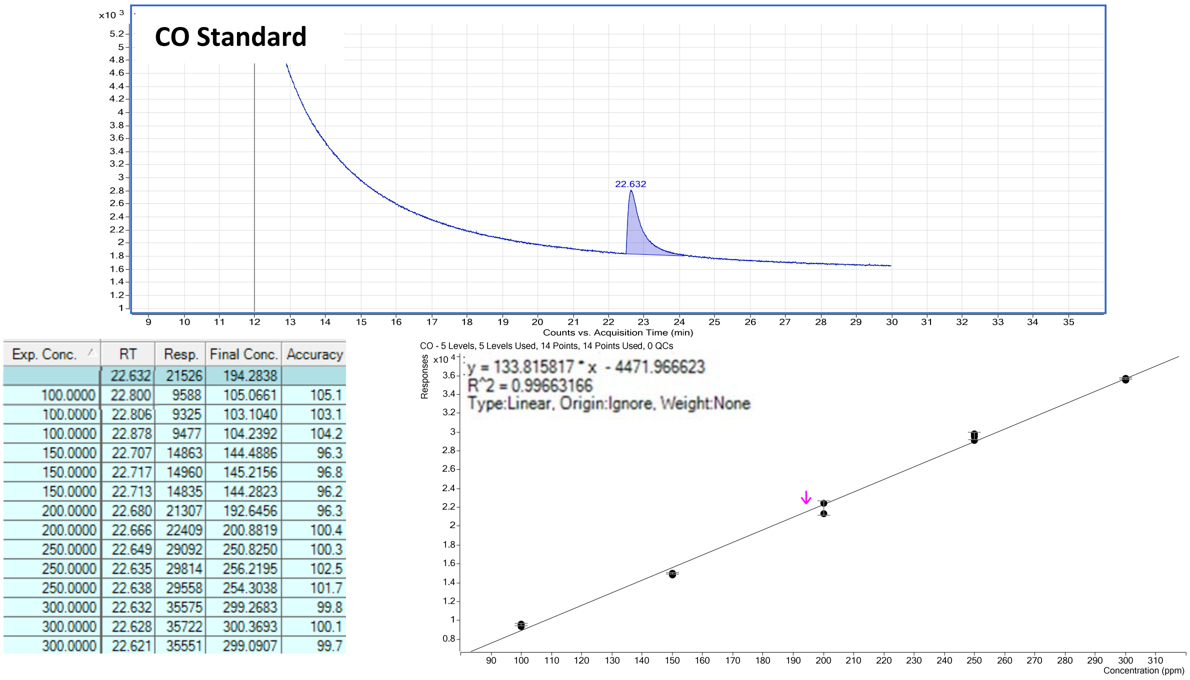
**Figure 4.1: Left: piece before cutting, right: one of the pieces after cutting**

## 4.3 Speciation

With respect to analytical requirements for speciation measurement during the third year of the project the work with the Gas Chromatograph and Ion Chromatography System was started.

### 4.3.1 Gas Chromatography coupled with Mass Spectrometry

Regarding the Gas Chromatograph (Agilent GC-MS 7890B), the column for analysing the permanent gases ($H_2$, $O_2$, $N_2$, CO), hydrocarbons C1 to C5 and $CO_2$ was chosen. At first, with the information given by Agilent Department and some bibliography it was expected that with the Molsieve 5A column (L = 50m; ID = 0.32 mm and F = 30µm) the permanent gases, hydrocarbons C1 to C5 and $CO_2$ could be analysed. However, after tests with a standard of $CO_2$ and varying some conditions, it was not possible to analyse $CO_2$ with this column. Therefore, the assays have been carried out only with a standard of CO in isothermal conditions (70ºC) and a Split Flow of 50 mL/min. With that, a good calibration curve has been obtained (Figure 4.2).



| Exp. Conc. | RT | Resp. | Final Conc. | Accuracy |
|---|---|---|---|---|
|  | 22.632 | 21526 | 194.2838 |  |
| 100.0000 | 22.800 | 9588 | 105.0661 | 105.1 |
| 100.0000 | 22.806 | 9325 | 103.1040 | 103.1 |
| 100.0000 | 22.878 | 9477 | 104.2392 | 104.2 |
| 150.0000 | 22.707 | 14863 | 144.4886 | 96.3 |
| 150.0000 | 22.717 | 14960 | 145.2156 | 96.8 |
| 150.0000 | 22.713 | 14835 | 144.2823 | 96.2 |
| 200.0000 | 22.680 | 21307 | 192.6456 | 96.3 |
| 200.0000 | 22.666 | 22409 | 200.8819 | 100.4 |
| 250.0000 | 22.649 | 29092 | 250.8250 | 100.3 |
| 250.0000 | 22.635 | 29814 | 256.2195 | 102.5 |
| 250.0000 | 22.638 | 29558 | 254.3038 | 101.7 |
| 300.0000 | 22.632 | 35575 | 299.2683 | 99.8 |
| 300.0000 | 22.628 | 35722 | 300.3693 | 100.1 |
| 300.0000 | 22.621 | 35551 | 299.0907 | 99.7 |

CO - 5 Levels, 5 Levels Used, 14 Points, 14 Points Used, 0 QCs

y = 133.815817 * x - 4471.966623
R^2 = 0.99663166
Type:Linear, Origin:Ignore, Weight:None

**Figure 4.2: CO calibration curve**

Further, with the column previously described it would be possible to analyse methane but at present the methane standard is not available in our facilities.

In June 2016, it was tested which column is suited to analyse the permanent gases, hydrocarbons and the $CO_2$. In accordance with reports from the literature it was decided to use a column Select Permanent Gases/$CO_2$ HR which is a combination of Molsieve 5A and PoraBondQ.

The optimal conditions to analyse different alcohol and aldehydes, in particular methanol, ethanol, formaldehyde (with a small amount of stabiliser, methanol, to suppress oxidation and polymerisation), acetaldehyde and propionaldehyde have been established. The column used was DB-624UI (L=60 m; ID=0.25 mm and F=1.40 µm). In this case the following gradient of temperature in order to separate the different peaks was applied: 40ºC (2 min); 1ºC/min to 45ºC (5 min.); 1ºC/min to 50ºC (5 min) and 50ºC (2 min) with a Split 100:1. The technique of head space sampling was used with 30 seconds of incubation time at 40ºC. A chromatogram performed with the standards, where it is possible to see different well-defined peaks, is shown in Figure 4.3.

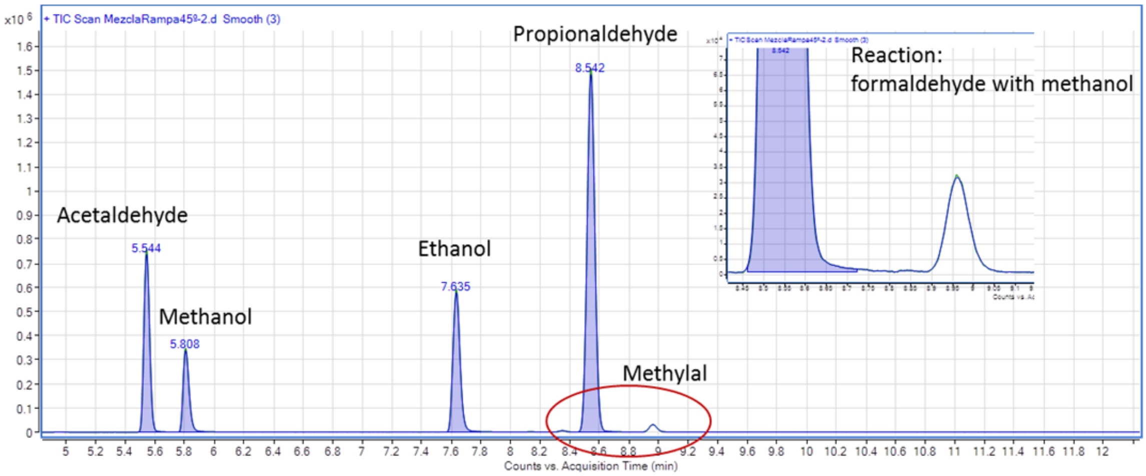


**Figure 4.3: Chromatogram performed with methanol, ethanol, formaldehyde, acetaldehyde and propionaldehyde standards**

### 4.3.2 Ion Chromatography

The conditions to operate the ion chromatograph using a conductivity detector, with samples corresponding to NaOH pH =12 leachant have been established. In this case the best results are obtained with the column AS-11, with a gradient of concentrations (1.5 mM KOH (0-8 min); 25 mM KOH (8-30 min) and 1.5 mM KOH (30-40 min) and a flow of 1 mL/min. The chromatograms obtained are shown in Figure 4.4 and the calibration curves in Figure 4.5.

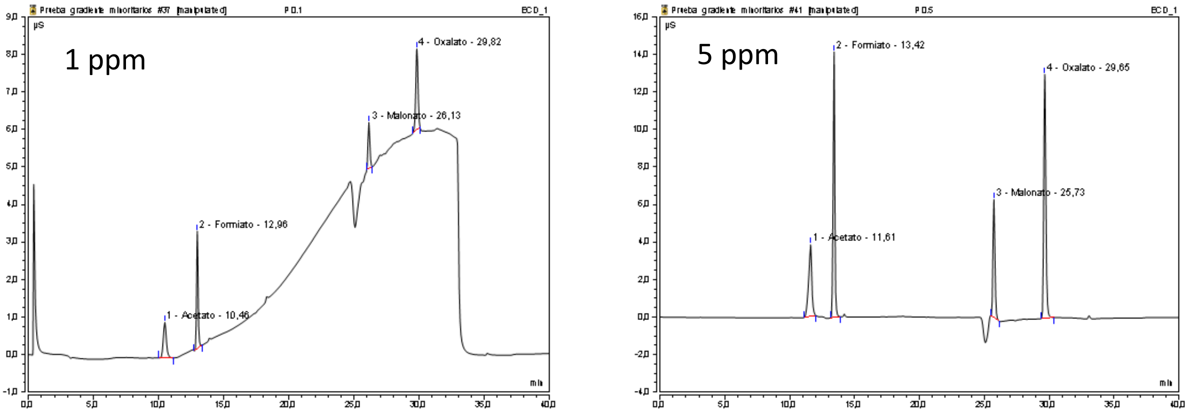


**Figure 4.4: Chromatograms performed with carboxylic acids standards (1 and 5 ppm)**

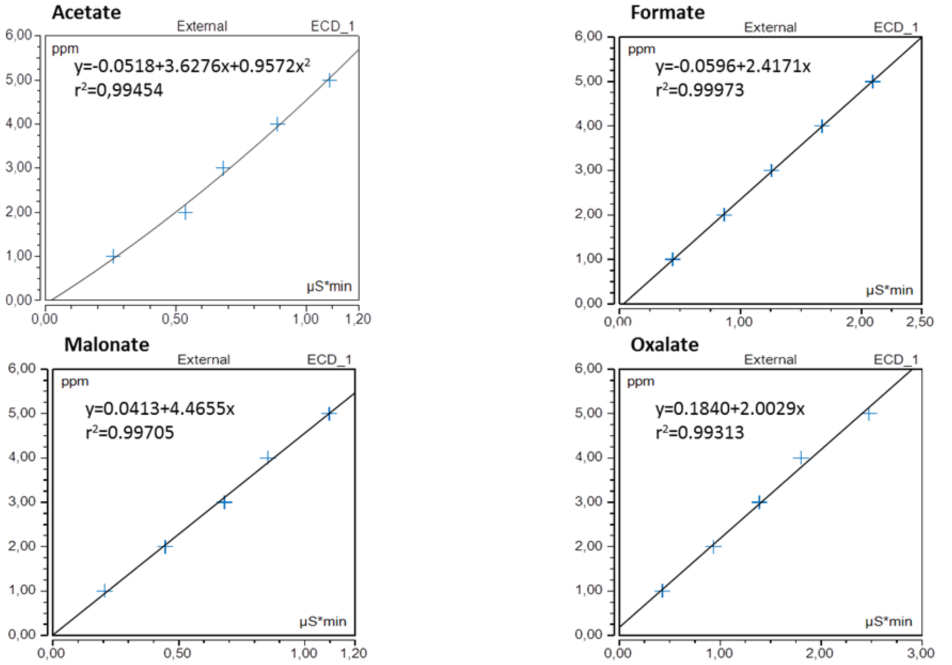


**Figure 4.5: Carboxylic acids (acetate, formate, malonate and oxalate) calibration curves**

## 4.4 Leaching Process

After cutting the sample pieces, the leaching process has been carried out as follows:

- Leaching experiments started in June 2016 with two samples. As leachant NaOH pH = 12 and $H_3PO_4$ 1M pH = 1.3 is used.

- The leachant container is made of PTFE (material recommended for its chemical inertness). The value of the ratio of the leachant to the exposed geometric surface area of the specimen is 0.2 m. This geometric surface area is calculated from measurements of the overall macroscopic dimensions of the specimen. During the leach tests carried out by now, although the tests have been conducted at room temperature, the losses of leachant by vaporisation are negligible.

- The specimen is suspended in 120 ml of leachant by means of a PTFE thread (Figure 4.6) and surrounded by at least 1 cm of liquid in all directions. The total volume of the vessel is 150 ml. Before using the containers, these were cleaned with milli-Q water. The stainless steel pieces were cleaned with acetone and milli-Q water.

**Figure 4.6: Leaching container**

- A mixture of $N_2$ and $O_2$ (21% oxygen, 79% nitrogen) gas has been introduced at a pressure of 1 bar in the containers to assure that the leaching process takes place under aerobic conditions. This synthetic air is supplied from a 5 litres pressure vessel.

- It is foreseen to renew both the gas and the leachate after 14, 28, 56, 90, 180 and 360 days from the start of the test. The periods corresponding to 14, 28, 56 and 90 days have been already covered.
- After each interval, first of all the gas sample (volatile species) is collected through the gas sample extraction valve by means of a gas tight syringe and immediately injected into the GC-MS system. After completing the previous step the container is opened, the specimen is removed from the leachant, and the leachate is transferred to a bottle which is labelled and stored for ulterior analysis (LSC, Gamma Spectrometry, GC-MS and IC).
- After storing the leachate, the PTFE is rinsed with milli-Q water, refilled with fresh leachant, the specimen immersed in the liquid and, after purging with synthetic air, the reactor is closed with the headspace.
- The leachate samples of the periods corresponding to 14, 28, 56 and 90 days have been taken to analyse $^{14}$C with a Quantulus LSC system, and gamma emitters with a Canberra BEGe 3830 HPGe Detector.
- The gas and leachate volatile species are being measured with an Agilent GC-MS 7890B system (Agilent DB624UI 60m column type for liquid samples and Molsieve 5A Porabond Q column for permanent gases and CO2) and the organic dissolved species (carboxylic acids) with an IC Dionex ICS-900 Ion Chromatography System with Ionic Reagent Free Controller (RFC) with an AS11-HC column.
- The data obtained up to now are in process.

# 5 ENRESA contribution to CAST WP2 Third Annual Report

## 5.1 *Scope of the test*

The goal of this work is to determine the behaviour of activated stainless steel under standard leaching test performed at El Cabril repository. The piece tested is a part of guide tube of the upper internals of the José Cabrera NPP that is being currently dismantled.

The work is mainly focused on the $^{14}C$ release, but also on other radionuclides measured in the piece with the aim to determine the retention capacity of the activated stainless steel, and therefore to assess the required treatment and additional barriers for the fulfilment of Waste Acceptance Criteria.

In the past project year, work focused on the development of the AMS scheme to analyse $^{14}C$ at very low concentration level.

## 5.2 *AMS scheme*

Currently the samples of every step in the leaching experiment of the activated piece of the internals are being analysed by AMS in the National Centre of Accelerators in Seville.

The standard sample preparation for the measurement of $^{14}C$ by using AMS technique is shown in Figure 5.1 and consists basically of:

1. Incorporating the carbon of the sample in a carbonate form by precipitation with calcium nitrate.
2. Bubbling the flask with He to remove $CO_2$.
3. Hydrolysis of the calcium carbonate by phosphoric acid.
4. Transport of the produced $CO_2$ to the graphitisation system.

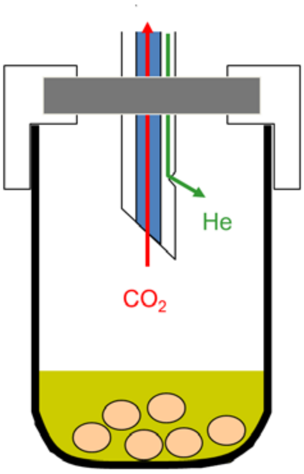


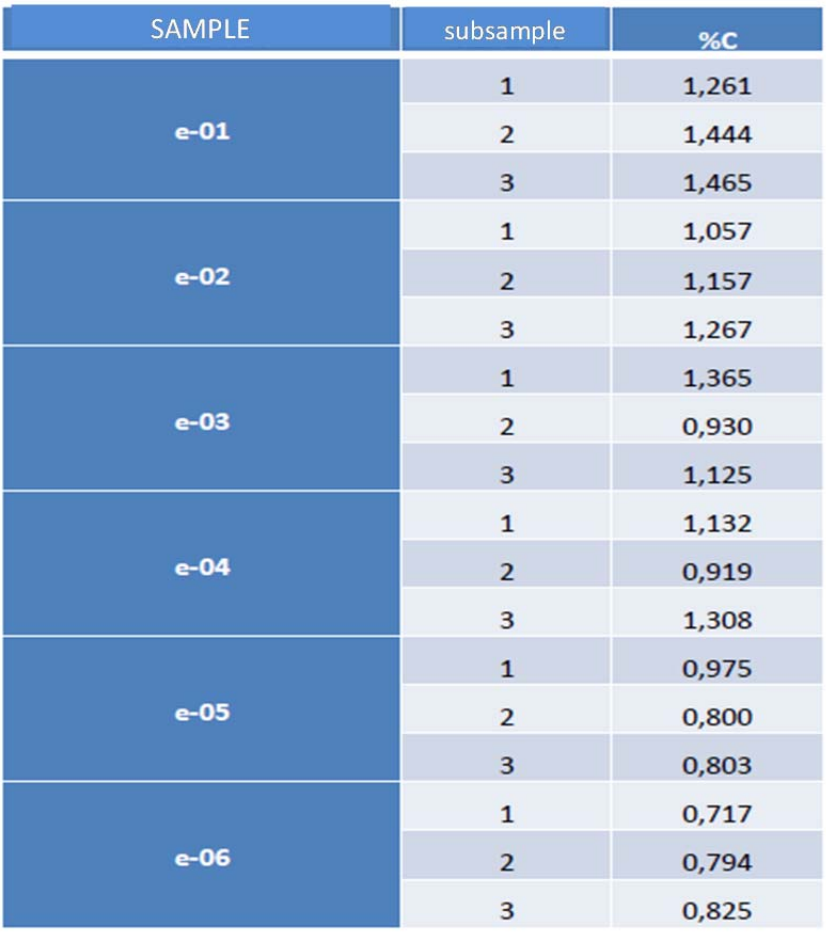
**Figure 5.1: Hydrolysis of calcium carbonate sample to produce $CO_2$ and to send to the graphitisation process**

Two approaches are used for the sampling preparation before the graphitisation process:

- Carbonate precipitation prior to the hydrolysis step, as indicated.
  No volume restriction is required in this case and the technique allows to measure very low $^{14}C$ content. On the other hand it takes longer time to be implemented.
- Direct Hydrolysis of the liquid sample without previous precipitation.
  This technique has a volume restriction and the carbonate concentration has to be above a threshold, but in this case, a direct measurement of the sample is possible.

Prior to these processes, a measurement of the carbon content in the different subsequent steps in a leaching experiment using an unirradiated test sample has been performed, obtaining values (weight percentage of the total carbon inventory of the sample, Table 5.1).

**Table 5.1: Percentage of carbon released from an unirradiated sample in the leaching steps e-01 to e-06**



| SAMPLE | subsample | %C |
|---|---|---|
| **e-01** | 1 | 1,261 |
| | 2 | 1,444 |
| | 3 | 1,465 |
| **e-02** | 1 | 1,057 |
| | 2 | 1,157 |
| | 3 | 1,267 |
| **e-03** | 1 | 1,365 |
| | 2 | 0,930 |
| | 3 | 1,125 |
| **e-04** | 1 | 1,132 |
| | 2 | 0,919 |
| | 3 | 1,308 |
| **e-05** | 1 | 0,975 |
| | 2 | 0,800 |
| | 3 | 0,803 |
| **e-06** | 1 | 0,717 |
| | 2 | 0,794 |
| | 3 | 0,825 |

# 6 JRC-ITU contribution to CAST WP2 Third Annual Report

## 6.1 *Materials*

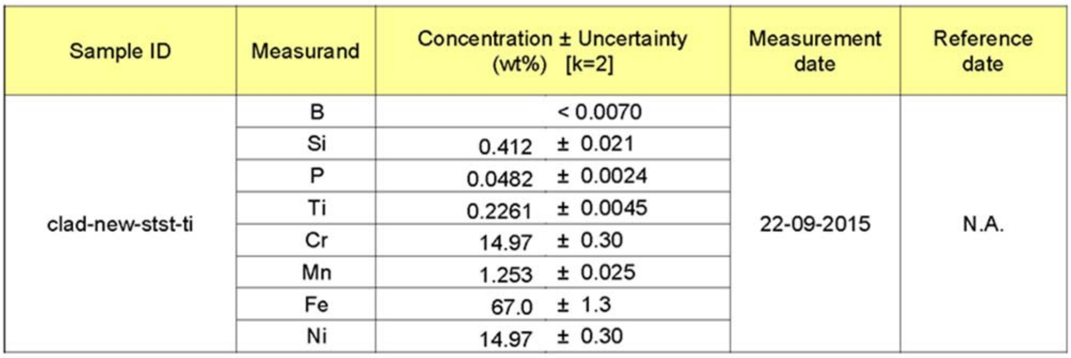
### 6.1.1 Cladding Analyses

The irradiated stainless steel cladding (15Ni-15Cr-Ti) was from a fast reactor fuel (NIMPHE) irradiated in the Phénix fast reactor. The fuels were mixed (U, Pu) carbide and nitride fuel. Ring samples of cladding have been cut from both carbide and nitride fuels. More details of the fuel have been given in the previous year's report.

The main analytical technique was ICP-MS for the metallic elements, while the inorganic elements (C, N, O) were measured by a metallurgical hot extraction technique to more accurately determine the elements that are responsible for $^{14}C$ production in the cladding.

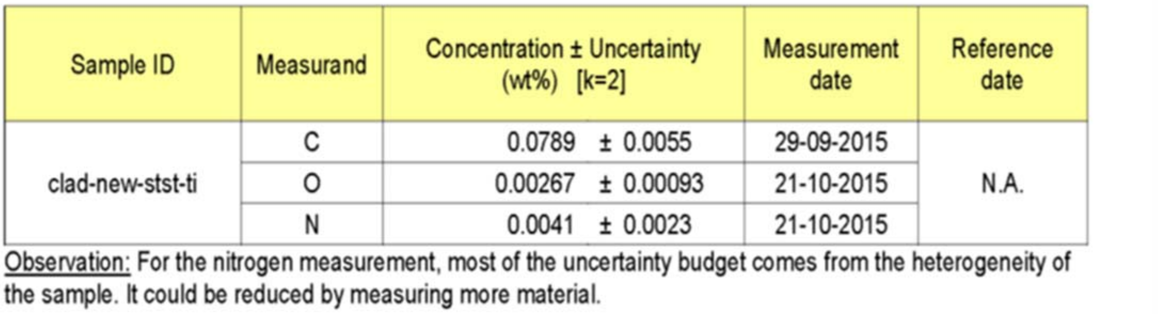
Tables 6.1 and 6.2 show the analysis of the (15-15-Ti) stainless steel cladding. The values for the main elements have been confirmed as14.97%Ni and 14.97% Cr with 0.22% Ti (and 0.4% Si). All these confirm the specified values for this material. The inorganic elements were given as C: 789 +/-55ppm, N= 41 +/-21ppm, and O 27 +/-9ppm. The carbon is specified as <0.1% and so within the specification.

**Table 6.1: Concentration results from ICP-MS measurements**



| Sample ID | Measurand | Concentration ± Uncertainty (wt%) [k=2] | Measurement date | Reference date |
|---|---|---|---|---|
| clad-new-stst-ti | B | < 0.0070 | 22-09-2015 | N.A. |
| | Si | 0.412 ± 0.021 | | |
| | P | 0.0482 ± 0.0024 | | |
| | Ti | 0.2261 ± 0.0045 | | |
| | Cr | 14.97 ± 0.30 | | |
| | Mn | 1.253 ± 0.025 | | |
| | Fe | 67.0 ± 1.3 | | |
| | Ni | 14.97 ± 0.30 | | |

**Table 6.2: Concentration results from ELANA measurements**



| Sample ID | Measurand | Concentration ± Uncertainty (wt%) [k=2] | Measurement date | Reference date |
|---|---|---|---|---|
| clad-new-stst-ti | C | 0.0789 ± 0.0055 | 29-09-2015 | N.A. |
| | O | 0.00267 ± 0.00093 | 21-10-2015 | |
| | N | 0.0041 ± 0.0023 | 21-10-2015 | |

Observation: For the nitrogen measurement, most of the uncertainty budget comes from the heterogeneity of the sample. It could be reduced by measuring more material.

Therefore there was a need to re-determine these values for the stainless steel. This was then performed by an external company (Bruker in June 2016) testing, cleaned and degreased ~0.5g ring samples (3-5x). The results are given in Table 6.3 along with the previous values (the Zircaloy values are given for comparison but are reported in the WP3 annual report).

The oxygen levels also appear to be low in the stainless steel cladding (~20 +/-10ppm) compared to the Zircaloy -4 cladding (1170ppm +/-190ppm). This is not unexpected given the great affinity that Zr has for oxygen.

**Table 6.3: Retesting of unirradiated small ring samples of Zircaloy -4 and 15—15 Ti stainless steel cladding material (Bruker)**

| **Cladding** | **Carbon Content (ppm)** | | **Nitrogen content (ppm)** | |
|---|---|---|---|---|
| | 1st test | Retesting | 1st test | Retesting |
| 15-15-Ti stainless steel | 789+/- 55ppm (4 samples x 0.4g) | 971 +/- 7ppm (5 samples x ~0.12g) | 41 +/- 23ppm (4 samples x 0.4g) | 75 +/-6 ppm (5x 0.1g samples) |
| Zircaloy -4 | <500 ppm | 91 +/- 3 ppm<br>(3 samples x 0.4g) | 44 +/-10 ppm<br>(4 samples x 0.5g) | 31 +/-5 ppm<br>(5x 0.1g samples) |

Finally the work shows that the stainless steel has low N and O content but high C contents. This indicates that C content can still have some impact on the total $^{14}C$ content given its high C content compared to the low Nitrogen content (10 x lower). The comparison shows that the $^{14}C$ inventory may come from different sources in the two materials.

### 6.1.2 Modelling data

The above values could be used for modelling the expected inventory for the cladding materials. Here R. Dagan (KIT-INR) has already performed some initial calculations using this data and that of INE's irradiated cladding. This preliminary data suggests an approximate value of 110 kBq/g for the stainless steel cladding. This suggests estimates of 250- 300 Bq for ~1µm of total corrosion of the stainless steel. There are no measurements at present at ITU to compare with these modelled values. Modelled estimates of INE's samples (with a more accurate C value) appear correspond well to their measurements. We have not yet had any feedback from NAGRA on their modelling.

## *6.2 Preparation of samples for leach tests*

Samples have been cut as 3-8mm long rings (1-0.5g) for the NIMPHE carbide & nitride breeder fuel. The NIMPHE nitride cladding has been defueled; the carbide cladding is to be defueled next.

a) Figure 6.1 shows a carbide fuel with a thin, dark adherent oxide. They are waiting for cleaning (& measurements) in preparation for leach testing. The cleaning is done by $HNO_3$ immersion for removal of the remaining fuel (2x 15 min in 8M $HNO_3$), rinsed followed by a final ultrasonic clean in distilled water for 15 min then finally dried in air. This may affect the external oxide film. Again the unirradiated material will cleaned (as with the Zircaloy 4 samples) with a degrease in alcohol, rinse in distilled water and then air dry.

a)  b)

**Figure 6.1: Sample of Nimphe carbide fuel that is defueled showing the dark thin adherent oxide on the cladding before cleaning.**

## 6.3 Preparation of an analytical glove box for carbon-14 analysis

The following progress in adaptations has been made:

- The furnace & round–bottomed flask heating have been tested; the balance was tested, stand for wash bottles set up, bottles mounted and gas lines connected (clasps to be ordered). Flowmeters and pumps installed and tested,

- Water cooling for the condenser of the flask (& pump) have been installed along with glove box filters on top of the glove box (GB)-see Figure 6.2,

- Protective metallic grids installed to prevent glove contact against hot surfaces on furnaces and tested (Figure 6.3).

Testing still needs to be on the gas line tightness with better clamps (already ordered). The GB will set up in wing B on a gallery area behind the hot cells together with GB atmosphere purification system. The gas connection system on the glove box needs to be added as well as fabrication of the gas collecting tube itself (see below).

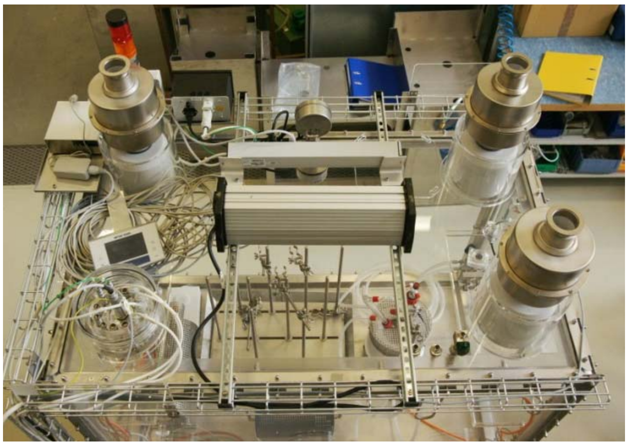
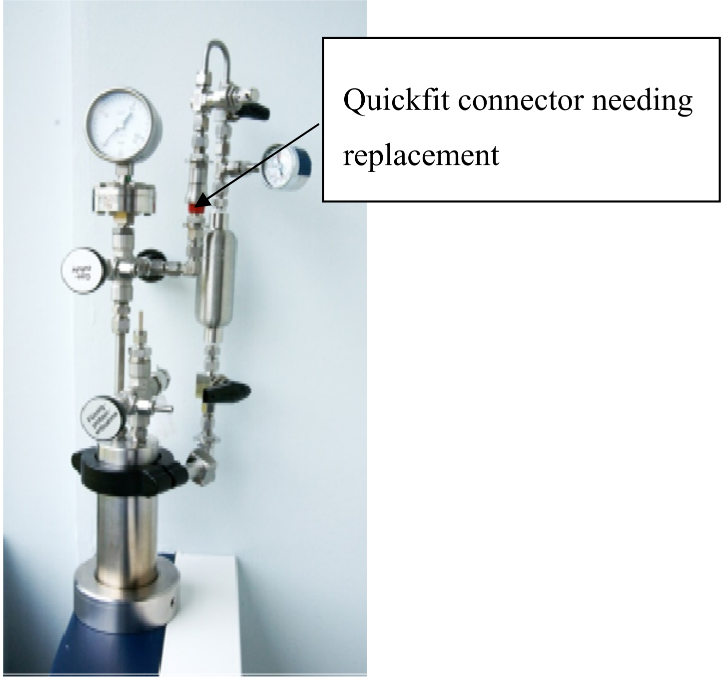


**Figure 6.2: Photograph showing the additional work on the glove box roof: glove box (GB) filter system and GB lighting placed on top**

**Figure 6.3: Horizontal view with the heating element and furnace with the additional shielding for protection against hot areas during operation of the furnaces**

## 6.4 Preparation of existing and additional autoclaves for leach tests

ITU will use an existing stainless steel autoclave that has been adapted and its PTFE lining replaced by PEEK. A heating plate & jacket is available (one inside the cell and another in reserve) and will be used for the higher temperature test at 80°C using the thermocouple in the heating block for approximate but more robust temperature control. The other tests at 30°C will be effectively at ambient hot cell temperatures. Tests will be of 3 months length with a single sampling (gas & liquid) at the end of the test. The pressure will be 1-2 bar. A gas collecting tube with special connections had been fabricated for ease of connection and detachment and the autoclave had been designed with matching connections. However during a visit to INE (July 2016) to examine the method in detail, it was noted that the connection system was not of sufficiently airtight to take a good sample from the autoclave without contamination transfer to the glove box (Figure 6.4). Therefore new connectors had to be ordered and added to the autoclave, the gas collecting tube (and finally the glove box). Also the liquid injection system and gas collecting tube volume estimation need to be performed before an active autoclave test can be carried out.



Quickfit connector needing replacement

**Figure 6.4: Autoclave with gas collecting tube attached. The connection requires improvement in order to allow optimum sampling and avoid transfer of contamination to the $^{14}$C analytical glove box.**

In order to try to recover time, new autoclaves have been purchased to perform the unirradiated testing capable of 10 bar up to 100°C; they have a borosilicate glass base and a PTFE cover with a sampling port. They need an injection/extraction system adding for sampling and transfer to the glove box line.

In addition, the purchase of further 150ml (200bar) stainless steel autoclave with PEEK lining is underway in order to increase the capacity for testing for the irradiated cladding samples.

## 6.5 *Progress in ICARUS installation for total carbon content*

A HF ICARUS G4 device has been purchased from Bruker, Karlsruhe. It can measure total inorganic carbon content of metallic samples. It has been designed specially with the transformer & rectifier separated from the induction furnace (where the sample is oxidised and $CO_2$ produced) and placed outside. In addition much of the analytical components will remain outside the hot cell. After construction and the initial testing at Bruker, delivery and successful commissioning took place at JRC-ITU-Karlsruhe in June/ July 2016. The device is now awaiting final cleaning of the lead hot cell. The hot cell can then be opened and the device installed and connected up. A small glove box will be added (in front of the hot cell next to the analysis unit) to include a filter on the exhaust gas line to collect all the $CO_2$ in the line for transfer to the $^{14}C$ analytical glove box for analysis. It is expected that the installation in the hot cell of the device will take place by the end of the year with active operation in 2017.

## 6.6 *Overall Schedule*

Some irradiated samples need only to have final characterisation before they are ready for testing. Until now only one unirradiated sample has been tested. A second (active) test has been delayed by finalising the last details of the gas collecting tube and liquid sampling systems. The construction is very dependent on the need to ensure that the gas collecting tube or liquid sample is not contaminated by gamma-emitting isotopes in a hot cell that has considerable contamination everywhere; thus we are following the advice and techniques of INE. The use of two autoclaves and a smaller autoclave for inactive testing should compensate for this loss of time. The second aspect is the design of the glove box. The construction is nearing completion but again the final details of connectors for the gas collecting tube and transfer of liquid samples need to be carefully worked out to optimise cleanliness.

The current schedule is to try to have the first irradiated test going by October 16 and carry out 3 Zry + 3 Stainless steel tests by October 17 (assuming the 2nd autoclave is active by January 17). Unirradiated samples will be done in parallel. This assumes post-test analysis (gamma–spectroscopy) as well as metallography & SEM-EDS of selected samples will be possible during this time.

The next aspect is the operation of the glove box. If this is ready by late 2016 with testing using $^{14}C$ calibration sources for verification, then it could be in operation from early 2017 until December 2017; this should be sufficient time to do all $^{14}C$ analyses of the gases and leach solutions.

Finally the installation of the Bruker device in the hot cell is due to be carried out late this year; final adaptations (the glove box) for the $^{14}C$ collection in the molecular sieve could be completed by early 2017. This could then be used for doing the key samples by June-October 2017.

The aim will be to obtain as many results by June-October 2017 to enable a reasonable time for integration and assessment of the new data.

# 7 KIT-INE contribution to CAST WP2 Third Annual Report

## 7.1 *Introduction*

After successful development and testing of the $^{14}C$ separation, quantification and speciation methods in the beginning of 2015, KIT started dissolution experiments involving irradiated Zircaloy-4 cladding specimens (within CAST WP3). Following further improvements of the separation and analysis techniques, $^{14}C$ was successfully separated from other radionuclides present in the irradiated cladding in gaseous and aqueous samples in the second half of 2015. In parallel to the $^{14}C$ dissolution, extraction and analysis experiments involving the irradiated Zircaloy-4 specimens (dose rates (DR) < 0.3 mSv/h) performed in a glove box, preparation of small subsamples of a highly activated plenum steel spring (DR ~1,600 mSv/h) in the shielded box-line of KIT-INE was performed. Moreover, the experimental set-up for the dissolution experiments of irradiated steel specimens in an autoclave equipped with gas sampling device was developed and installed in a shielded box.

Finally, dissolution experiments involving small subsamples of the irradiated stainless steel spring (X7CrNiAl17.7 steel, DR < 150 mSv/h) and separation and analysis of $^{14}C$ in the irradiated material has started in the beginning of 2016. Sample preparation, sample dissolution and first preliminary results obtained from investigation of irradiated steel samples are summarised in the following sections.

## 7.2 *Preparation of steel subsamples*

Preparation of specimens from the stainless steel plenum spring of an irradiated $UO_2$ fuel rod segment was conducted by means of remote handling in a shielded box. Until now, three specimens were dry cut using an IsoMet® low speed saw (11-1180, Buehler Ltd.) equipped with an IsoMet® diamond wafering blade (11-4254, Buehler Ltd.). Cutting was very slow (ca. 5-10 hours per sample) to prevent overheating of the material. Characteristics of the subsamples are given in Table 7.1 as well as photos of the preparation in Figure 7.1. Due to the high dose rate of the subsamples, also dissolution experiments had to be performed in a shielded box.

**Table 7.1: Characteristic data of the irradiated steel subsamples**

| specimen | #1 | #2 | #3 |
|---|---|---|---|
| **mass [g]** | 0.283 | 0.356 | 0.047 |
| **dose rate [mSv/h]** | < 150 | < 230 | < 25 |

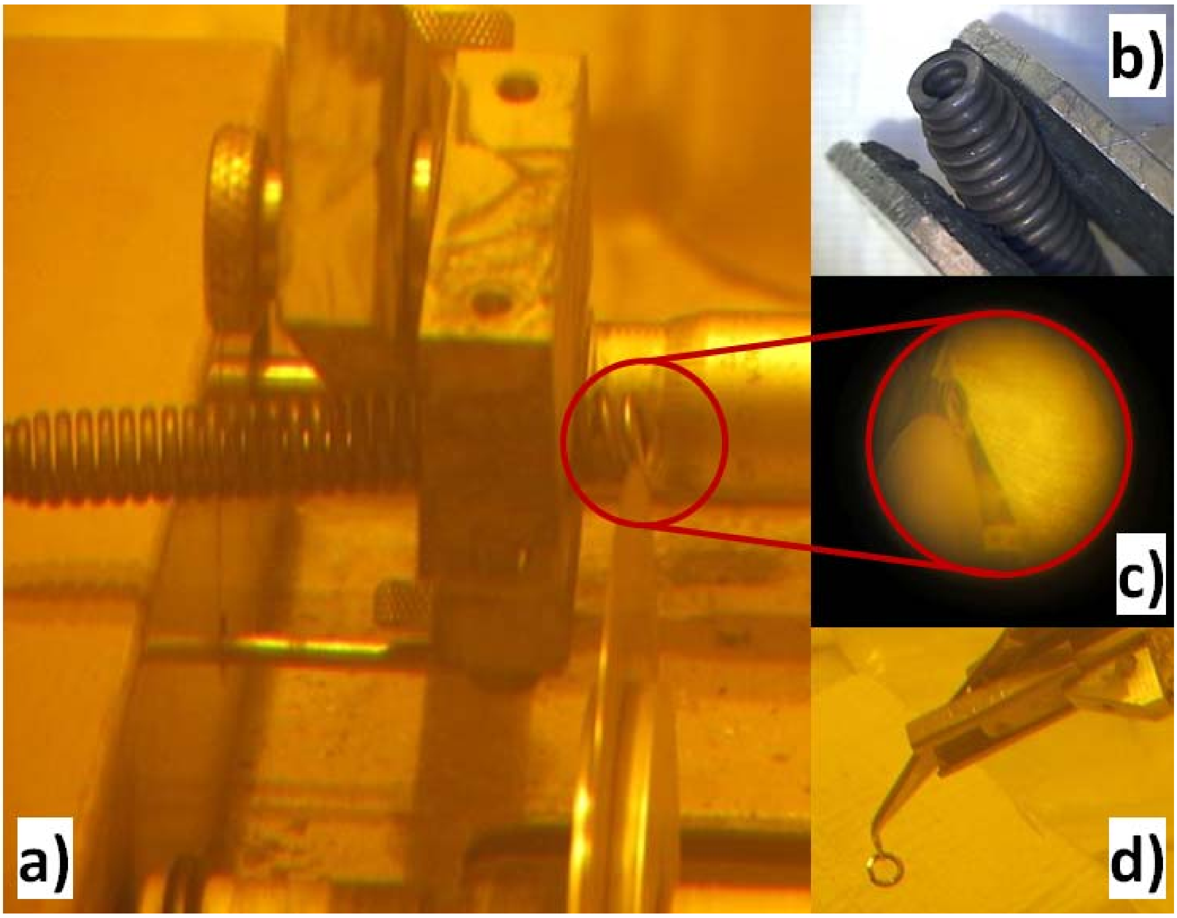


**Figure 7.1: a) low speed saw and steel spring during the cutting process, b) plenum spring before cutting, c) detailed view of the blade, cutting slowly through the sample, d) subsample prepared for the dissolution experiment**

## 7.3 Subsample dissolution in an autoclave

A stainless steel specimen was placed in an autoclave equipped with a PTFE liner and a double ended gas collecting cylinder. The autoclave was flushed with argon for about 20 minutes. A mixture of 150 mL 24% $H_2SO_4$ + 3% HF was added through a tube using a syringe. After the addition, all valves in the lid of the autoclave were closed. The sample was digested within a day. However, to ensure complete digestion, sampling of the gaseous and aqueous phase was performed on the following day. Photos of the experimental set-up are shown in Figure 7.2.

The evacuated gas collecting cylinder was opened and the gas phase collected within two minutes. Finally, the autoclave was opened and the digestion liquor was sampled. The gas collecting cylinder was removed from the shielded box and the collected gas phase was analysed by means of a multipurpose mass spectrometer with customised gas inlet systems (GAM 400, InProcess Instruments). Aliquots of the digestion liquor (after dilution due to dose rate) as well as the remaining gas phase in the gas collecting cylinder were also analysed for $^{14}C$ in the extraction and analysis system installed in a glove box, as described in detail elsewhere [HERM *et al.*, 2014].

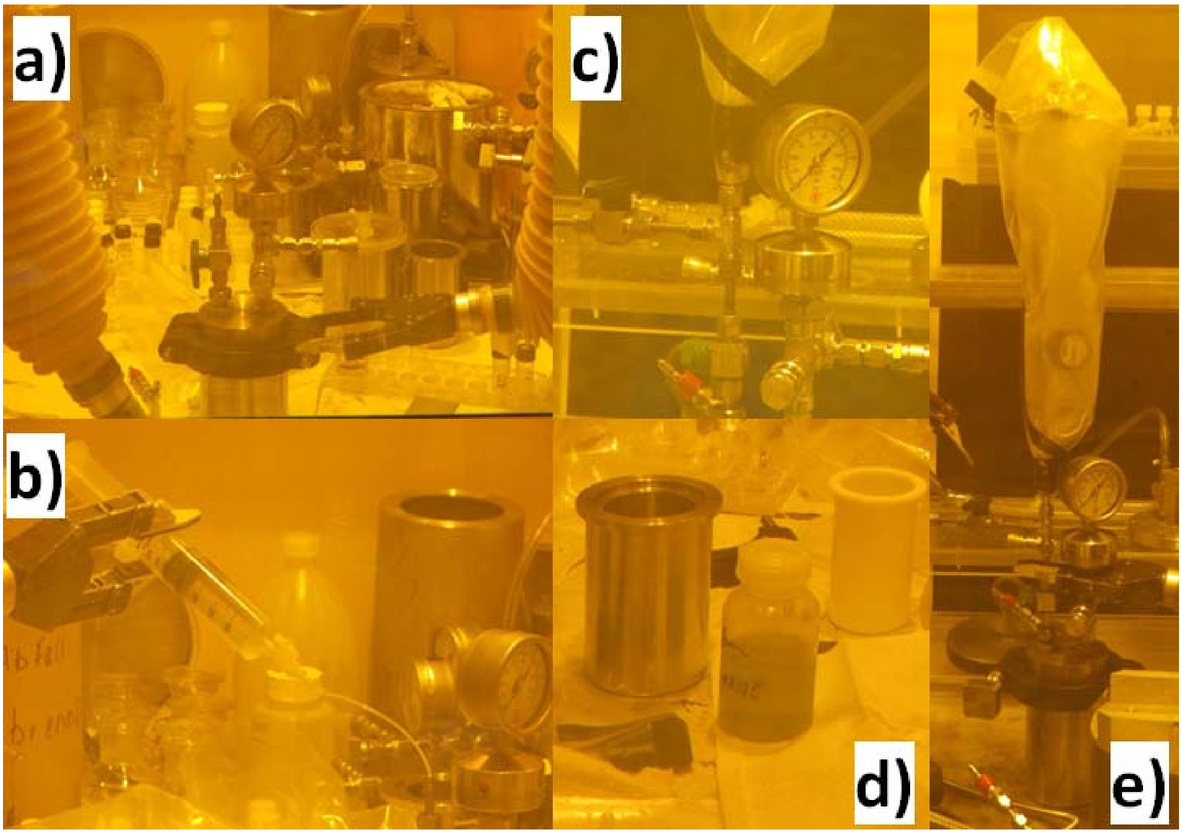


**Figure 7.2: a) autoclave for dissolution experiments, loaded with a steel specimen, inside a shielded box (gas collecting cylinder not yet connected to the autoclave); b) addition of the acid mixture to the sample placed in the autoclave; c) valves, connection for the gas collecting cylinder and pressure gauge in the lid of the autoclave; d) open autoclave (left) as well as the blueish/greenish digestion liquor (middle) and the PTFE liner (right) after digestion of a subsample; e) whole set-up, including autoclave and gas collecting cylinder mounted on top (inside the bags)**

## *7.4 Preliminary results of dissolution experiments involving irradiated steel*

Table 7.2 summarises the experimental outcome of the $^{14}C$ inventory analysis of the irradiated stainless steel plenum spring. The experimentally determined $^{14}C$ inventory is further compared to theoretically predicted inventory obtained by Monte Carlo N-particle calculations (MCNP-X).

Experimental and calculated results agree within a factor of about three. Given the limited knowledge of the nitrogen impurity in the irradiated steel and the great uncertainty of nitrogen contents in stainless steel in general (0.04–0.1 wt.%, [SCHUMANN *et al.*, 2014]), the experimental results obtained in the digestion experiments for $^{14}$C is in good agreement with the calculated value. The experimental $^{14}$C inventory in irradiated stainless steel, recently assessed by [SCHUMANN *et al.*, 2014], exceeds the calculated value by a factor of four. It is noticeable that in both studies the experimentally determined inventory exceeds the calculated inventory by similar factors. Moreover, about 99% of the $^{14}$C is found as gaseous or dissolved organic $^{14}$C bearing compounds after release from steel. These results are in accordance with results obtained on the chemical form of $^{14}$C after release from irradiated Zircaloy-4 cladding within CAST WP3.

**Table 7.2: Results of inventory analysis of the first steel subsample**

| | **experimental [Bq/g]** | **calculated [Bq/g]** | **factor** |
|---|---|---|---|
| $^{14}$C | $2.7(\pm0.3)\times10^5$ | $8.5(\pm0.9)\times10^4$ | 3.1 |

# 8 NRG contribution to CAST WP2 Third Annual Report

## 8.1 *Introduction*

Within the CAST EU project, WP2, NRG perform experimental investigation of the release of $^{14}$C from irradiated steels. The leaching experiment on stainless steel samples will be performed in the hot cell G1 (chemical hot cell) in the Hot Cell Laboratory (HCL) at Petten. The leaching experiment will be realised in 0.1M NaOH (pH 13) under anaerobic conditions (in a nitrogen atmosphere) at the temperature present in the hot cell, which is to be expected to be slightly above room temperature. Two duplicate experiments will be carried out for irradiated steel samples. Additionally an identical experiment will be set up, with an un-irradiated steel sample, for reference. The stainless steel samples had been acquired and characterised, detailed information has been presented in previous Annual Reports.

For the experiments with irradiated and unirradiated stainless steel, gas and solution phase sampling will take place 6 times during the 1 year run of the experiment (1 week, 3 weeks, 6 weeks, 3 months, 6 months and 1 year). Two liquid samples will be taken for each of the three experiments, one sample for $^{60}$Co measurements and one for $^{14}$C analysis. The gas phase from each experiment will be periodically purged with nitrogen gas through a gas sampling rig to collect as separate fractions $^{14}$C released into the gas phase as $^{14}CO_2$, $^{14}$CO and volatile $^{14}$C-containing organic species.

The experiments have been started in June 2016.

## 8.2 *Progress in the reporting period*

The design, construction and commissioning of the experimental equipment was undertaken outside the CAST project. This was a cooperation project involving Amec Foster Wheeler and Radiocarbon Dating Limited; funded by Radioactive Waste Management. In that project all preparations required for the starting of experimental work within CAST were performed including a blank test to determine any background levels of $^{14}$C. The CAST experiments have now been started. The progress in this reporting period is discussed in following sections.

### 8.2.1 Container design

The leaching experiment takes place in a suitable container. The container design could significantly affect the experiments. Many aspects have been considered during the container design, and in consultation with Amec Foster Wheeler and Radioactive Waste management Limited (RWM) a number of options have been considered. The final container design (Figure 8.1) consists of an outer vessel with cover, both made from borosilicate glass. An inert zirconia crucible serves as an insert where the leachant is placed during the leaching experiment to avoid contact between leachant and glass that could potentially affect the experiment. It is known that silicate ions can affect the corrosion rate of steels [FRANCIS & MERCER, 1983], and the borosilicate glass container would react with the high pH solution to release silicate species into solution. A gas sampling system is formed by inlet and outlet, where inlet is connected to nitrogen source and outlet to the RCD rig. Liquid sampling and leachant addition are performed via a dip leg (quartz).

Stainless steel samples will be placed on a triangle that will be placed on the zirconia insert. The compact tension (CT) samples will be fixed with stainless steel hooks and will be hung from the triangle. First, a prototype of the container has been fabricated and fully tested during the blank tests.

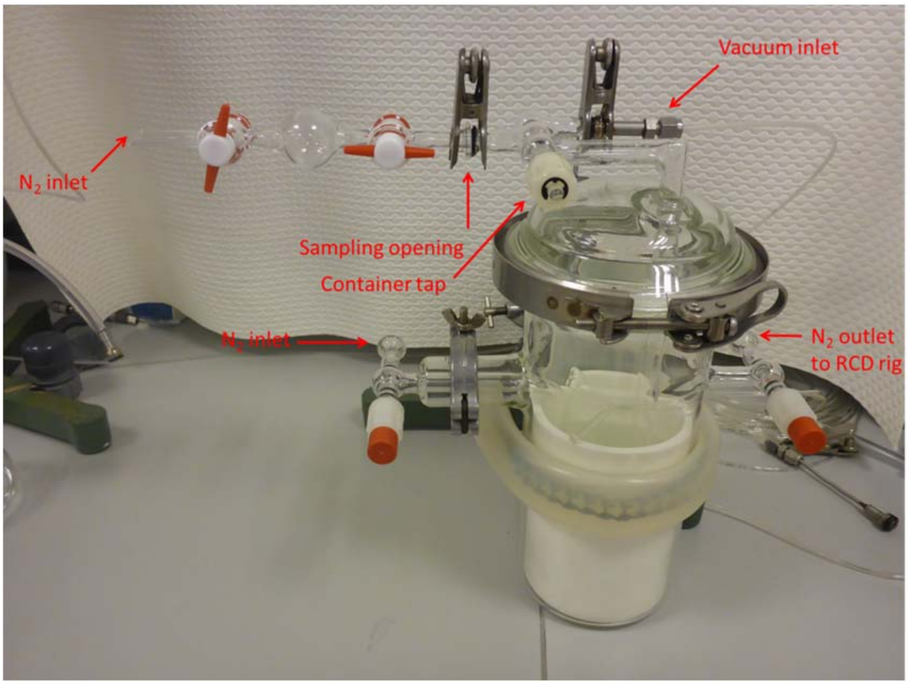


**Figure 8.1: A picture of the leaching container prototype**

### 8.2.2 Methods development

The method for $^{14}C$ measurements in the solution has been setup and validated. The method is based on separation of $^{14}C$ from the solution by acidification of the solution by nitric acid and capture of $CO_2$ by Carbosorb (Figure 8.2). These methods have been tested and validated by using a $^{14}C$ tracer. The measurements have been done by Liquid Scintillation Counting.

The methods for leachant addition and sampling have been setup and tested. Details have been presented in previous annual reports [MIBUS *et al.*, 2015a, b].

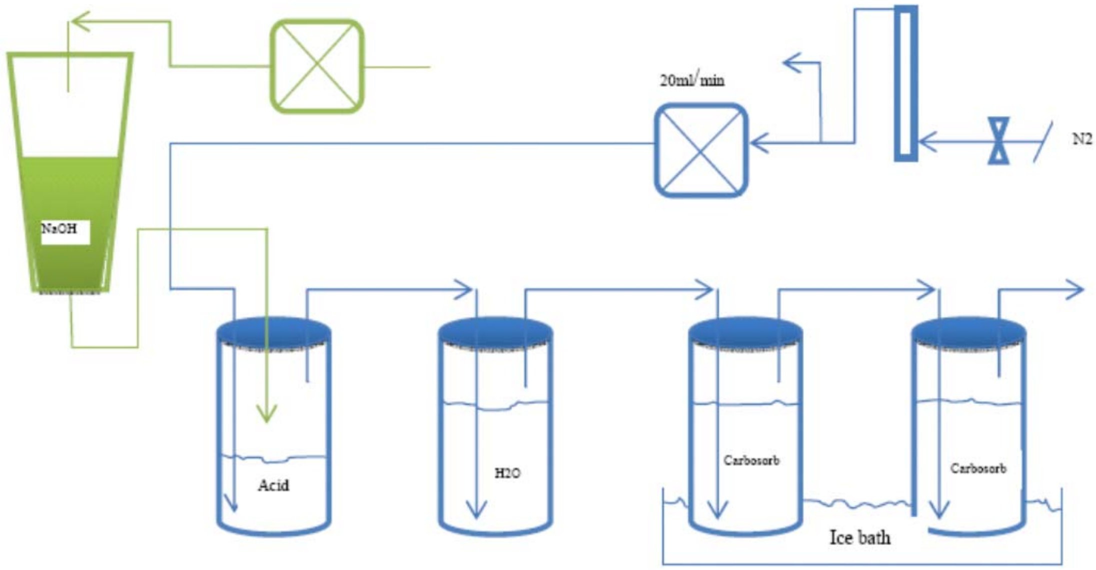


**Figure 8.2: Schematic design of $^{14}$C-carbonate separation method**

### 8.2.3 Blank tests

The blank tests have been performed following the outline experimental procedure (Figure 8.3). The setup has been commissioned, tested and approved for blank tests.

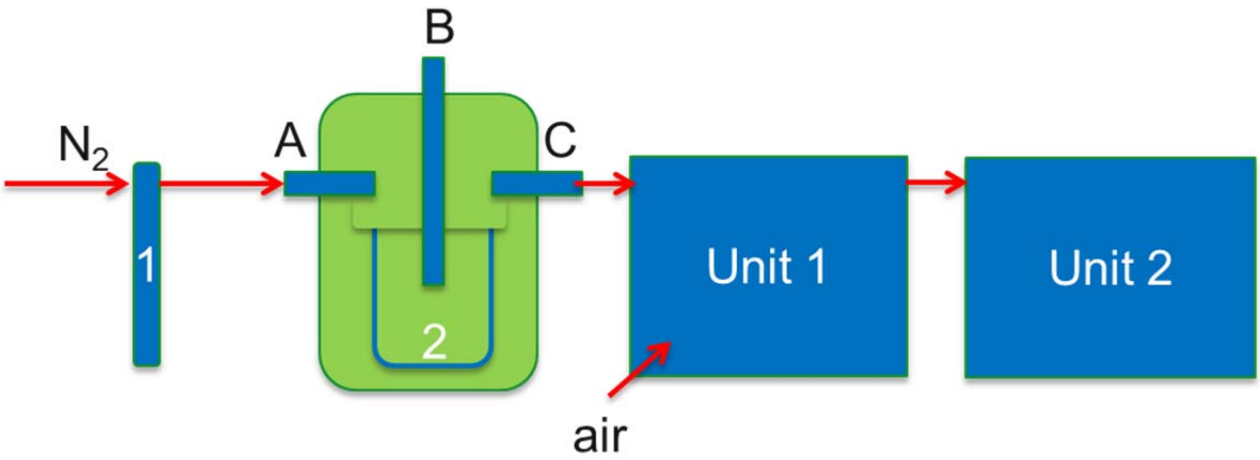


**Figure 8.3: Setup for blank tests: 1 is soda lime column for removing carbon-14 from nitrogen feed, 2 is leaching container where A is $N_2$ inlet, B is dip leg and C is $N_2$ outlet, Unit 1 and Unit 2 are the parts of RCD rig**

The blank tests have been started by setting the RCD rig's furnaces on the required temperature, nitrogen feed has been switched on, the setup has been flushed by nitrogen. The flow rate of nitrogen was kept on 100 ml/min. There is also air inlet necessary for the oxidation catalysts to ensure sufficient oxygen for the oxidation over the catalysts, the flow rate of the air was 100 ml/min as well. The ovens of the RCD rig had to reach required temperatures for proper working of the catalysts for oxidising the carbon-14 species. When these temperatures (Unit 1 at 350ºC and Unit 2 at 425ºC) were reached and maintained for a period of 1 hour, the RCD has been connected to the leaching container.The leachant has been added and the blank test has been started. After 24 hours of running, the setup has been switched off, the columns with carbon-14 have been removed, marked and stored. Liquid sampling took place, a sample of 5 ml has been taken, treated for separation of carbon-14 from the solution, InstaGel has been added and moved to LCS laboratory for analysis.

The new fresh columns have been placed in the RCD rig, the same procedure has been followed as for one day experiment. The second blank test run for 9 x 24 hours. When finished, the RCD rig has been switched off, columns have been removed, marked and stored. Liquid sampling took place and the sample has been prepared for LSC analyses.

Columns from both gas samplings have been properly packaged and sent to RCD Lockinge for analyses.

#### 8.2.3.1 Blank tests results

*Liquid phase analysis*

A sample of leachant (5 ml) has been acidified by $HNO_3$, whereby carbon-14 present as carbonate in solution released as $CO_2$ which was subsequently trapped by columns filled by Carbosorb E (10 ml in each bottle) which traps $CO_2$ only. The method is validated only for carbonates in solutions, there is uncertainty regarding organic species if they would be oxidised as well.

The carbon-14 in the solution has been determined by liquid scintillation counting method (LSC). A LSC apparatus Packard TriCarb 3180 TR/SL from Perkin Elmer has been used for the carbon-14 analysis. This apparatus had been installed, tested and validated. Carbon-14 measurements in solution (Carbosorb + InstaGel) had been validated, the detection limit is 0.1 Bq in a measured sample, with uncertainty 1σ of 15%.

The LSC measurement took 60 minutes as in the validated method for carbon-14 measurements. The low level count mode has been applied as validated for this matrix.

The carbon-14 activity, $A$, in the sample has been calculated as follows:

$$A\ (Bq) = \frac{CPM\ sample - CPM\ (Average)\ Blank}{60} * \frac{100}{Eff}$$

Where:

| | |
|---|---|
| *CPM sample* | is the number of counts per minute measured for the sample; |
| *CPM (Average) Blank* | is the average CPM measured for blank measurements; and |
| *Eff* | is the efficiency of detection in counts per second per Bq of carbon-14 activity, expressed as a percentage. |

The results of the analysis of the solution phase samples from the blank experiment along with the blank and standard measurements are presented in Table 8.1.

The carbon-14 measurements show that the amounts of carbon-14 in solution samples from the blank experiments after 1 day and 10 days are below the detection limit of LSC. The uncertainty of the measurement *2s* is 3%.

**Table 8.1: Results of LSC analysis of blank, standard and blank experiment sample solutions for carbon-14**

| Sample name | CPM | Efficiency (%) | Activity in sample (Bq) |
|---|---|---|---|
| Blank A (0.1 M NaOH) | 5.4 | 78.9 | - |
| Blank B (0.1 M NaOH) | 6.2 | 78.6 | - |
| Average Blank A&B | **5.8** | 78.8 | - |
| Blank C (Carbosorb + InstaGel, 50:50) | 4.9 | 78.5 | **-** |
| Standard A (carbon-14 tracer) | 109.8 | 79.5 | 2.18 |
| Standard B (carbon-14 tracer) | 112.1 | 79.2 | 2.24 |
| Blank Sample A (1-day sampling) | 5.3 | 78.8 | **<0.1** |
| Blank Sample B (1-day sampling) | 6.3 | 78.7 | **<0.1** |
| Blank Sample C (10-days sampling) | 5.0 | 79.0 | **<0.1** |
| Blank Sample D (10-days sampling) | 4.4 | 79.5 | **<0.1** |

*Gas phase analysis*

Two sets of soda lime columns were supplied to NRG with the $CO_2$/CO and $CH_4$ samplers in March 2015 ready for use in the Blank Experiment. The columns were filled with soda lime which had been pre-loaded with fossil $CO_2$. An aliquot of the pre-loaded soda lime was processed to benzene and the carbon-14 content measured by LSC to provide a system background.

The columns were returned to RCD Lockinge in December 2015 for processing. The samples were acidified and the $CO_2$ converted to benzene for LSC. A further aliquot of the batch of pre-loaded soda lime was processed and counted alongside the samples as a second check on the system background.

Samples were counted together with background samples made from material containing no carbon-14, e.g. marble, and standards of ‘known activity’, e.g. National Bureau of Standards oxalic acid. Samples were counted 20 times and, in each cycle, counted for either 100 minutes or the time needed to collect 3000 counts. For these low activity samples a total counting time of 2000 minutes was required.

The results of LSC analysis of the gas phase samples are presented in Table 8.2 in terms of specific activity and in Table 8.3 in terms of total activity measured in each soda lime column. The results are compared with the measurements of the intrinsic background of the pre-loaded soda lime batch presented on an equivalent basis.

**Table 8.2: Measured carbon-14 specific activities of soda lime columns from the Blank Experiment compared with soda lime background**

| Run time (days) | RCD reference No. | Carbon-14 specific activity (Bq kg$^{-1}$ carbon) | | | |
|---|---|---|---|---|---|
| | | Soda lime | $CO_2$ | CO | $CH_4$ |
| 1 | RCD-8517 – $CO_2$ | | 9 ± 0.9 | | |
| | RCD-8518 - CO | | | 8 ± 0.9 | |
| | RCD-8519 – $CH_4$ | | | | 9 ± 0.9 |
| 9 | RCD-8520 – $CO_2$ | | 8 ± 1.0 | | |
| | RCD-8521 - CO | | | 8 ± 0.8 | |
| | RCD-8522 – $CH_4$ | | | | 10 ± 1.0 |
| Background | RCD-8334 | 8 ± 0.8 | | | |
| | RCD-8538 | 9 ± 0.9 | | | |

**Table 8.3: Measured total carbon-14 activities of soda lime columns from the Blank Experiment compared with soda lime background**

| Run time (days) | RCD reference No. | Total carbon-14 activity in sample (Bq) | | | |
|---|---|---|---|---|---|
| | | Soda lime | $CO_2$ | CO | $CH_4$ |
| 1 | RCD-8517 | | 0.023 ± 0.003 | | |
| | RCD-8518 | | | 0.021 ± 0.002 | |
| | RCD-8519 | | | | 0.023 ± 0.003 |
| 9 | RCD-8520 | | 0.020 ± 0.002 | | |
| | RCD-8521 | | | 0.021 ± 0.002 | |
| | RCD-8522 | | | | 0.025 ± 0.003 |
| Background | RCD-8334 | 0.026 ± 0.003 | | | |
| | RCD-8538 | 0.023 ± 0.003 | | | |

There is no significant difference between the carbon-14 specific and the total activities measured in the samples and those measured in the aliquots of pre-loaded soda lime and it can be concluded that no carbon-14 was absorbed from the laboratory air during the sampling periods.

### 8.2.4 Preparations of the experiments in the Hot cells

#### 8.2.4.1 Containers

Based on the blank tests results, small changes have been made in the container design; the dip leg diameter decreased and the placing of the sampling valves. Finally, three containers have been fabricated for the leaching experiments with irradiated and unirradiated samples.

To handle the containers in the cell in a safe way, some additional tools and racks have been designed (see Figure 8.4). A massive metal rack has been designed to fix the container to minimise the possibility of damaging the glass container during the manipulation.

**Figure 8.4: CAST leaching container placed in a rack with tools for manipulation in the HCL (front side – left and back side –right)**

#### 8.2.4.2 Hot cells preparation

After the approval of the placing of the glovebox on the top of G1 cell, the glove box could be placed. The glovebox has been site accepted, carefully placed on the top of the cell and leak tested.

The glovebox has been connected via the other one to the connection box of the cell. The gloveboxes are connected via hose and flanges. The gas line coming from the hot cell is fed through the hose between the gloveboxes. All the gas lines in the hot cell and old glovebox are equipped with Staubli quick connectors.

The RCD rig has been placed in the glovebox (see Figure 8.5); the glovebox has been again leak tested.

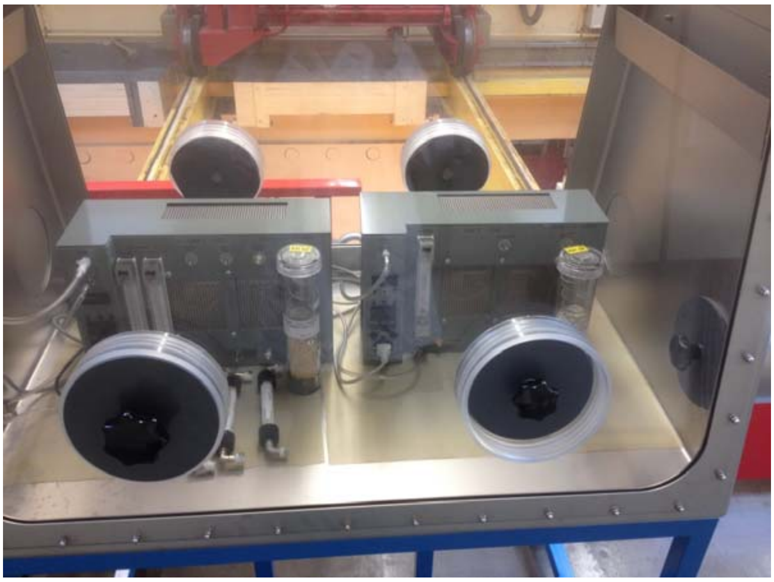


**Figure 8.5: RCD rig placed in the glovebox in the HCL**

After all the preparations of hardware, the experimental setup has been placed in the hot cell to perform some tests:

- the manipulation with containers;
- manipulation (open/close) with the valves;
- hanging the CT specimen in the container;
- put the cover on the container;
- closing the container;
- fixing the clamp;
- liquid addition (see Figure 8.6); and
- liquid sampling

All these tests have been successfully completed.

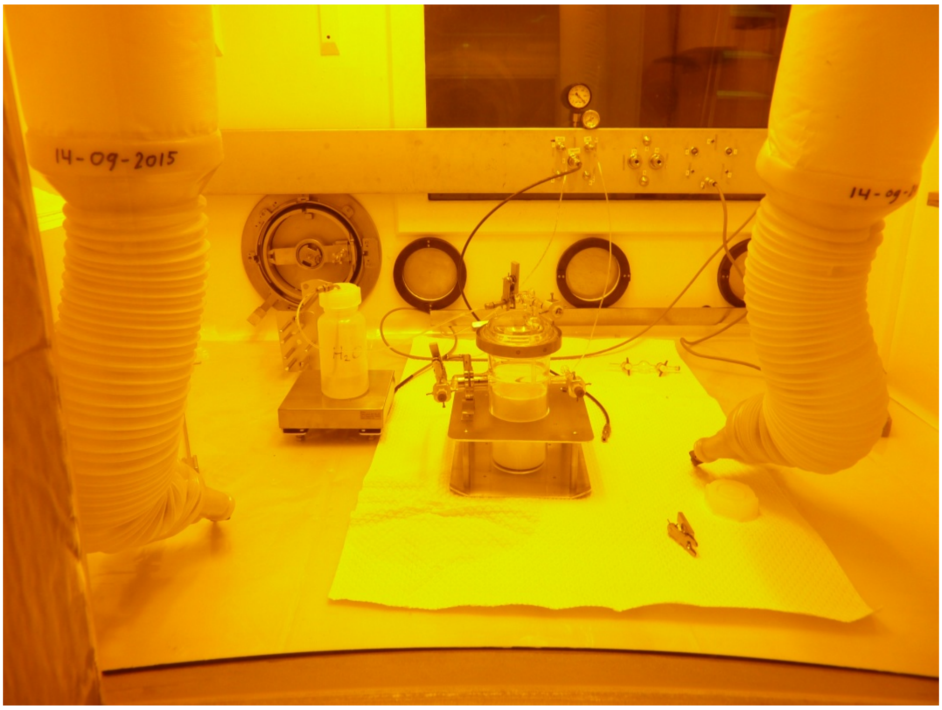


**Figure 8.6: Liquid addition tests in the hot cell**

#### 8.2.4.3 Experiment preparations

Unirradiated specimens have been cut from the same batch steel as the irradiated samples. These specimens have the size, but they are missing the V - cut.

All CT specimens have been weighed before being fixed in the leaching containers.

The irradiated samples have been divided in two containers according to the scheme in Table 8.4.

**Table 8.4: Overview of samples in the containers**

| | **Container 1** | | | **Container 2** | | |
|---|---|---|---|---|---|---|
| Sample | b102 | b116 | b121 | b103 | b112 | b117 |
| $^{14}$C activity (Bq g$^{-1}$) | 1.55E+05 | 2.87E+05 | 2.21E+05 | 1.81E+05 | 2.85E+05 | 2.01E+05 |
| Total **$^{14}$C** activity in container (Bq) | **5.17E+7** | | | **5.24E+7** | | |
| $^{60}$Co activity (Bq g$^{-1}$) | 5.13E+07 | 9.36E+07 | 7.25E+07 | 5.96E+07 | 9.32E+07 | 6.60E+07 |
| Total **$^{60}$Co** activity in container (Bq) | **2.17E+08** | | | **2.19E+08** | | |

The unirradiated samples have been all put in the last container. The containers with the CT specimens inside have been closed and leak tested.

### 8.2.5 Leaching experiment

The leachant (0.1 M NaOH) has been prepared outside the cell and transported into the cell. The leachant is prepared $^{14}$C free by bubbling the solution by helium in a glovebox .

The experiments have been started by addition of the leachant. The experiments have been running for almost three months; one week, three and six weeks sampling have taken place. The gas samples have been collected by the use of RCD rig, transported to RCD Lockinge and are being analysed for $^{14}$C. The liquid samples have been taken and being analysed for $^{14}$C- and $^{60}$Co at this moment.

The results of the experiments will be presented in the deliverable of NRG.

## 8.3 *Milestones & Deliverables*

No milestones or deliverables scheduled in the third reporting period. An abstract related to this research has been submitted for the KONTEC 2017 conference.

# 9 PSI contribution to CAST WP2 Third Annual Report

## 9.1 *Development of the Analytical Techniques: Gas Chromatography coupled to thermal conductivity detection*

Modifications of the previously installed gas chromatographic system equipped with mass spectrometry detection (GC-MS) [MIBUS *et al.*, 2015a] were undertaken to enable direct detection of the target analytes by thermal conductivity detection (TCD). Installation of the TCD will enable us to monitor the oxidation of alkanes and alkenes in the oxidation reactor in connection with the development of compound-specific $^{14}C$ accelerator mass spectrometry (AMS) for gaseous species (see section 9.4.3).

The TCD was installed and tested. It allows the non-destructive analysis of gaseous compounds of interest and thus opens up the possibility to collect the target analytes in the fraction sampling system after detection by TCD. The analytical procedure was adapted in accordance with the specifications of the detector and tests were carried out to assess linearity and capacity of the detector. The following temperature programme was developed for separating gaseous compounds using the Restek Rt®-Msieve 5A column (30 m × 0.32 mm with 0.025 mm film): initial temperature 45°C for 4 min followed by a ramp of 20°C/min up to 290°C (1 min hold). To optimise detection of the compounds, the column flow rate was set to 5mL/min using a detector make-up flow rate of 10 mL/min and a detector reference flow rate of 15 mL/min, respectively, and helium as carrier gas. Note that the addition of a significant amount of carbon (20 µg carbon-12 per target analyte) as carrier is required for the preparation of AMS samples. Therefore, capacity of the chromatographic column and the TCD was tested. Both devices showed no saturation effect for $CO_2$, methane and ethane up to a total concentration of 250 µg carbon. Hence, it is possible to prepare AMS samples with 20 µg carbon per target analyte using a procedure consisting of the separation of the gaseous compounds with the Restek Rt®-Msieve 5A column in combination with TCD detection of the compounds. The next step towards compound-specific $^{14}C$ AMS for gaseous species will include installation of the oxidation reactor and the fraction sampling system (section 9.4.3)

## 9.2 *Corrosion Experiments with Non-activated Iron Powders*

### 9.2.1 Batch experiments in different pore waters

Additional batch-type experiments with non-activated carbon-bearing iron powders were carried out in the reporting period with the aim of checking the speciation of organic compounds formed in the course of the anoxic corrosion of iron as reported earlier [MIBUS *et al.*, 2015a]. In particular, the objective of the new series of experiments was to check whether or not the carbon speciation is different if corrosion experiments are carried out in sodium hydroxide (NaOH) solution instead of Ca containing artificial cement porewaters (ACW) as reported in the previous reports [MIBUS *et al.*, 2015a,b]. For the sake of comparison the NaOH solutions had a pH of 11.5 and 12.5, respectively, corresponding to the pH of the previously used ACWs. Note that the WP 2&3 consortium decided to consider a NaOH solution (pH 12 or higher) as a possible electrolyte solution for experiments.

### 9.2.2 Time-dependent formation of organic compounds in sodium hydroxide (NaOH)

The main findings from the time-dependent corrosion experiments under anoxic alkaline conditions that had been reported in detail in the previous reports [MIBUS *et al.*, 2015a,b] can be summarised as follows: 1) Reduced hydrocarbons (e.g. alkanes and alkenes) as well as oxidised hydrocarbons (e.g. carboxylic acids, alcohols and aldehydes) are produced during anoxic corrosion of iron powders, 2) fast formation of the organic compounds occurs within the first day of corrosion, 3) the long-term production of the organic compounds occurs at much lower rate after the first day.

The same kind of organic compounds were identified in NaOH as in the previously used Ca containing ACWs (Figure 9.1). Carboxylic acids were identified in the liquid phase and hydrocarbons in the gas phase as the predominant corrosion products. However, in case of the hydrocarbons, the measured concentrations were significantly higher in NaOH compared to Ca containing ACW (Table 9.1). For example, the methane concentration in NaOH (pH 12.5, Figure 9.1B) was around 10 µM whereas the methane concentration in ACW with the same pH was only 2 µM ([MIBUS *et al.*, 2015a] Figure 9.2A). By contrast, the concentration of the carboxylic acids is comparable in NaOH and Ca containing ACW.

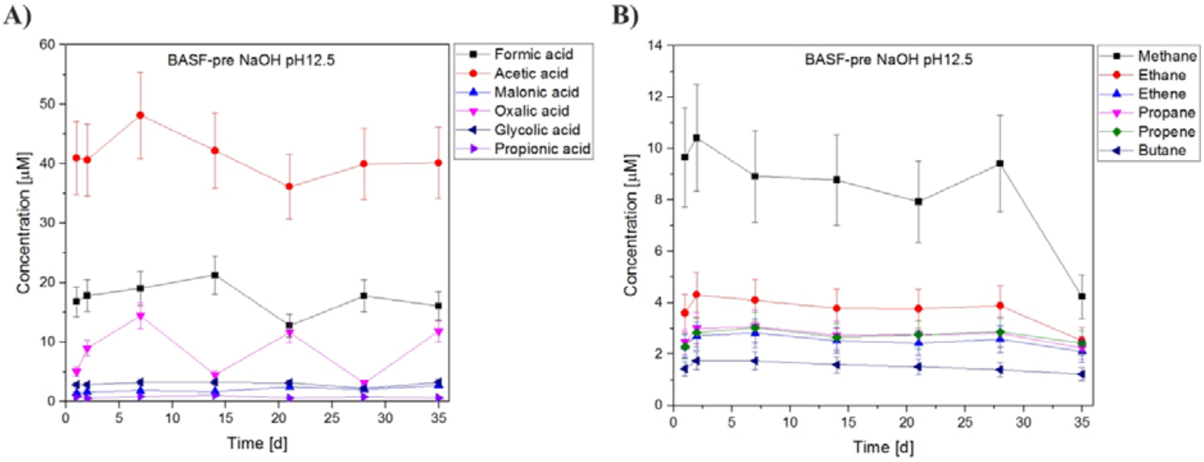


**Figure 9.1: Concentration of carboxylic acids (A) and hydrocarbons (B) formed during the anoxic corrosion of iron powders in NaOH (pH 12.5)**

**Table 9.1: Comparison of the concentrations of corrosion products observed after 28 days in ACW-I/NaOH (pH 11) and ACW-II/NaOH (pH 12.5)**

| **Compound** | **Concentration [µM]** | | | |
|---|---|---|---|---|
| | pH 11 | | pH 12.5 | |
| | ACW-I | NaOH | ACW-II | NaOH |
| Formic acid | 12 ± 2 | 16 ± 2 | 15 ± 3 | 18 ± 3 |
| Acetic acid | 36 ± 6 | 38 ± 6 | 40 ± 7 | 40 ± 6 |
| Malonic acid | n.d. | 0.6 ± 0.1 | n.d. | 2 ± 0.3 |
| Oxalic acid | 0.2 ± 0.0 | 0.6 ± 0.1 | 0.8 ± 0.1 | 3.1 ± 0.5 |
| Glycolic acid | n.d. | 1.4 ± 0.2 | n.d. | 2.2 ± 0.3 |
| Propionic acid | n.d. | 0.7 ± 0.1 | n.d. | 0.8 ± 0.1 |
| Methane | 5.2 ± 1.0 | 52.7 ± 10.5 | 1.9 ± 0.4 | 9.4 ± 1.9 |
| Ethane | 1.4 ± 0.2 | 47.7 ± 9.5 | 0.8 ± 0.1 | 3.9 ± 0.8 |
| Ethene | 1.9 ± 0.4 | 7.8 ± 1.6 | 0.8 ± 0.2 | 2.6 ± 0.5 |
| Propane | 1.1 ± 0.1 | 28.8 ± 5.8 | 0.7 ± 0.1 | 2.8 ± 0.6 |
| Propene | 1.7 ± 0.3 | 24.3 ± 4.9 | 0.7 ± 0.1 | 2.9 ± 0.6 |
| Butane | 0.4 ± 0.1 | 10.8 ± 2.2 | 0.3 ± 0.1 | 1.4 ± 0.3 |

The higher concentration of hydrocarbons in NaOH solutions found within the course of the experiment (up to 35 days) is possibly the result of enhanced iron corrosion. The amount of oxidised compounds, however, is comparable in all experiments which supports the idea that oxidised species are formed in the course of a preceding corrosion process (e.g. exposure to air, during pre-treatment etc.).

The corrosion experiments in NaOH further revealed the presence of additional gaseous compounds up to C7. A ZEBRON™ ZB-624 column (60 m × 0.25 mm with 1.4 µm film) was used for the separation of the compounds. A large number of unidentified peaks were detected upon analysis of the organic corrosion products formed in NaOH (Figure 9.2A). A library search using the identified masses of the unknown compounds showed that most of the gaseous compounds are hydrocarbons with a chain length > C3. Additional measurements with standards (butane, pentane, 1-hexene, hexane, heptane) as shown in Figure 9.2B (chromatogram in blue and red) were carried out in order to identify some of the unknown compounds (Table 9.2). The results show that besides the previously observed hydrocarbons with chain length up to C3, also hydrocarbons up to C7 are produced, although at much lower concentration. These compounds could only be detected as a result of the higher corrosion rate of iron in NaOH in the time period of the batch experiments.

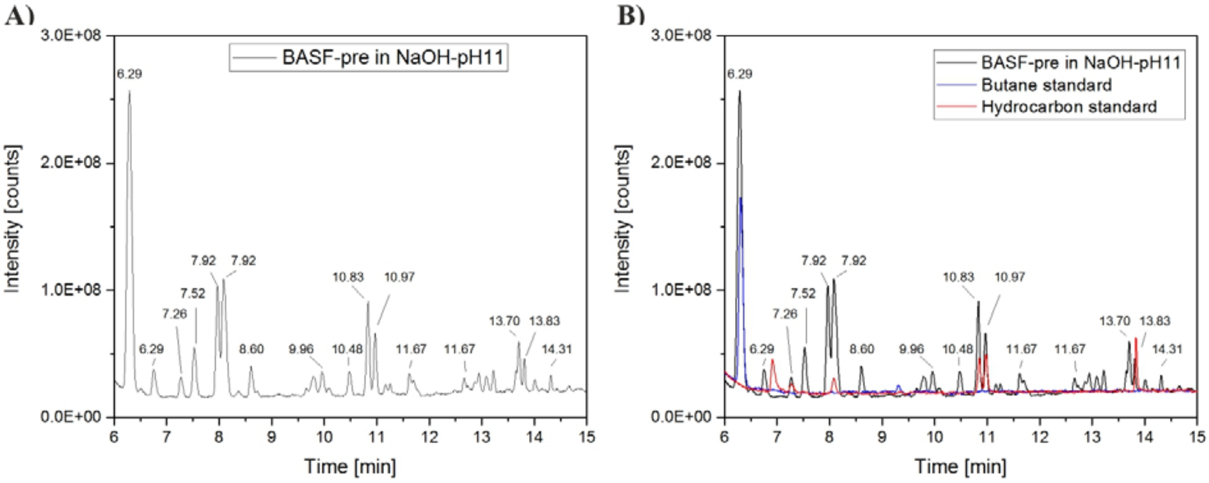


**Figure 9.2: A) TIC-MS chromatogram of a BASF iron powder corroded in NaOH (pH 11.5) for 14 days, B) Chromatogram of the same sample including measurements with standards, i.e. butane (blue) and a mixture of several hydrocarbons (pentane, 1-hexene, hexane, heptane) (red)**

**Table 9.2: Carbon species produced during corrosion of iron powders in NaOH (bold: confirmed by standards, regular: confirmed by mass spectrometry library search)**

| Retention time [min] | Compound | Formula |
|---|---|---|
| **6.29** | **butane** | **$C_4H_{10}$** |
| 6.75 | 2-butene | $C_4H_8$ |
| 7.26 | 2-pentene | $C_5H_{10}$ |
| 7.52 | pentene/2-methylbutane | $C_5H_{12}$ |
| 7.92 | 1-pentene | $C_5H_{10}$ |
| ***8.08*** | ***n-pentane*** | ***$C_5H_{12}$*** |
| 8.6 | 2-pentene/3-methyle-2-butane | $C_5H_{10}$ |
| 9.96 | 2-methylpentane | $C_6H_{14}$ |
| 10.48 | 3-methylpentane | $C_6H_{14}$ |
| **10.83** | **1-hexene** | **$C_6H_{12}$** |
| ***10.97*** | ***n-hexane*** | ***$C_6H_{14}$*** |
| 11.67 | 2/3-hexene | $C_6H_{12}$ |
| 12.66 | 3-methyl-hexene | $C_7H_{14}$ |
| 13.7 | 1-heptene | $C_7H_{14}$ |
| ***13.83*** | ***n-heptane*** | ***$C_7H_{16}$*** |
| 14.31 | 2/3-heptene | $C_7H_{14}$ |

## 9.3 *Development of a Reactor for the Corrosion of Activated Steel Samples*

### 9.3.1 Experimental set-up

An experimental set-up for the long-term corrosion experiment with the activated steel nuts from the Gösgen nuclear power plant was developed in the reporting period. The setup consists of a custom-made gas-tight overpressure reactor placed within a 10 cm thick lead shielding (Figure 9.3). The reactor is equipped with a digital pressure transmitter and a sensor to detect dissolved oxygen (Visiferm DO Arc, Hamilton, USA). The Visiferm DO Arc is an optical oxygen sensor without electrolyte, thus eliminating the risk of contamination of the aqueous phase, and an oxygen detection limit as low as 4 ppb. The overpressure reactor is designed in such a way that all manipulations necessary for regular sampling can be carried out outside the lead shielding to minimise exposure of the experimentalist to radiation (Figure 9.3 C).

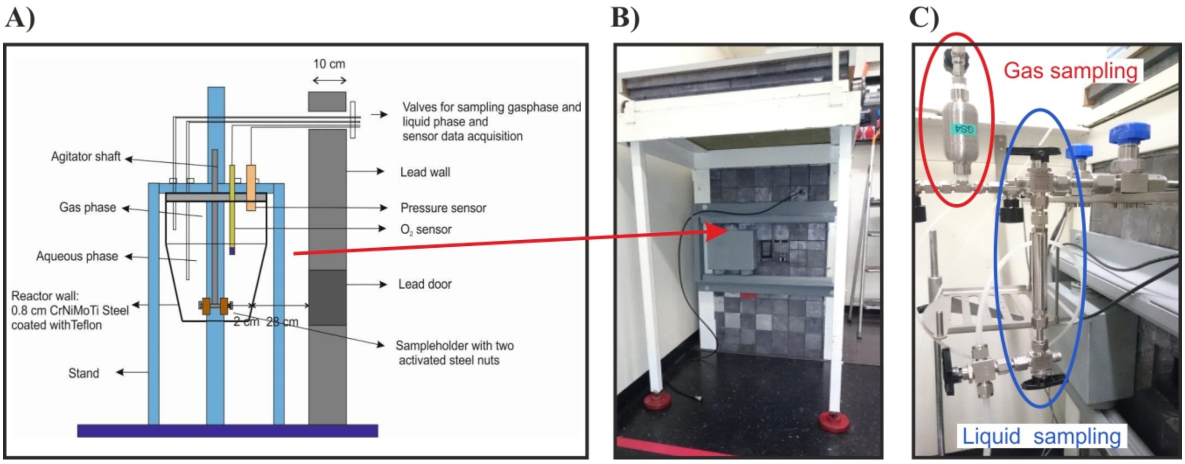


**Figure 9.3: A) Sketch of the reactor, B) picture of the lead shielding with door and C) the sampling system for liquid and gaseous samples placed outside of the shielding**

Transfer of the activated steel nut into or out of the reactor takes place via a door in the lead shielding (Figure 9.3B). In 2015, construction of the reactor was completed and "cold" experiments, i.e. without activated material, were carried out to check the tightness of the reactor, to test the proper functioning of the different sensors (dissolved $O_2$, pressure) and their response to $O_2$ contamination, and to evaluate the extent of $O_2$ contamination during the sampling procedure. Furthermore, the sampling procedure was tested several times, which includes a gas phase sampling step (50 mL gas), a liquid phase sampling step (7 mL liquid) followed by a re-adjustment of the liquid volume with 7 mL $O_2$-free solution and the re-adjustment of the $N_2$ overpressure. For these tests, the reactor was filled with 300 mL ACW (pH 12.5), a piece of iron wire (length: 1 m, ID = 0.5 mm) was submerged and a $N_2$ overpressure of 4 bar was applied. A typical record of the evolution of pressure and dissolved oxygen with time for one of these tests is displayed in Figure 9.4.

Sampling is clearly visible as short pressure drop. During initial filling of the reactor, a small amount of $O_2$ could enter the reactor which is consumed by subsequent oxidation of the Fe wire. Thus, sequential samplings do not result in significant $O_2$ accumulation. The tests show that the reactor is gas-tight and that $O_2$ concentration, temperature and pressure can be monitored accurately during an experiment.

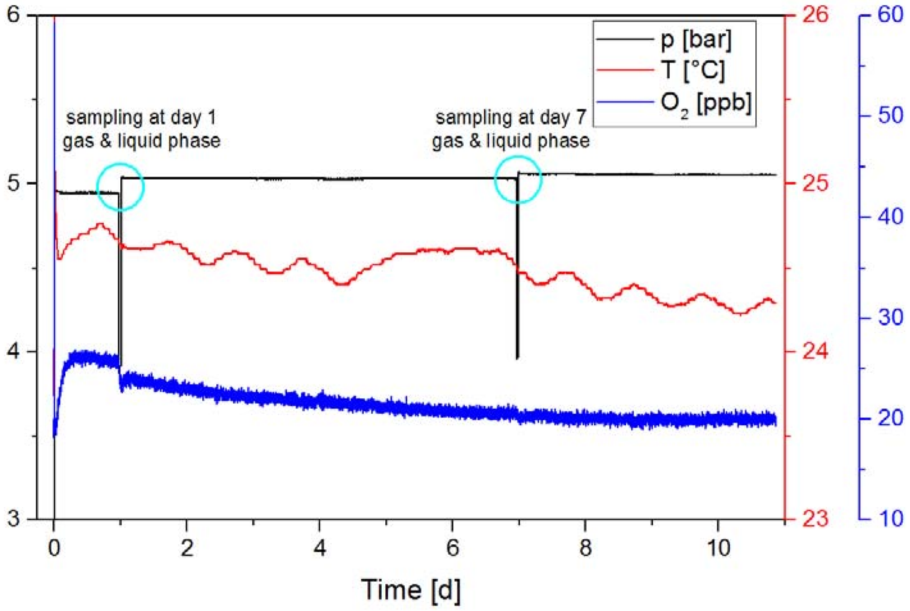


**Figure 9.4: Graph of the recorded temperature (red), pressure (black) and dissolved oxygen (blue)**

### 9.3.2 Determination of the carbon-14 background in the reactor

The $^{14}C$ background in the reactor was determined with the aim of assessing future measurements of $^{14}C$ concentrations in the corrosion experiment with activated steel. In a first test the reactor was filled with 300 mL Milli-Q water and the sampling procedure was carried out several times. The liquid phase was analysed by AMS to determine the $^{14}C$ activity in solution. AMS measurements are commonly reported in fraction modern ($F^{14}C$), which is defined as $^{14}C/^{12}C = 1.18 \cdot 10^{-12}$. Knowing the amount of $^{12}C$ used for the measurement, the amount of $^{14}C$ can be calculated. The $^{14}C$ background in Milli-Q water sampled from the reactor was about 0.06 $F^{14}C$ which is identical to the analytical background level of 0.06 ± 0.02 $F^{14}C$ determined during fractionation with ion chromatography (IC) [MIBUS *et al.*, 2015a].

In a subsequent test the reactor was filled with 300 mL ACW (pH 12.5) to simulate experimental conditions in the future corrosion experiment with activated steel. The sample solution which had been incubated for up to 36 days was analysed for TOC (total organic carbon) and by LSC (liquid scintillation counting) in addition to $^{14}$C AMS (Table 9.3). In addition, single compound analysis was performed using GC-MS and IC-MS.

**Table 9.3: Chemical analysis of the ACW aliquots sampled from the reactor. AA: Acetic acid, FA: Formic acid, MA: Malonic acid, OA: Oxalic acid**

| | | | **GC-MS** | | **IC-MS** | | **AMS** |
|---|---|---|---|---|---|---|---|
| **Sample** | **TOC [ppm]** | **LSC [cpm]** | **Compound** | **Conc. [µM]** | **Compound** | **Conc. [µM]** | **Conc. [F$^{14}$C]** |
| Start KPWeq-II | 1.2 | 0 | - | -- | AA/FA/MA/OA | 5/4/0/0.2 | 0.200 |
| Reactor after 1d | 69.5 | 0.7 | $CH_4/C_2H_6/C_2H_4$ | <0.06/<0.04/<0.06 | AA/FA/MA/OA | 12/12/0/1.1 | 0.156 |
| Reactor after 7d | 70.3 | 0.9 | $CH_4/C_2H_6/C_2H_4$ | <0.06/<0.04/<0.06 | AA/FA/MA/OA | 11/13/0/1.1 | 0.141 |
| Reactor after 36d | 70.1 | 0 | $CH_4/C_2H_6/C_2H_4$ | <0.07/<0.04/<0.06 | AA/FA/MA/OA | 18/19/0/1.0 | 0.511 |

GC-MS revealed very low concentrations of the $^{12}$C containing gaseous organic compounds while the concentrations of the $^{12}$C containing carboxylic acids were relatively high according to the IC-MS analysis. AMS measurements showed an enhanced background of total $^{14}$C (> 0.1 F$^{14}$C) in the samples. Nevertheless, determination of the $^{14}$C containing single compounds by compound-specific $^{14}$C AMS shows that the enhanced $^{14}$C background was not due to the presence of $^{14}$C containing carboxylic acids. After fractionation the $^{14}$C activity of single compounds was significantly reduced and comparable to the previously determined analytical background of 0.06 ± 0.02 F$^{14}$C (Table 9.4). The results hence show that the observed high $^{14}$C background in the reactor has no detrimental effect on the identification and quantification of $^{14}$C containing carboxylic acids by compound-specific $^{14}$C AMS. Note that the source of $^{14}$C in the reactor has not yet been identified.

**Table 9.4: Carbon-14 activities of the samples taken from the overpressure reactor. AA: Acetic acid, FA: Formic acid, MA: Malonic acid, OA: Oxalic acid**

| Sample | Conc. [F$^{14}$C] |
|---|---|
| Corrosion reactor | 0.360 |
| AA fraction | 0.020 |
| FA fraction | 0.006 |
| MA fraction | 0.043 |
| OA fraction | 0.071 |

## 9.4 *Coupling Separation Techniques with AMS for Compound-specific Carbon-14 Analysis*

### 9.4.1 Recovery of Carbon-14 Labelled Carboxylic Acids in ACW

Recovery of the compound-specific $^{14}$C AMS method for dissolved organic compounds was further assessed in the reporting period. Recovery tests using the four different $^{14}$C labelled carboxylic acids ($^{14}$C-AA, $^{14}$C-FA, $^{14}$C-MA and $^{14}$C-OA) dissolved in ACW (pH 12.5) were carried out in addition to those in Milli-Q water that had been reported earlier [MIBUS *et al.*, 2015b]. The samples were sequentially injected into the IC system as single compounds. The corresponding fractions of the $^{14}$C labelled carboxylic acids were collected and analysed by AMS. The start solutions were also analysed by AMS in addition to the collected fractions which enabled us to estimate the recovery from a comparison of the $^{14}$C activities before and after fractionation. The $^{14}$C activities of the injected start solutions ranged between 25 - 60 F$^{14}$C depending on the analyte. Recoveries (%) were calculated for each compound taking into account the dilution factor during IC separation and fractionation (Table 9.5).

**Table 9.5: Recoveries (%) of the single carboxylic acids after IC separation**

| Compound | Recovery | Δ % |
|---|---|---|
| AA | 132 | 9 |
| FA | 129 | 14 |
| OA | 86 | 5 |
| MA | 88 | 19 |

The recoveries for acetic and formic acids were found to be higher than 100 %, i.e. ~ 130%, while the recoveries for oxalic and malonic acids were less than 100 %, i.e. ~ 90%. At present, the enhanced recoveries for the former compounds cannot be explained while recoveries below 100 % for the latter compounds are conceivable. Additional experiments are ongoing with the aim of further exploring recoveries, in particular for recoveries above 100 %. Also, additional tests are ongoing with the aim of checking whether the observed recoveries are constant. If so, the recoveries listed in Table 9.5 can be used for the quantification of $^{14}$C containing carboxylic acids.

### 9.4.2 Application of Compound-specific Carbon-14 AMS

The compound-specific $^{14}$C AMS method was applied to determine the $^{14}$C containing carboxylic acids in a leach solution in contact with activated steel. An activated steel nut segment was immersed in the solution and leached over a period of approximately 3 years. The steel segment was placed in a closed container filled with 30 mL ACW (pH 12.5). The container was stored in a hot cell under atmospheric conditions. Thus, the leach solution was not fully protected against ingress of $^{14}CO_2$. The leachate was pretreated, separated and analysed using the previously described IC-AMS procedure.

The activities of the single compounds were determined by compound-specific $^{14}$C AMS and the total $^{14}$C activity by AMS with no preceding separation of the single compounds. The results are listed in Table 9.6. The activity after separation amounts to about 0.14 - 0.40 Bq/L or 36 -201 µBq/fraction (fraction of 250 µL) for the different carboxylic acids. Thus, the measured $^{14}$C activity of each single compound is clearly below the limit of detection (LOD) of LSC (LOD: 10.000 µBq) commonly used for $^{14}$C radioanalysis. Note that analysing the solution with LSC would require collection of more than 50 fractions for $^{14}$C quantification above the LOD of LSC. The results further show that acetate and formate are the main $^{14}$C containing carboxylic acids present in the leach solution. This finding is in line with the results obtained from the corrosion experiments with non-activated iron powders in ACW.

The total $^{14}$C activity of the leach solution was estimated from the $^{14}$C activities of the two compounds at 38 ± 15 Bq/L taking into account dilution in the course of chromatographic separation. Direct measurement of the leach solution by AMS prior to chromatographic separation resulted in a $^{14}$C activity of 21 ± 5 Bq/L. Thus, the two values agree well within the uncertainties indicating that $^{14}CO_3^{2-}$ is only a minor species in the leach solution.

**Table 9.6: Activities determined in a leachate of an activated steel nut segment immersed in ACW under oxic conditions**

| Sample | AMS [F$^{14}$C] | AMS-Activity [Bq/L] | AMS-Activity [µBq/fraction] |
|---|---|---|---|
| Acetate fraction | 0.85 ± 0.35 | 0.38 ± 0.16 | 192 ± 78 |
| Formate fraction | 0.59 ± 0.23 | 0.26 ± 0.11 | 132 ± 53 |
| Malonate fraction | 0.34 ± 0.23 | 0.15 ± 0.10 | 38 ± 26 |
| Oxalate fraction | 0.32 ± 0.11 | 0.14 ± 0.05 | 36 ± 12 |
| Total carbon-14 | Σ: | 0.96 ± 0.40 | |
| | Σ (dilution corrected): | 38 ± 15 | |
| | Direct measurement | 21 ± 5 | |

## 9.4.3 Compound-specific carbon-14 AMS for gaseous species

Preparation of the gas samples for compound-specific $^{14}$C AMS is novel and therefore requires instrumental development. The GC system operated at PSI has to be coupled to a combustion reactor and a fraction sampling system for $CO_2$ collection. The mixture of $^{14}$C labelled gaseous organic compounds will be separated in the GC and subsequently oxidised to $^{14}CO_2$ in a combustion reactor. Therefore, the fractions collected with the fraction sampler correspond to single $^{14}$C labelled compounds oxidised to $^{14}CO_2$. Modification of the GC system for the preparation of AMS samples was designed by Brechbühler AG (Schlieren, Switzerland), the commercial partner involved in this project. Recently, the combustion reactor was coupled to the GC-MS system. At present, first tests are being carried out with the aim of determining the efficiency of the oxidation process with alkanes and alkenes to $CO_2$. The fraction sampling system is currently being developed by Brechbühler AG.

## 9.5 *Summary and Outlook*

The GC-MS system available at PSI was modified with a view to the development of compound-specific $^{14}C$ AMS for gaseous species. Installation of a non-destructive TCD was realised and enables us to directly detect hydrocarbons in the gas phase.

Corrosion experiments with non-activated iron powders immersed in NaOH (pH 11 and 12.5) were performed. The experiments show that the same carbon species are produced in NaOH and Ca containing ACW. The concentration of the hydrocarbons was found to be significantly higher in NaOH solution compared to the ACW solutions suggesting that the corrosion rate is higher in NaOH within the experimental time investigated. By contrast, the concentrations of the carboxylic acids are similar in both solutions suggesting that their release is not the result of the ongoing corrosion process. This finding supports the idea that carboxylic acids had been produced in a preceding oxidation process, e.g. due to exposure of the surface of the iron particles to air or acid (oxidising) pre-treatment of the iron powders, and are instantaneously released to solution in the first stage of the corrosion process. Furthermore, we were able to identify a series of additional gaseous species with a longer carbon chain length up to C7 (e.g. pentane, 1-hexene, hexane, heptane) possibly due to the higher corrosion rate in NaOH we observed within the course of our experiment. These compounds could not be detected in the previous experiments carried out in the ACW solutions. Note, however, that the concentration of the compounds with a chain length > C4 is very low.

A gas-tight overpressure reactor was developed and tested which will be used for the long-term corrosion experiment with activated steel from the Gösgen nuclear power plant. Gas-tightness and absence of $O_2$ in the reactor was demonstrated over a time period of more than 10 days by monitoring dissolved oxygen in solution and the pressure inside the reactor. Furthermore, the $^{14}C$ background activity in solution sampled from the reactor was determined for the target carbon species. The $^{14}C$ background was found to be in the range of the previously determined analytical background (~0.06 $F^{14}C$).

The compound-specific $^{14}C$ AMS method for dissolved carboxylic acids was applied to identify and quantify $^{14}C$ containing carboxylic acids in a leach solution in contact with an activated steel nut segment. The concentration of $^{14}C$ containing acetic and formic acids released from activated steel was successfully determined in solution after a three years leaching period under oxic conditions. The $^{14}C$ activities of the two compounds were found to be well below the typical LOD of LSC.

The experimental program in the coming year will include the start of the corrosion experiment with two activated steel nut segments. The segments will be immersed in ACW (pH 12.5) in a controlled anoxic atmosphere in the reactor. Regular sampling, separation and analysis of the liquid phase will be undertaken in the first phase of the project with the aim of determining the $^{14}C$ speciation in solution. Furthermore, development of the compound-specific $^{14}C$ AMS method for gaseous and volatile compounds will be accomplished and applied in the analysis of gas samples collected from the reactor.

# 10 RWMC contribution to CAST WP2 Third Annual Report

The corrosion rate of the 18Cr-8Ni austenitic stainless steel under a condition of a dilute NaOH solution of pH 12.5 at 303K was reported last year [MIBUS *et al.*, 2015b; SAKURAGI *et al.*, 2016]. Here, we report the stainless steel corrosion obtained in deionised water. This is aimed to understand the corrosion behaviour in a fundamental condition and the pH influence on the corrosion rate of stainless steel.

A gas flow system was applied to measure the amount of gaseous hydrogen that evolves from the corrosion reaction. In this system, foils of stainless steel were immersed in a glass vessel through which an Ar gas was passing to carry and measure the evolved hydrogen by an atmospheric pressure ionisation mass spectrometry (API-MS). Details of the specimen and the experimental system are described in the last year report [MIBUS *et al.*, 2015b; SAKURAGI *et al.*, 2016].

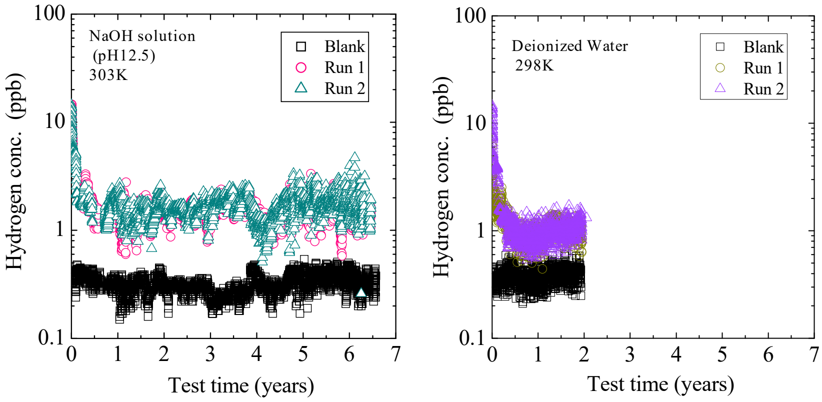


**Figure 10.1: Gaseous hydrogen concentration generated from stainless steel. Left represents the data in a dilute NaOH solution of pH 12.5 [MIBUS *et al.*, 2015b; SAKURAGI *et al.*, 2016]. Right represents the data in deionised water.**

Figure 10.1 shows the evolved hydrogen concentration in the argon carrier gas in the system. Two sets of experiments have been performed. The hydrogen concentration decreased from over 10 ppb to below 1 ppb within a year. This trend is similar to that reported last year obtained in a dilute NaOH solution at 303K [MIBUS *et al.*, 2015b;

SAKURAGI *et al.*, 2016]. The slight lower hydrogen concentration in this year may be attributed to the temperature difference of 5°C.

Figure 10.2 shows the corrosion rate of stainless steel, $R_c$ (µm/year), obtained from the evolved hydrogen gas in Figure 10.1 and by assuming the following corrosion reaction and equation:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 8H,$$

$$R_c = \frac{3}{8} \cdot \frac{A_{gas} \cdot M_{Fe} \cdot 10^6}{\rho_{Fe} \cdot t},$$

where $A_{gas}$ is the cumulative atomic molar amount of gaseous hydrogen per unit surface area (mol/m$^2$), $M_{Fe}$ is the molecular weight of iron (55.85 g/mol), $\rho$ is the iron density ($7.87\times10^6$ g/m$^3$), and $t$ is the test time (years). The corrosion rates decrease with time. As mentioned above, the corrosion rate in deionised water at 298K is slightly lower than that reported last year obtained in a dilute NaOH solution at 303K [MIBUS *et al.*, 2015b; SAKURAGI *et al.*, 2016], but the overall trend is similar. Therefore, it is expected that the corrosion rate in deionised water will be constant after the 2 years. In the next step, we will analyse the oxide film formed in the deionised water and discuss the characteristics and roles of the oxide.

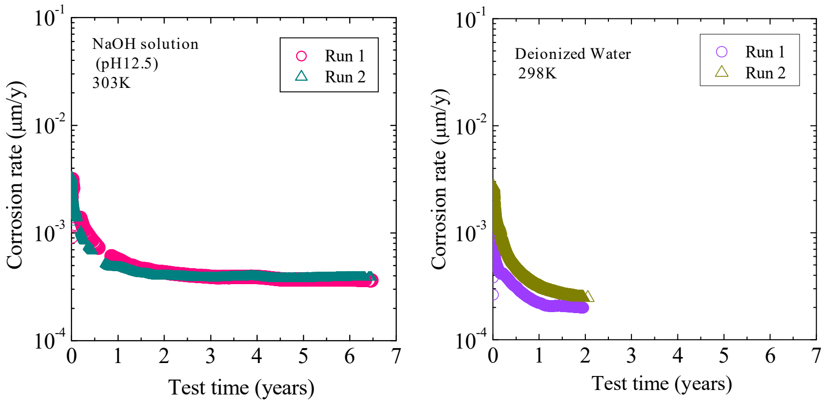


**Figure 10.2: Corrosion rate of stainless steel as a function of time obtained from the gas flow test. Left represents the data in a dilute NaOH solution of pH 12.5 at 303K [MIBUS *et al.*, 2016; SAKURAGI *et al.*, 2016]. Right represents the data in deionised water at 298K.**

This research is a part of the “Research and development of processing and disposal technique for TRU waste (FY2015)” program funded by the Agency for Natural Resources and Energy in Ministry of Economy, Trade and Industry of Japan.

# 11 SCK•CEN contribution to CAST WP2 Third Annual Report

## 11.1 *Materials*

SCK•CEN has at its disposal both unirradiated and irradiated JRQ (ASTM A533 grade B class 1 steel) carbon steel samples. The available irradiated JRQ specimens originate from the SCK•CEN`s BR-2 reactor and are ready for the static and accelerated corrosion experiments. They were cut to the appropriate size.

## 11.2 *Methods and experiments*

### 11.2.1 Preliminary test on corrosion rate determination from Cobalt-60 release

Objective

The objective of this task was to test if corrosion rate can be determined radiometrically by measuring the release of activation products, like $^{60}$Co, after contacting an irradiated steel sample with $Ca(OH)_2$ portlandite pore water solution. This approach assumes a homogeneous distribution of $^{60}$Co in the material and same chemical behaviour as the carbon steel under alkaline conditions.

Description

A piece of irradiated JRQ carbon steel sample was immersed in a Teflon test cell containing approximately 20 mL of 0.01 M $Ca(OH)_2$. After some pre-defined periods 10 mL liquid samples were taken, transferred into a 20 mL HDPE liquid scintillation vial and closed with a cap. The released $^{60}$Co activity concentration was determined with gamma-ray spectrometry at the Low-level radioactivity Measurements Unit (LRM) at SCK•CEN. The measurement lasted between two and three days and after that, this 10 mL liquid sample was poured back to the original test cell to continue the corrosion experiment and let $^{60}$Co accumulate in the electrolyte. This procedure was repeated after each sampling, except the last one. The last sampling was planned after 30 days from starting the test but it was changed to 50 days.

Planning

The contact time of the metal and $Ca(OH)_2$ solution was 50 days in total. Samples were taken on regular intervals during the test period. The experiment started on 24.02.2016 and finished on 12.04.2016.

Results

The `a priori` assumption on the $^{60}$Co release kinetics and concentration profile in the solution was based on the carbon steel corrosion behaviour in alkaline solution. Under these conditions two regions can be distinguished: 1) an instantaneous and rapid corrosion region where the corrosion rate, and then the $^{60}$Co release, increases linearly and 2) a slow corrosion region, sometimes below the detection limit, where the corrosion rate is close to zero due to the formation of passive corrosion layer. This would lead to a plateau in the graph of the $^{60}$Co concentration in function of the time.

After obtaining the originally planned five measurement results (until 30 days), a fluctuation of results can be observed (Figure 11.1). The only plausible explanation at this moment is the interference of the visible small sized precipitate particles. Under alkaline conditions the released $^{60}$Co can be precipitated as hydroxide. It is difficult to homogenise completely the solution/suspension and take a representative sample. Another error source might be that these precipitates already absorbed on the wall of the test cell. The third error can originate from the gamma-ray spectrometry measurement, where $^{60}$Co was assumed to be homogenously distributed in whole the solution. While, in our case the precipitate can be settled to the bottom of the vial. It was shown that the calibration correction factor in this case can differ by a factor of two. Furthermore, the amount of precipitate after each sampling might have been different and it is not possible to quantify retroactively.

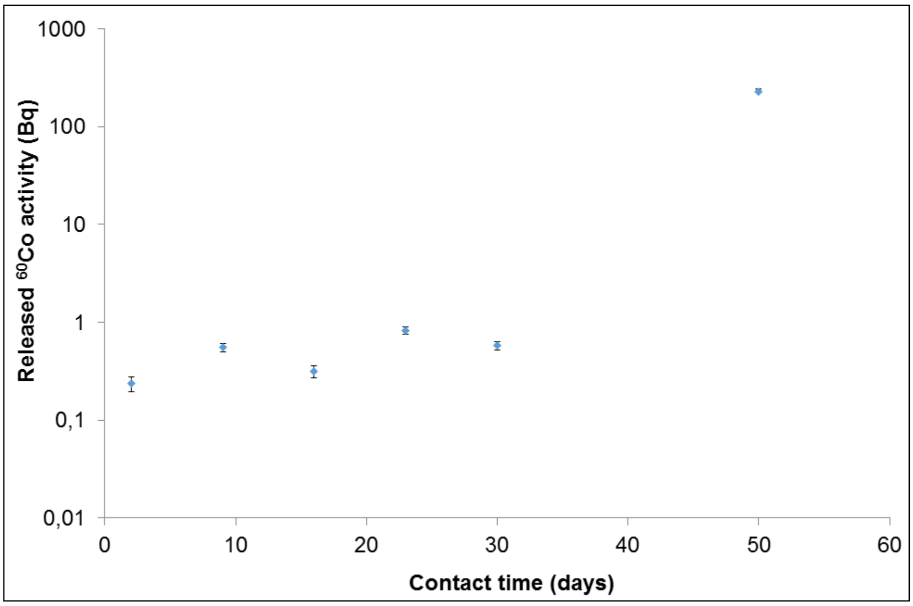


**Figure 11.1: The total released $^{60}$Co activity as a function of contact time**

The experiment continued up to 50 days and the whole 20 mL liquid phase was analysed by gamma-ray spectrometry (Figure 11.1).

After 50 days, an unexpectedly high $^{60}$Co activity was observed in the liquid phase. The reasons are unclear but it may have happened that a very small piece of irradiated metal was transferred accidentally into the liquid scintillation vial.

Possible reasons for the discrepant results:

- Visible precipitates
- Sampling difficulties: inhomogeneous samples
- Precipitate absorption on the experimental cell wall
- Gamma spectrometry: correction for inhomogeneous activity distribution
- Small piece of irradiated material (unclear, 50 days result)

For more accurate $^{60}$Co release results the following actions could be considered to improve the reliability of results:

- Sample acidification before analysis to avoid the cobalt hydroxide precipitation,
- Careful sampling to avoid contamination from the corroded irradiated samples.

### 11.2.2 Carbon-14 production estimation

The released $^{14}C$ quantity was estimated on the basis of a liquid scintillation measurement where an OptiPhase HiSafe3 cocktail was used and a Quantulus liquid scintillation counter.

The $^{14}C$ release was estimated to be 21 ± 14 Bq/L which equals to 1.05 ± 0.7 Bq in the original 20 mL volume. The detection limit was 6 Bq/L.

It can be concluded that there was already detectable $^{14}C$ release after 50 days from the irradiated samples. However, this quantity is very low and has high relative uncertainty. Therefore, determining the distribution of $^{14}C$ between different carbon species will be very difficult.

## 11.3 *Corrosion experiments*

Static leaching and accelerated corrosion tests are planned for unirradiated and irradiated samples. After consulting with the SCK•CEN's radiation protection officers, experiments are allowed to be performed in glove bags under fume hoods respecting the safety regulations. The final experimental setup was designed accordingly and presented in this document. Hot cells at the SCK•CEN are fully occupied and they have to be shared with other experiments which may jeopardise the integrity of our experimental setup and samples.

### 11.3.1 Static leaching test

During the static leaching test a piece of irradiated metal sample is placed in a container filled with saturated $Ca(OH)_2$ aqueous solution. After closing the test cell airtight with a lid, the whole setup is left for six months. At the end of the experiment gas and liquid samples are taken and analysed for carbon species. All the manipulations are performed under anaerobic atmosphere. The static leaching experiments will be performed in glove bags having underpressure inside. The atmosphere in the glove bag will be anaerobic which is maintained by a flow of argon gas. The gas flow of the argon will be regulated and filtered with HEPA filters. Three irradiated sample will be run parallel in one batch.

The schematic layout of the static leaching test setup and the technical drawing of the test cells are presented in Figure 11.2.

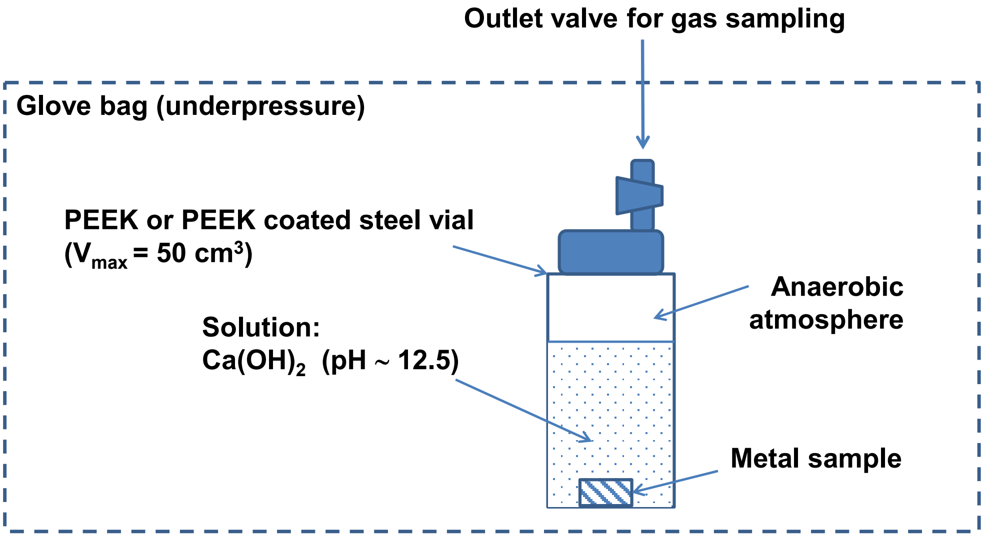


**Figure 11.2: Proposed design of the static leaching test setup**

The irradiated samples will be put immediately into the test cells. Then, before starting the experiment the glove bag will be flushed with argon to reduce oxygen level in the system, eventually obtaining anaerobic condition.

Irradiated samples will be placed manually with tweezers in a test cell filled with saturated Portlandite pore water. The samples will be placed at the bottom of the vial and 35 mL pore water will be filled into the test cells. The liquid phase will occupy approximately 70 % of the test cell volume and the rest is for the headspace (15 mL).

The test cell will be covered immediately with the lid and closed gas tight by tightening with the screws. The test cells will be left for six months without opening behind a lead shielding wall. After this contact time, gas and liquid samples will be taken. Sampling will be done from the gas and liquid phase only once at the end of the experiment.

First, the gas samples are taken through a special gas tight valve (Mininert) with a gas tight syringe. The Mininert valve is fixed to the outlet just before the sampling to avoid any damage in the Teflon valve material due to radiation. A gas tight syringe with a 5 cm long needle is used for this purpose. The carbon compounds accumulated in the test cell will be transferred to the analytical instrument with a 0.5 mL gas tight syringe after checking for surface contamination. After sampling, the needle is stuck into (not through!) a septum or a rubber piece. Then the syringe is placed in a small transport box, so that the piston will not be pushed or pulled on. After disassembling the test cell, a small aliquot (2 mL) liquid sample is taken with a pipette and transferred into vial with screw cap and septum.

After taking the gas samples, the lid of the test cell will be removed and a liquid sample will be taken for gamma-ray spectrometry and gross alpha beta counting to see the gamma emitting contaminants and the level of alpha/beta radioactivity. After the contamination check, the total $^{14}C$ content of the liquid phase would be measured by liquid scintillator counting.

On the basis of these measurement data, the radiation and contamination risk related to the chromatographic separation can be further assessed. Out of the 35 mL solution, approximately 5 mL solution is needed for the gamma spectrometry analysis, which could be recuperated and used for the gross alpha/beta measurement by liquid scintillation counting. Another 2 x 2 mL aliquot could be used for the total released $^{14}C$ measurement and for the speciation analysis respectively. The total sample consumption of these tasks is 9 mL, which still enables us to perform more replicates from the liquid phase (total $^{14}C$ and speciation analysis).

### 11.3.2 Accelerated corrosion test

The accelerated corrosion tests would consist of imposing a pre-determined potential to the samples that would result in accelerated active corrosion of the sample. To determine this potential, polarisation measurements should be performed to determine the E-i behaviour of the sample in the tested environment. Depending on the active corrosion rate, a single accelerated experiment can last from few days till some weeks. The proposed design of the accelerated corrosion test setup and the glass cell are shown in Figure 11.3.

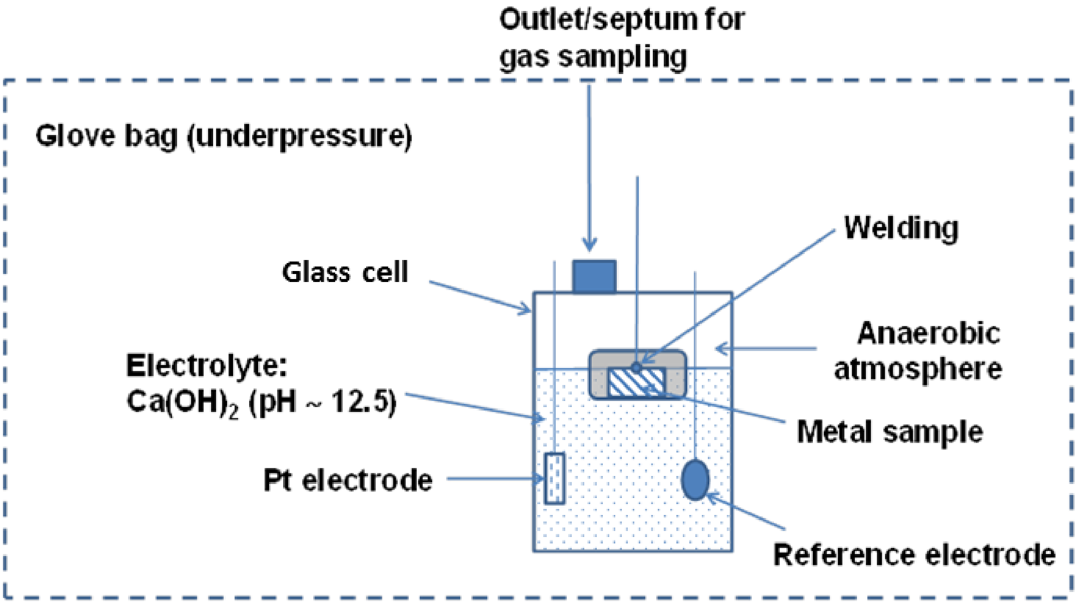


**Figure 11.3: Proposed design of the accelerated corrosion test setup**

After point welding a wire to the back of the sample which serves as an electric connection, the metal sample is embedded in a radiation resistant resin under fume hood and then polished to obtain a fresh non oxidised surface. Samples have to be clean, i.e. free from spent fuel or any external radionuclide contamination.

Special glass wares and electrodes have been designed for the accelerated corrosion setup (Figure 11.4).

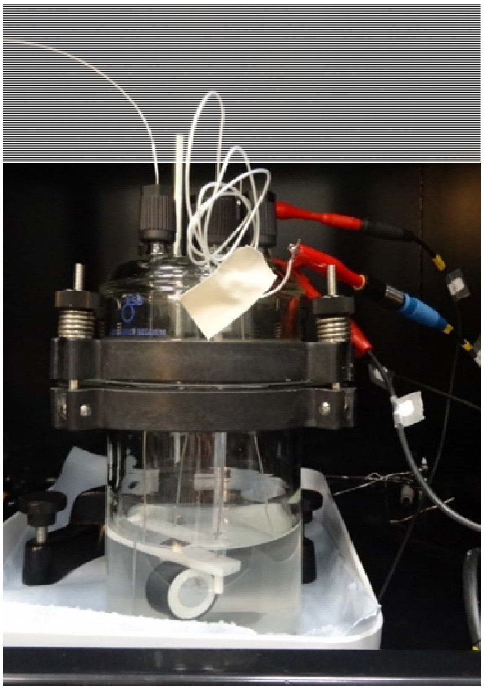


**Figure 11.4: Picture of the accelerated corrosion test 3-electrodes setup**

This test cell contains 3 electrodes: (1) the working electrode (metal sample), (2) the platinum counter electrode and (3) the home made Ag/AgCl reference electrode. These electrodes will be introduced through the cell cap.

The experiment will be stopped after dissolving sufficiently enough material. For the accelerated leaching test, one sample will be taken at the end of the experiment. Gas sample will be taken through one of the connections by a gas tight syringe with a 5 cm long needle. After sampling, the needle is stuck into a septum or a rubber piece. Then the syringe is placed in a small transport box, so that the piston will not be pushed or pulled on. After disassembling the test cell, a small aliquot (2 mL) liquid sample is taken with a pipette and transferred into vial with screw cap and septum.

## 11.4 *Procurement of an analytical instrument*

For the determination of the $^{14}$C speciation, a gas chromatography system was installed in September 2016. The acquired system is a Shimadzu GC-2010 Plus, which is tailor-made to meet our requirements. Detectors include a Flame Ionisation Detector (FID), a Barrier Discharge Ionisation Detector (BID), and a Pulse Discharge Helium Ionisation Detector

(PDHID). The operation of the FID is based on the detection of ions formed during combustion of organic compounds in a hydrogen flame. The generation of these ions is proportional to the concentration of organic species in the sample gas stream. The response of a FID is semi-universal: all hydrocarbons can be detected. Our FID has a detection limit of approximately 1 ppm. In a BID detector, a plasma is generated by applying a high voltage to a quartz dielectric chamber, in the presence of helium. Compounds that elute from the GC column are ionised by this He plasma, then captured with collection electrodes and described as peaks. The limit of detection of our BID is approximately 500 ppb. The PDHID uses a stable, low powered, pulsed DC discharge in helium as an ionisation sources. Compounds coming from the GC are ionised by photons from the helium discharge and the resulting electrodes are captured in a collector electrode where the current is quantified as the detector output. The limit of detection of our PDHID is approximately 50 ppb. To determine the total amount of $^{14}$C in the leachant, samples will be taken for liquid scintillation counting.

# 12 VTT contribution to CAST WP2 Third Annual Report

## 12.1 *Experiments with inactive material*

The experiments with inactive materials were started in 2015. Unirradiated $Fe_3C$ and AISI316Ti steel powders are being investigated in two simulated groundwater solutions, CA85 and CA125. The compositions of the solutions are presented in CAST WP2 Annual Progress Report - Year 1 (D2.2) by [Mibus *et al.*, 2015a]. Duran® laboratory glass bottles (100, 150 and 250 mL) are used as experiment vessels. The bottles were placed in a glove box with Ar atmosphere ($O_2$< 1ppm, low $CO_2$). The solid to liquid ratio in AISI316Ti powder experiments is 100g/200mL and in $Fe_3C$ experiments varied as follows: 20g/80mL, 50g/100mL and 20g/200mL. In addition to that, the experiments in 100 mL anaerobic media bottles with a septum stopper were started. From these samples we will try to analyse the gas phase and determine the quantity and composition of carbon compounds in gas phase.

### 12.1.1 Sampling and carbon-12 analyses

The total amounts of dissolved inorganic carbon (DIC) and organic carbon (DOC) were determined in the solution phase after semi-sequential leaching periods. The first sampling for $Fe_3C$ experiments was done after the leaching time of 20 days and the second one after 361 days from the start. For AISI316Ti experiments, the first sampling was done after 48 days and the second one after 302 days. The more detailed description of the sampling procedure is giving in CAST WP2 Annual Progress Report - Year 2 (D2.5) by [Mibus *et al.,* 2015b] DIC and DOC analyses were done by Ramboll analytics with TOC analyser (Analytika Jena N/C UV HS) as reported earlier [Mibus *et al.*, 2015a].

The compositions of the organic carbon compounds in liquid phase were analysed at VTT Expert Services Oy and at VTT Oy. Volatile organic alcohols were analysed by gas chromatography with a flame ionisation detector (HS-GC-FID). 5 mL of sample was put into 20 mL Headspace (HS) vial and heated at 60 °C for 23 min. Volatile organic alcohols were detected from the gas phase of the vial. The concentrations were detected by means of the external calibration with standards made of pure substances and the identifications were confirmed with standard additions. Other volatile organic compounds (VOCs) were analysed by HS-GC-MS instrument (headspace technique with gas chromatography and mass spectrometry). 3 mL of sample was put into 20 mL Headspace (HS) vial and heated at 80 °C for 30 min. Sample was taken from the gas phase. The compounds detected were identified by using commercial mass spectrum library and the concentrations were determined semiquantitatively with an external toluene standard. ESI-MS/(MS) and LC-MS/(MS) (electrospray ionisation tandem mass spectrometry, liquid chromatography tandem mass spectrometry) with C18 column were used for the qualitative analysis of polar molecules sharing similar structures. The analyses were tested with undiluted and diluted samples. It was observed that quite high salt concentrations in the samples disturbed analyses and only adduct signal clusters coming from salt and LC-eluent (water-acetonitrile) were detected. Therefore, the solid phase extraction (SPE) procedure was used to remove the salts and to concentrate the samples. Both positive and negative ionisation modes were used in the measurements. For the compounds detected, the product ion spectra were measured. Possible organic acids, such as oxalic, formic, succinic, glycolic, acetic, lactic, levulinic, butyric and Valeric acids were analysed by using a P/ACE MDQ capillary electrophoresis (CE) instrument equipped with a photodiode array UV-Vis detector working at a wavelength of 230 nm (Beckman-Coulter Inc., Fullerton, USA). The acid standards were prepared and analysed prior to the analyses of the actual samples. The electrolyte solutions were commercial from Analis (Ceofix Anions 5 (Ordior/Analis, PART NUMBER: 10-0004650)). Bare fused silica capillary with inner diameter 75µm were used; the detector length to the UV detector was 50 cm and the total length was 60 cm. The separation voltage of -30kV and polarity of positive to negative were applied. Samples were injected using 0.5 psi pressure for 8 s. The separation of acids was carried out after diluting the sample by CE.

### 12.1.2 Results of analyses

The total amounts of dissolved organic (DOC) and inorganic (DIC) carbon were analysed after the chosen time periods. The results from the leaching tests with $Fe_3C$ and AISI316Ti powders at pH 8.5 and 12.5 are presented in Figure 12.1 (solid to liquid 1/2). The content of organic carbon is higher compared to inorganic carbon (in all the experiments) at both pH in the leaching solutions of both carbon containing solid phases. The content of dissolved carbon was higher in the experiments with $Fe_3C$ than in AISI316Ti experiments. This was expected, because $Fe_3C$ had a higher carbon content (6.2). The pH difference had a small influence on the dissolved organic carbon, while the concentration of inorganic carbon was higher at alkaline pH 12.5.

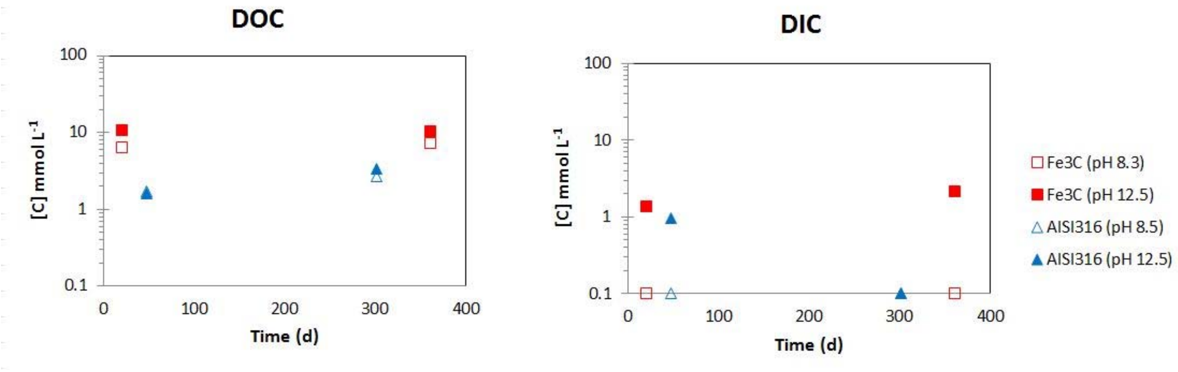


**Figure 12.1: Measured contents for dissolved organic (DOC) and inorganic (DIC) carbon in simulated groundwaters in the leaching experiments of $Fe_3C$ and AISI316 powders**

The volatile organic alcohols, which were analysed from the leaching solutions, were methanol, ethanol and 1-propanol. Other volatile organic alcohols were not analysed. The results of the measurements are presented in Table 12.1. Only the concentration of 1-propanol in $Fe_3C$ experiments was above the limit of quantification. On the other hand, the limit of quantification was relatively high, especially for methanol, with the method used (GC-FID) under these conditions. Methods to improve the sensitivity will be explored.

**Table 12.1: Results from the HS-GC-FID alcohol analyses**

| Sample | Methanol (mg/L) | Ethanol (mg/L) | 1-Propanol (mg/L) |
|---|---|---|---|
| $Fe_3C$ pH 8.3 | < 2 | < 0.6 | 1.2 |
| $Fe_3C$ pH 12.5 | < 2 | < 0.6 | 2.7 |
| AISI316 pH 8.5 | < 2 | nd | < 0.3 |
| AISI316 pH 12.5 | < 2 | nd | < 0.3 |

< = detected, but concentration was below detection of quantification (<LOQ)
nd = not detected

Other volatile organic compounds (VOCs), see Table 12.2, were determined with gas chromatography using MS detection in the samples from the leaching experiments with alkaline pH 12.5. Minor amounts of toluene, ethyl benzene and xylenes were found in the samples from the leaching experiment with $Fe_3C$ powder.

**Table 12.2: Results from the HS-GC-MS analyses**

| Sample | Toluene | Ethyl benzene | Xylenes, sum | *Sum* |
|---|---|---|---|---|
| $Fe_3C$, pH 12.5 | 0.04 | 0.01 | 0.02 | *0.06* |
| AISI3,16 pH 12.5 | nd | nd | nd | *nd* |

nd = not detected

The LC-MS total ion chromatograms (positive ionisation mode) of the samples after the solid phase extraction (SPE) procedure are presented in Figure 12.2. The compound peaks coming from the samples are filled with black colour. The ESI-MS-spectra taken from the three peaks detected in the sample from $Fe_3C$ test (pH 12.5) are given in Figure 12.3.

Based on the product ion spectra and literature, the organic compounds detected in the sample from $Fe_3C$ test (pH 12.5) were surfactants (tensides). The peaks at the retention times of 4.91 (m/z 360) and 5.1 min (m/z 388) are probably hexadecyl (C16) and octadecyl (C18) benzyldimethylammonium chlorides. At the retention time of 4.98 min, the compounds detected were probably a mixture of alcohol ethoxylates (AE) or polyethylene glycols. The compounds with signal m/z 654 (Figure 12.3, middle spectrum) could not be identified but probably it is also a surfactant compound. These compounds were observed also in the sample from AISI316 test (pH 12.5). In the LC-MS/MS analyses with negative ionisation mode, also linear alkylbenzene silphonate (LAS) surfactants (tensided) were identified in the samples from $Fe_3C$ test (pH 12.5) and from AISI316 test (pH 12.5). Without reference standards the determination of exact concentrations could not be done. The rough estimation for the sum concentration of the surfactants was 1-5 mg/L. In CE analysis no organic acids were detected. All the results were below the detection limit.

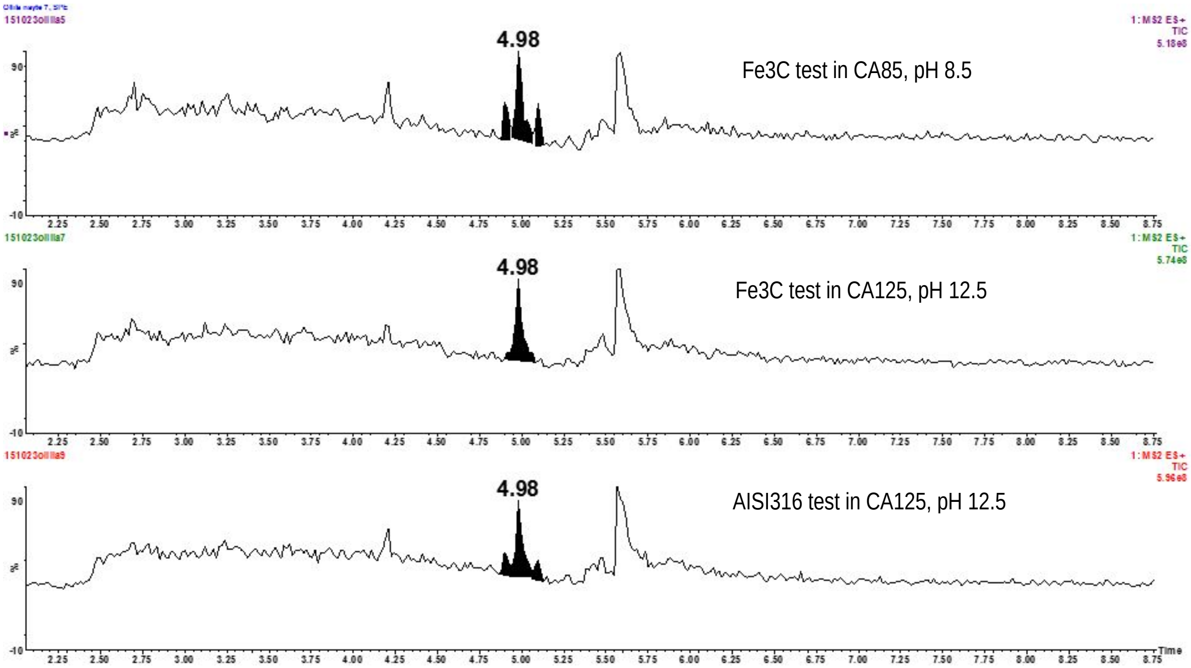


**Figure 12.2: The LC-MS total ion chromatograms (positive ionisation mode) of the samples after SPE (solid phase extraction)**

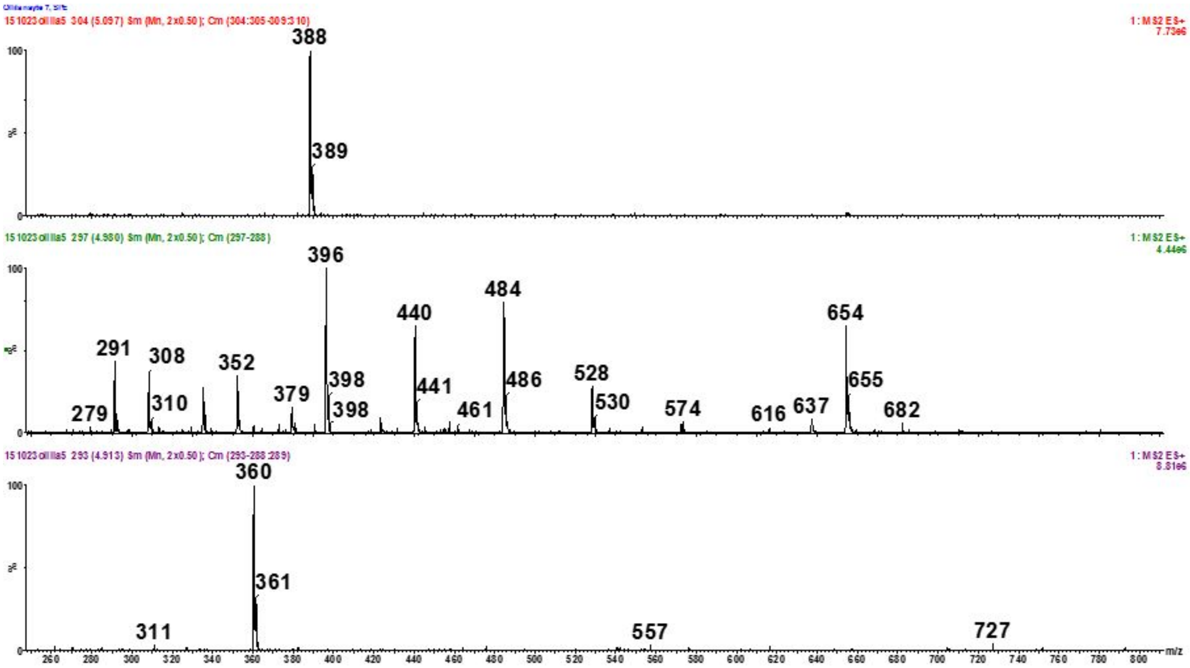


**Figure 12.3: The ESI-MS-spectra taken from the three peaks detected in the sample from the $Fe_3C$ test (pH 12.5). Upper spectrum is a peak at the retention time 4.91 min, middle at 4.98 min and bottom at 5.2 min**

## 12.2 Experiments with active material

The samples chosen for the active experiments come from the surveillance capsule chains from the Loviisa nuclear reactor (Figure 12.4). These capsule chains were loaded in Loviisa reactor in autumn 2011 and were removed in autumn 2015. They were used to determine the irradiation embrittlement of the pressure vessel during the operation of the reactor. The capsule chains arrived to VTT Nuclear Reactor Materials team for testing in spring 2016. The two specimens for $^{14}C$ leaching experiments were cut from these capsule chains. The analytical data for the composition of the capsule material, which is stainless steel, is given in Table 12.4. The nitrogen content of the inactive capsule steel was analysed. On the basis of this initial $N_2$ content and the neutron dose fluence of the capsule, the theoretical maximum content of $^{14}C$ after exposure was calculated to be2 x $10^3$ Bq $^{14}C$/g.

The $^{60}Co$ activities for the two specimens were measured to be: Specimen A) 227.27 MBq and Specimen B) 619.23 MBq. The schematic drawing of the experiment set-up is presented in Figure 12.5. The specimens are in zirconia crucibles (Vol. 175 mL), which are inside of a 500 mL Duran glass bottle. The set-up was placed inside an underpressure glove-box (Ar) behind a lead shield (Figure 12. 6). Synthetic groundwater CA85 (pH 8.5) and 0.01 M NaOH solution (pH 12) are being used as the leaching solutions. Synthetic groundwater CA125 (pH 12.5) was replaced with 0.01 M NaOH solution due to the difficulties in carbon analysis (Table 12.3). The high $Cl^-$ concentration in CA125 solution disturbs the sensitive measurements. The experiments were started on June 29th 2016 by immersing the active samples in the solution. Prior to that the specimens were quickly rinsed with ethanol and weighed. Specimen A (227.27 MBq) weighed 2.975 g and was immerged in CA85 solution. The more active Specimen B weighed 9.211 g and was immersed in 0.01M NaOH solution.

**Table 12.3 Compositions of the synthetic groundwaters used as leaching solutions**

| | | CA85 | CA125 |
|---|---|---|---|
| *pH* | | *8.5* | *12.5* |
| $Na^+$ | mg/L | 2680 | 2730 |
| $Ca^{2+}$ | mg/L | 630 | 590 |
| $K^+$ | mg/L | 25 | 25 |
| $SO_4^{2-}$ | mg/L | 560 | 560 |
| $Cl^-$ | mg/L | 4840 | 4840 |
| $Br^-$ | mg/L | 18 | 18 |

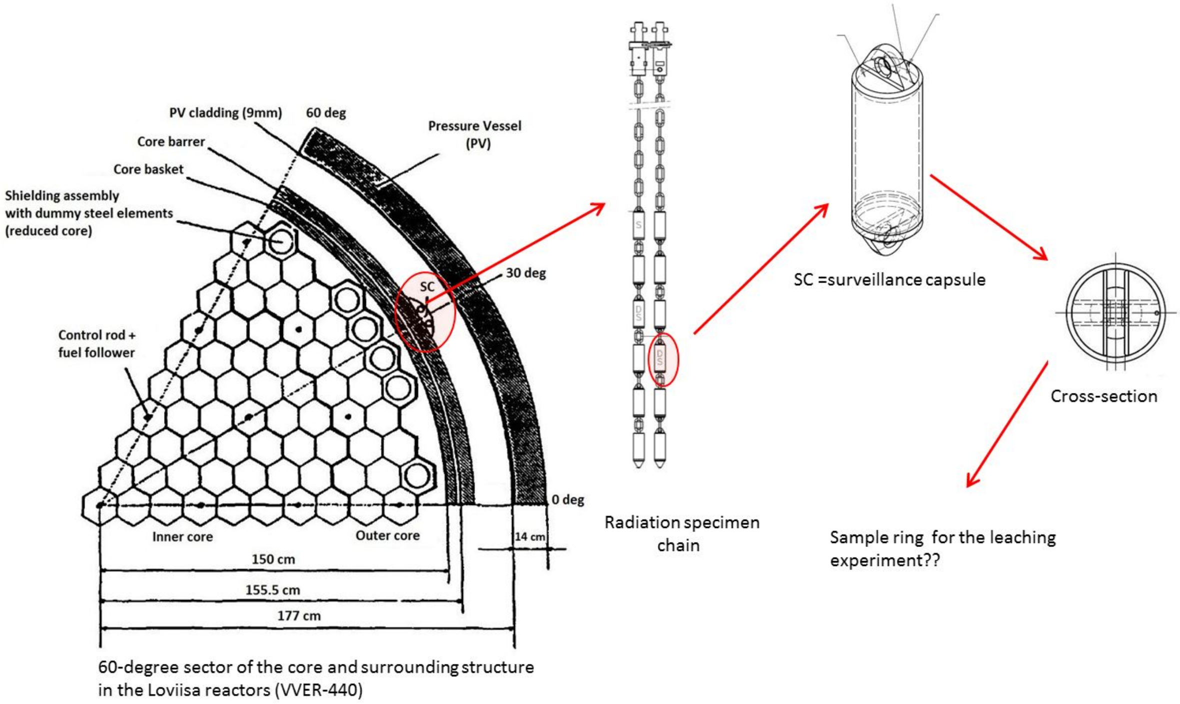


**Figure 12.4: Schematic drawing of the surveillance capsule and its position in the reactor (Pictures by Fortum Power and Heat Ltd.)**

**Table 12.4: The composition of the inactive surveillance capsule material**

| Sample | Composition % | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Capsule cover | *C* | *Si* | *Mn* | *S* | *P* | *Cr* | *Ni* | *Mo* |
| | 0.023 | 0.34 | 1.81 | - | 0.027 | 16.7 | 11.1 | 2.06 |
| | *Cu* | *Al* | *W* | *V* | *Ti* | *Co* | *N* | *Fe* |
| | 0.26 | 0.023 | 0.02 | 0.05 | 0.22 | 0.07 | 0.04 | (rest) |

The first samplings are planned to be performed three months after the start of the experiments for measuring the total activity of the leaching solutions. The $^{60}$Co activity of the solutions will be analysed by γ-spectrometer and the $^{14}$C activity is determined by LSC (Liquid Scintillation Counting), if possible. If the sensitivity of LCS is not sufficient, the possibilities for the measurements with AMS (Accelerated Mass Spectrometry) will be explored. AMS is available at Helsinki University. After a better knowledge of the activity level of the solutions the speciation analyses are planned. Treatment of the samples with ion-exchange resin is probably necessary. Thereafter, the total carbon content will be analysed, as well as the amounts of total organic and inorganic carbon, with TIC/TOC analyser. A plan is to try to identify the organic compounds from the solution using the same methods as in the inactive experiments. The gas phase analysis will be performed only for the inactive experiments. Our possibility to identify the organic compounds present in the gas phase is under investigation.

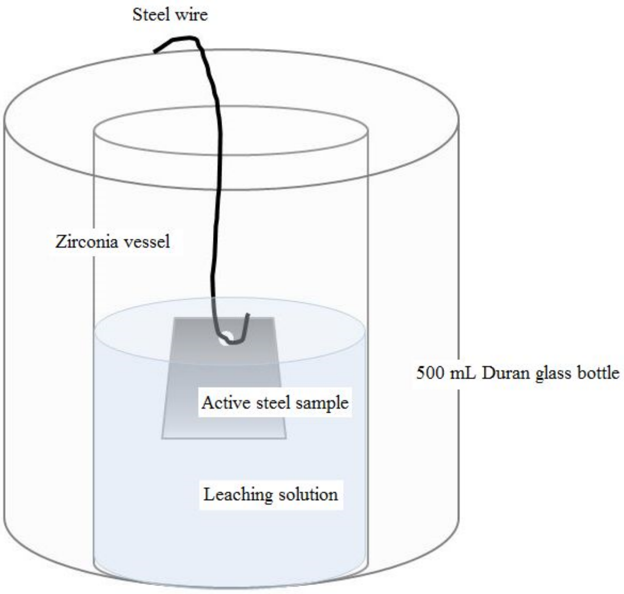


**Figure 12.5: The schematic picture of the experimental set-up.**

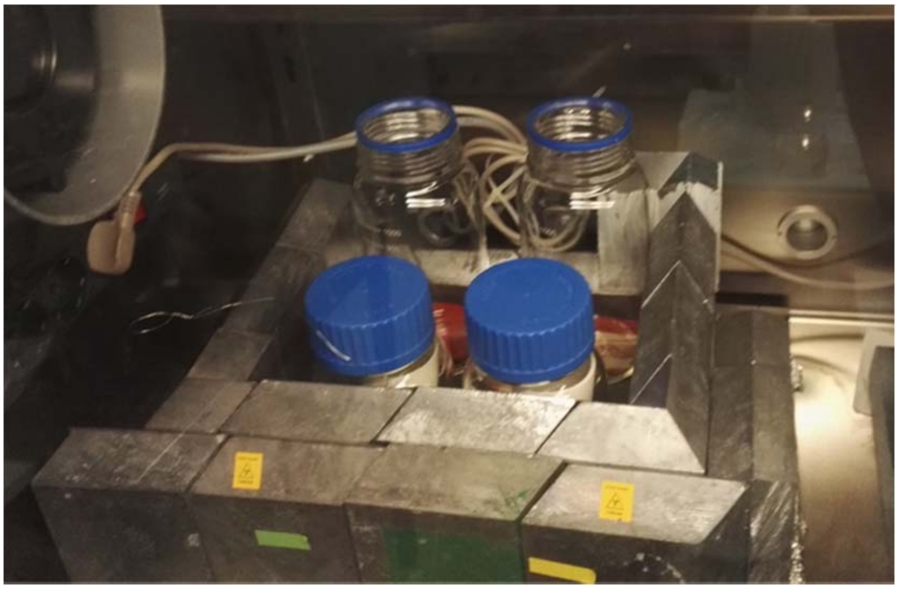


**Figure 12.6: The experimental set-up inside the glove-box (Ar) behind the lead shield.**

# 13 Conclusions

In the third project year (October 2015 to September 2016), further refinements to the analytical methods for speciation measurement of $^{14}C$ in liquid and gaseous phase have been made. The experimental setup and the preparation and characterisation of samples could be achieved and consequently all experiments (with one exception) could be started in the past project year.

In the fourth and last project year (October 2016 to September 2017), the corrosion experiments will be continued and the release and speciation of $^{14}C$ will be measured. Interpretation of the experimental results and a final synthesis will be a main task of the last project year.

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