CArbon-14 Source Term

CAST

WP2 Annual Progress Report - Year 2 (D2.5)

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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 ion-exchange materials.

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

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

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

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WP2 Annual Progress Report - Year 2 (D2.5)

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 organizations 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 second project, year the participants were mainly engaged in Tasks 2.2 and 2.3.

The literature review, carried out by AMEC with support from all participants, has been issued with slight delay in the beginning of the reporting period as deliverable D2.1. The results of the review provide a basis for the experimental design and the interpretation of the results. With that, Task 2.1 is concluded and milestone M6 is reached.

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 has been started in the first project year. This Task 2.2 is done by PSI and Armines in close cooperation with the partners from WP3. Experiments with non-irradiated iron samples have been performed and analytical strategies for sampling, separation and quantification of possible ^{14}C species

were developed. For the separation and identification of low molecular weight organic molecules, High-Performance Ion Exchange Chromatography and Gas Chromatography, both coupled to Mass Spectrometry, are proposed for aqueous and gaseous samples, respectively. It is estimated that 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.

The corrosion experiments to measure the release and speciation of ^{14}C in Task 2.3 have been prepared within the reporting period. Materials cover activated stainless steel and mild steel but also non activated samples of iron and iron carbide. Methods for characterizing the sample surface have been tested. Data on the activation of the samples were compiled to start a comparative calculation of the ^{14}C inventory. The experimental setup for the corrosion experiments is being prepared and tested (delayed in some groups). The leaching solution in the experiments has been intensely discussed including thermodynamic calculations. A representative cement pore water of pH 12 to 12.5 is recommended. It can be prepared from NaOH (higher background from atmospheric $^{14}CO_2$ possible) or $Ca(OH)_2$ (potential precipitation of $Ca^{14}CO_3$) depending on the chosen experimental conditions.

During the second project year, a common Technical Meeting with WP3 was held during the General Assembly Meeting on 21 – 22 October 2014 in Brussels. A further Technical Meeting was organized by Nagra on 27 – 28 May 2015 in Wettingen (CH) with a subsequent Workshop on analytical methods held on 29 May 2015 at PSI (organized by E. Wieland). Three deliverables are due in the second project year. The report on selected analytical procedures at PSI (D2.3) is expected to be issued by the end of December 2015 and a draft of the corresponding report from Armines (D2.4) is expected on the same timescale. This annual report (D2.5) is the third deliverable.

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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 organizations participate in WP2: Amec Foster Wheeler, (former AMEC, 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 second project year (October 2014 to September 2015). The report is edited by Nagra and contains contributions from all participants. In addition to the authors mentioned, M. Bahri (Armines), Enrique Magro Lozano (Ciemat), E. Wieland (PSI) and K. Ollila (VTT) made contributions.

2   Amec Foster Wheeler contribution to CAST WP2 Second Annual Report

2.1 *Introduction*

During Year 2 of the CAST project, Amec Foster Wheeler[1] has contributed two activities to WP2:

- revision and publication of the state of the art review of the understanding of steel corrosion rates and carbon-14 releases from irradiated steels [SWANTON *et al*., 2015], which had been written during Year 1; and

- through our sub-contractor RadioCarbon Dating limited (RCD), designed and manufactured equipment for the selective capture of volatile carbon-14 species from the gas phase for subsequent quantitative analysis.

This report focuses on the second of these two activities.

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 will be performed in the G1 chemical hot cell in NRG's Hot Cell Laboratories (HCL) at Petten. Amec Foster Wheeler through RCD is contributing the expertise in selective capture and quantitative analysis of gas phase carbon-14 to these experiments. The methods used have been applied previously by Amec Foster Wheeler and RCD to measure gas-phase carbon-14 releases from irradiated graphite [BASTON *et al*., 2012, 2014]. Under a parallel project to CAST (called Pre-CAST), RCD have manufactured equipment for installation in the HCL. The equipment was delivered to NRG in March 2015. The RCD equipment will be installed in a glovebox adjacent to the G1 hot cell from which it will be connected to the leaching experiments for gas-phase sampling.

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[1] AMEC merged with Foster Wheeler in November 2014 to form Amec Foster Wheeler and henceforth will be referred to as Amec Foster Wheeler in CAST.

Further details of the analysis method and equipment design are outlined below. Further details of the planned leaching experiments on steels are provided in the NRG contribution to this Annual Report (see Section 8).

2.2 *Apparatus for gas-phase carbon-14 capture*

The RCD methodology is based on solid-state (soda lime) absorbent technology linked to the selective oxidation of gas phase carbon-14 containing species to $^{14}CO_2$.

Humidified soda lime is a highly efficient absorbent for CO_2. Tests carried out by RCD have demonstrated that CO_2 capture by the soda lime columns used (containing 36g of humidified soda lime (30g soda lime in the dry state)) is near-quantitative at about 96% [BASTON *et al*., 2014]. The use of soda lime enables the absorbed $^{14}CO_2$ to be recovered quantitatively by acidification and converted to benzene for liquid scintillation counting (LSC). The limit of detection for carbon-14 by this method is 0.03 Bq.

A schematic diagram of the gas-phase sampling apparatus is shown in Figure 2.1. The apparatus has been constructed as two transportable units, the first for the collection of inorganic carbon-14 ($^{14}CO_2$ and ^{14}CO, each on separate soda lime columns) and the second for volatile organic carbon-14 containing species (e.g. $^{14}CH_4$). The units have been manufactured to vacuum engineering standards and operate at slightly less than atmospheric pressure. The sample gas is drawn through the apparatus by means of a pump located near the outlet of the second unit.

In the planned irradiated steel leaching experiments, the carbon-14 containing gases that are released will be collected periodically by flushing the headspace of the leaching vessel with nitrogen gas and drawing the gas stream through the sampling apparatus. The gas stream first passes through a soda lime column to collect any $^{14}CO_2$ released from the experiments. After passing through a non-return valve, the sample gas is then mixed with CO_2-free air[2] and passed over a CuO catalyst at a temperature of 350°C. This catalyst is designed to

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[2] It is anticipated that bottled air will be used. The air will be passed through a soda lime column to remove any CO_2 present before mixing with the sample gas.

selectively convert CO to CO_2 in the presence of volatile hydrocarbons. The $^{14}CO_2$ produced by the oxidation of ^{14}CO is then collected on the second soda lime column.

The sample gas then passes into the second unit, where it is first passed through a silica gel column pre-loaded with tritium-free water to re-humidify the gas stream (this is necessary to avoid drying out of the soda lime over time, which will reduce its collection efficiency) before it passes through a second catalyst bed containing Pd at a temperature of 450°C, which converts all remaining volatile carbon-containing species to CO_2. The $^{14}CO_2$ produced is then collected on the third soda lime column.
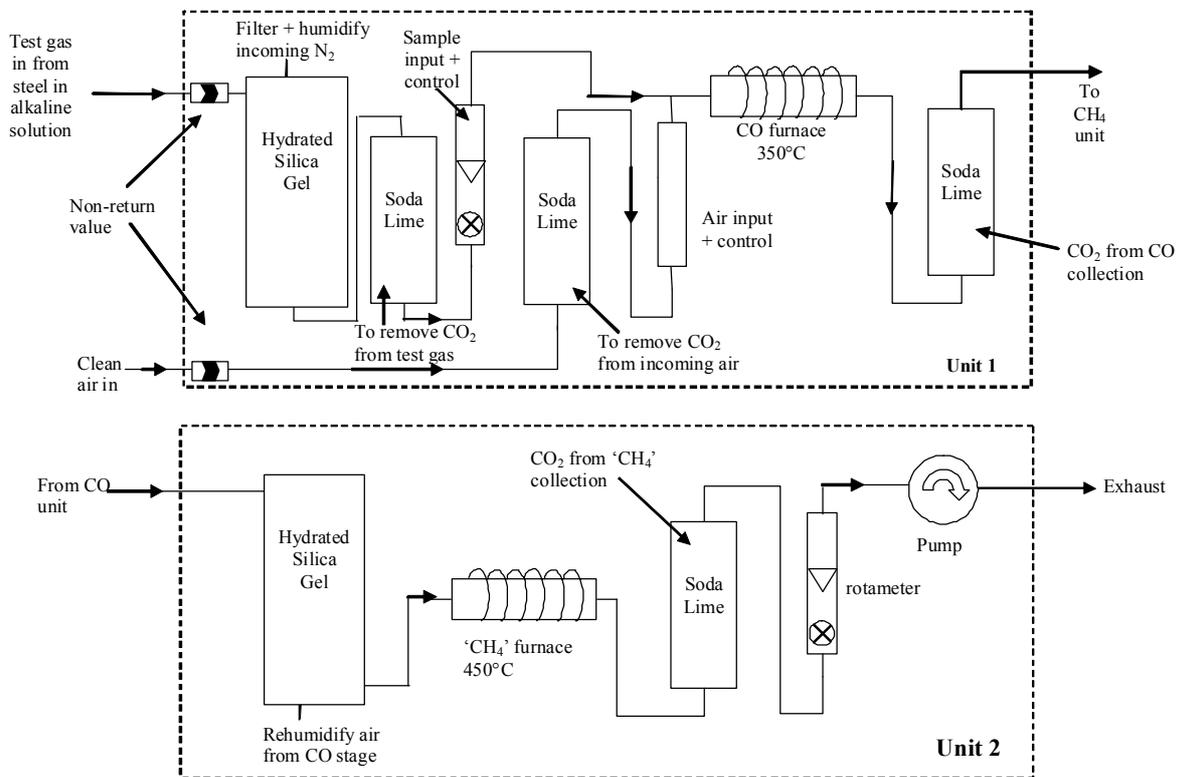
Figure 2.1: Schematic design of the RCD sampling apparatus for collection of gas-phase carbon-14 species

After a suitable collection period, purging will be stopped, the experiments sealed and the soda lime columns will be removed for return to RCD for analysis. The soda lime columns are fitted with quick release couplings that ensure that both the rig and the columns are sealed once disconnected. A particular advantage of this method is that the entire carbon-14

gas phase release (over any given period) is collected, maximizing the amounts of carbon-14 species available for analysis.

2.2.1   Testing of the apparatus

In the experimental arrangement that will be built in the G1 hot cell for the leaching tests, the RCD apparatus will be located at some distance from the leaching container. In addition, narrow bore tubing is specified for gas lines in the hot cell. Tests were carried out successfully which confirmed that the pump in the RCD apparatus could draw the sample gas through 15m of narrow bore tube effectively.

Prior to delivery of the apparatus to NRG in March 2015, the efficiencies and selectivities of the two catalysts for CO and CH_4 oxidation respectively were tested. These tests were performed using certified mixtures of bulk gases at low concentrations (CH_4 2.5% and CO 0.2% by volume) with cryogenic collection coupled to calibrated volumetric measurements of the amounts of CO_2 produced. After some initial trials to establish the optimum procedures, high efficiencies of conversion to CO_2 were obtained:

- CO to CO_2 over CuO at 350°C   94.6%
- CH_4 to CO_2 over Pd at 425°C   95%

In addition, less than 2% of CH_4 was converted over the CuO catalyst, showing good selectivity for CO; as expected, the residual CO (5.4%) that passed the CuO catalyst was converted quantitatively over the Pd catalyst. It is noted that these efficiencies were measured at relatively high carbon concentrations. Much lower concentrations of volatile carbon species would be expected in the steel leaching experiments, and so yields could well be higher in the experiments.

2.3 *Next steps: blank experiment*

A prototype experimental container for the leaching experiments with stainless steel is currently under manufacture for NRG (see Section 8.2.3). Once this has been checked and tested, it is planned to undertake a blank experiment. The aim is to test the container design and all of the experimental procedures before these are finalized and the apparatus is

installed in the G1 hot cell. The blank experiment is also designed to measure the carbon-14 background in the experiment without steel being present. It is intended that two sets of gas phases samples will be collected: one after 24 hours and one after a further 9 days purging of the headspace of the experimental container (a longer pumping time than is expected for any of the sampling periods in the hot cell experiments). The two sets of soda lime columns will be returned to RCD for analysis. The blank experiment is currently scheduled to begin in late September 2015 with the analysis results being available by early December 2015.

3   Armines contribution to CAST WP2 Second Annual Report

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.

The proposed strategy aims to detect and quantify low molecular weight organic compounds released with extremely low concentrations. The details of the strategy are documented in deliverable D2.4 [BAHRI *et al. in prep.*].

We focused on carboxylic acids molecules dissolved in the liquid phase and having short carbon chains of ≤ 4 carbon atoms (the main released compounds). No studies will be carried out for gaseous and volatile compounds.

The analytical strategy was implemented firstly by using reconstituted solutions simulating cementitious environments (NaOH solution, pH 12) and taking account of the expected composition and activity of the leaching solution.

3.1 *Analytical strategy*

Figure 3.1 gives an overview of the analytical strategy for speciation of the dissolved carbon-14 species in the liquid phase of the leaching solution.
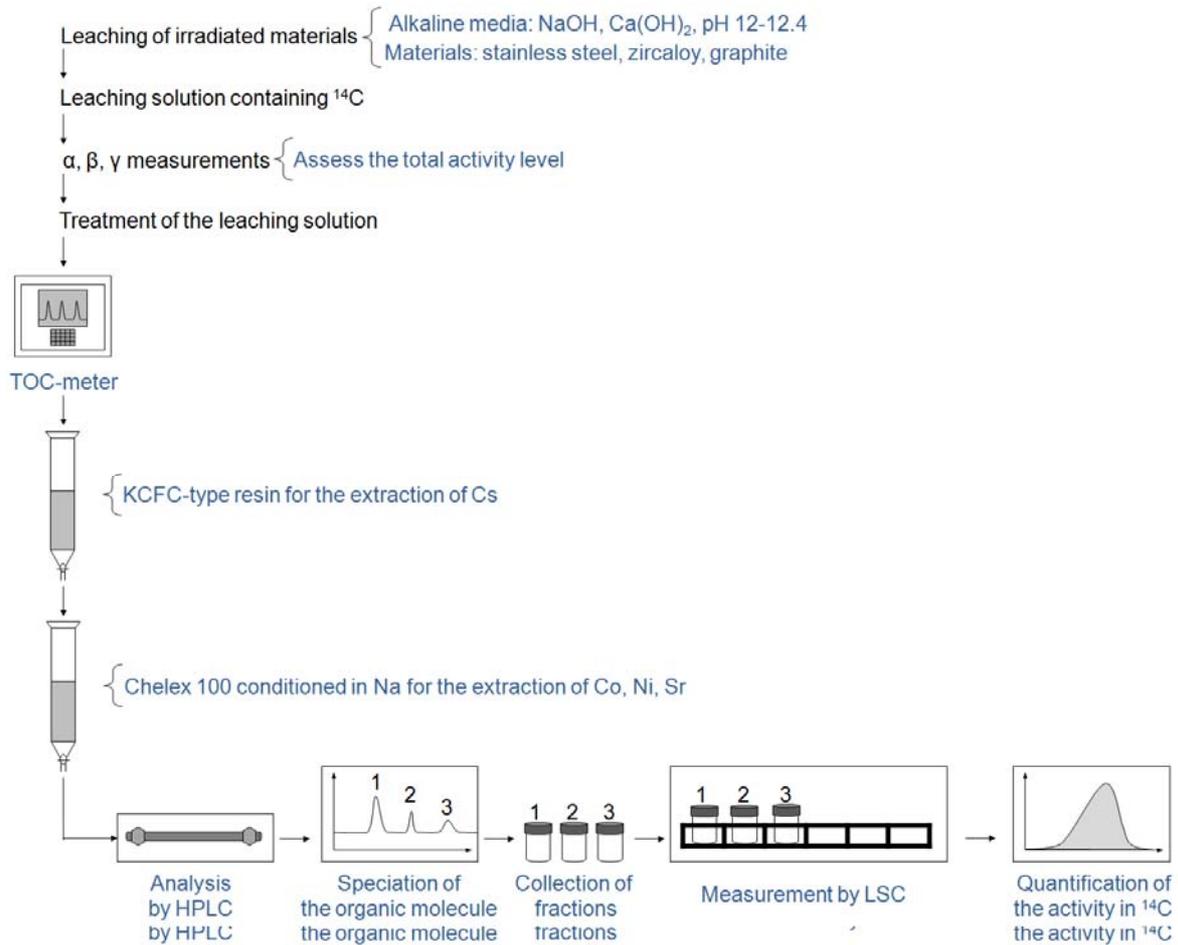
Figure 3.1: Analytical strategy for the speciation of organic carbon-14 in the liquid phase

The strategy for the speciation of organic carbon-14 dissolved in the liquid phase is based on the use of ionic chromatography suitable for the identification and separation of small ionized molecules. Individual fractions of carboxylic acids have to be collected and measured separately using liquid scintillation counting LSC for the quantification of the [14]C. LSC allows the detection of very low activities of [14]C. Compared to other analyzers used for quantification of very low concentrations (especially AMS), liquid scintillation counters offer the advantage to be more available, far cheaper and requiring less maintenance.

Given that ionic chromatography is not adapted for detection of very low ^{14}C concentrations which are expected in the leaching solution, carboxylic acids composed of stable carbon

(^{12}C) will be added to leachates to amplify the chromatographic signals. An optimal separation of chromatographic peaks is then needed to ensure an individual collection of carboxylic acids fractions. On the other hand, collected fractions must be free of beta emitter radionuclides other than ^{14}C, which cannot be discerned by LSC; this is why a selective extraction of interfering beta emitter radionuclides ahead of the chromatographic separation is required. This treatment stage based on ion exchange resins will also reduce the activity level of the leaching solution to be admitted in the different laboratories without a further dilution of the leaching solution.

3.2 *Speciation of organic carbon-14 in the liquid phase*

3.2.1 Composition of leaching solution

In the leaching solution, dissolved organic compounds are substantially in small carboxylic acids form. An exhaustive list of carboxylic acids released during steel and iron corrosion is drawn up by CAST partners (see [MIBUS *et al.*, 2015], Table 9.1). The cited molecules are: formate, acetate, propanoate, butanoate, oxalate and malonate.

Furthermore, the leaching solution contains other radionuclides such as ^{137}Cs, ^{134}Cs, ^{125}Sb, ^{60}Co, ^{59}Ni, ^{63}Ni, ^{55}Fe and ^{90}Sr which are also expected to have significant activity levels compared to ^{14}C.

According to Eh-pH diagrams in NaOH pH 12 media, some radionuclides such as ^{60}Co, ^{59}Ni, ^{63}Ni, ^{55}Fe and ^{125}Sb are partially or totally negatively charged as hydroxides or oxoanions forms. These radionuclides may appear in the chromatographic retention time window of carboxylic acids anions and therefore in the collected fractions preventing an accurate quantification of ^{14}C by LSC.

3.2.2 Treatments of the leaching solution

Chelex 100 resin conditioned on sodium form was selected for the elimination of respectively ^{60}Co, ^{59}Ni, ^{63}Ni, ^{55}Fe and ^{90}Sr, whereas for the removal of ^{125}Sb the ferric form was used. This ion exchange resin is more selective for multivalent metals than the standard cation exchange resins. Chelex 100 will scavenge multivalent metallic anions without altering nonmetallic ^{14}C target anions, *i.e.* carboxylic acids molecules. Furthermore, Chelex

100 is a radiation resistant resin and is currently used for extraction and preconcentration of radionuclides [ALLIOT *et al.*, 2013; PAKALNS, 1980].

For the ^{137}Cs removal (the main contributor to the total activity), we use one selective extraction method based on potassium hexacyanonickel (II) ferrate (II), abbreviated KCFK, that is a highly selective absorbent for the caesium ion and showing a high stability in alkaline solutions. [COLLINS *et al.*, 1995; PROUT *et al.*, 1965]. Similar to Chelex100, KCFC is a radiation resistant resin and has weak interaction with organic anionic species [SEBESTA AND STEFULA, 1990].

Tests on resins are occurring to validate the retention efficiency of radionuclides and the absence of interaction with carboxylic acids. The batch method with a large excess of resins is used to ensure a quantitative extraction of radionuclides, resins are directly added into the samples followed by stirring. Resins are beforehand conditioned in NaOH or KOH, rinsed with copious amounts of MilliQ water and their equilibrium pH is carefully adjusted to the required values, i.e. the leaching solution pH.

The solution with radionuclides is contacted with resins under agitation for at least 24 hours; after centrifugation, the supernatant is recovered and the remaining activity is quantified by liquid scintillation counting.

3.2.3   Ionic Chromatography

In order to implement the analytical strategy described above, a separation of a mixture of carboxylic acids using ionic chromatography is carried out. The chromatographic parameters are optimized to enable an individual collection of carboxylic acids fractions.

Figure 3.2 shows the chromatogram related to a mixture of formate, acetate, propanoate and oxalate in NaOH pH 12 solution.
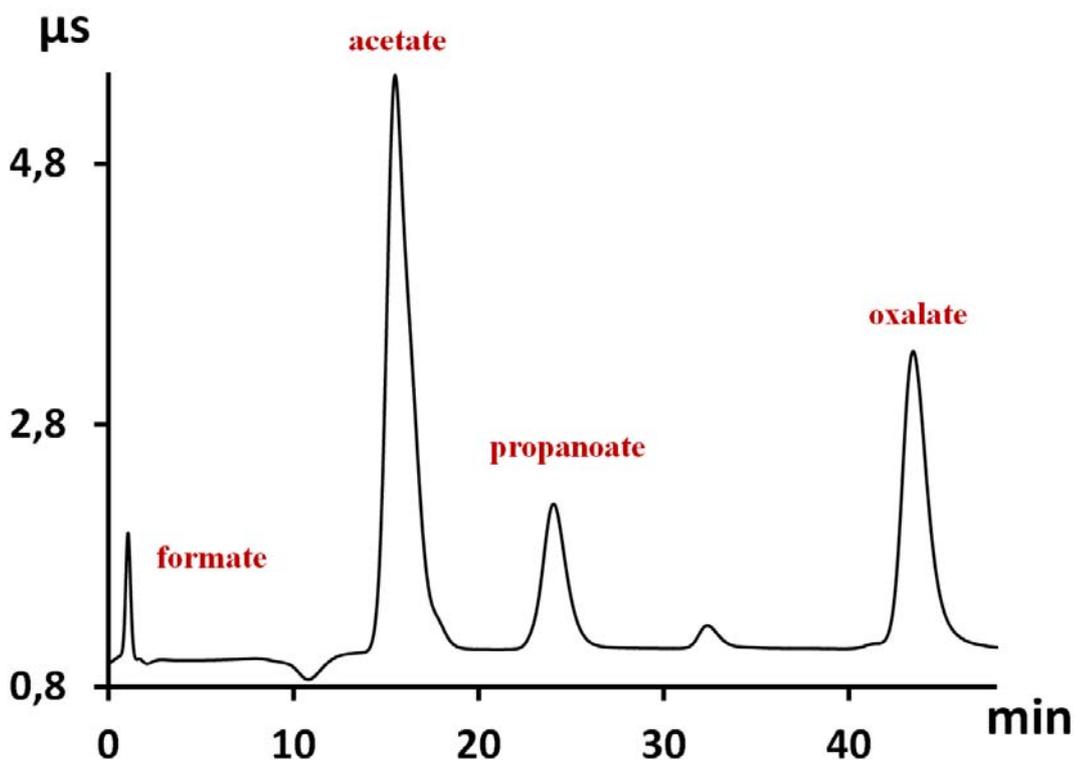
Figure 3.2: Chromatogram for the separation of small carboxylic acid 1ppm

Analyses are performed using an IC Compact 881 Metrohm liquid chromatography with a conductimetric detector. The separation column used was a Metrosep Asupp 16 250-2.0 column specifically designed for the separation of inorganic and small carboxylic acid anions; the injected volumes have been 200 µl. The pump flow is maintained at 0.3 mL/min to maximize the separation peaks. Alternatively, one can use a gradient elution to reduce analysis time.

Another feature related to the chromatographic analyses is the detection of carbonates due to the quick carbonation of NaOH solutions. Carbonates coelute and interfere with the quantification of anions of interest, i.e. carboxylic acids. To overcome this issue, samples are prepared and kept into a controlled atmosphere glove box filled with argon.

A separation of a mixture of the six carboxylic acids expected to be produced during steel and iron corrosion is under investigation. After the optimal separation conditions were found, fractions with individual carboxylic acid were collected and their analysis using liquid scintillation counter was performed.

3.2.4   Liquid scintillation counting

A liquid scintillation counter Tri-Carb is used to measure the ^{14}C activity in the collected fraction of carboxylic acids. Preliminary tests are performed by separation and quantification of a carboxylic acids mixture spiked with few Becquerels of ^{14}C of corresponding carboxylic acids, to give 5 Bq per collected fraction. The collected fraction is mixed to a scintillation cocktail (Hionic Fluor, PerkinElmer) selected to determine the ^{14}C activity in alkaline solutions. The cocktail volume ratio is optimized to have the best counting efficiency. For the oxalate fraction, 83 % of the ^{14}C activity was recovered after the chromatographic separation and fraction collection.

For the low and unknown carbon-14 concentration samples, like the ones that are expected for leaching solutions, high quenching and other possible matrix effects may appear. To fulfil the objectives of this work, it is paramount to use an ultra-low level counter (Quantulus type). Maximum sensitivity can then be obtained using quench correction curves with optimizing the scintillation cocktail volume ratio.

4 Ciemat contribution to CAST WP2 Second Annual Report

4.1 *Introduction*

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

- the preparation of the samples of activated stainless steel from reactor upper internals of José Cabrera NPP,

- the design of the containers for the leaching experiments and

- the set-up of the equipment acquired in the last quarter of 2014: Gas Chromatograph coupled to a Mass Spectrometer (GCMS) and an Ion Chromatography system (IC). This equipment will allow measuring the speciation of carbon compounds formed during the leaching process.

4.2 *Sample Preparation*

The four samples of activated stainless steel (approximate dimensions of 20 cm x 5 cm x 0.5 cm) prepared in the C.N. José Cabrera by ENRESA arrived at the facilities of Ciemat on 09 April 2014. Due to the dimensions of the reactor (150 mL capacity) where the leaching tests will be carried out, additional cuts of the pieces have to be performed.

Although a "Procedure for cutting irradiated metallic pieces which will be used for performing leaching assays" PT-LCRR-21-02 (30/10/2014) was developed, this procedure still has to be modified as was communicated by the head of the Radiological Protection Department in June 2015.

As soon as all requirements are fulfilled, cutting tests with conventional material will be started, also to train staff. These tests are performed with an electric grinder (Figure 4.1) which is connected to a container for collecting the chips of steel produced during the process.
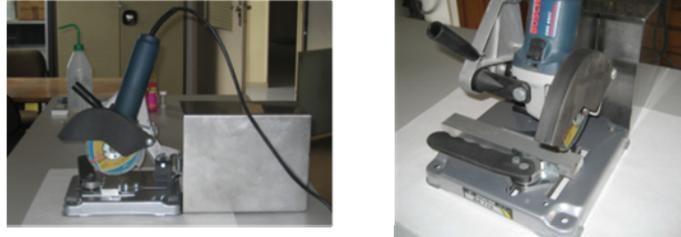
Figure 4.1: Electric grinder with container trailer

4.3 *Leaching Process and Speciation*

The leaching experiments to analyze gas and liquid phase are being designed:

- The procedure foreseen for developing the leaching tests is based on the standard procedure ISO 6961. In this case, the leaching rate (R_n) will be expressed in cm/day (units given by ENRESA in the acceptance criteria of the surface disposal of radioactive waste located in "El Cabril"; note that R_n is not referring to the corrosion rate)

$$R_n = \frac{a_n}{a_o} \times \frac{V}{S} \times \frac{1}{t_n}$$

where:

a_o: Initial amount of the component in the assay specimen, Bq or mg

a_n: Amount of the component that has passed from the assay specimen to the leachant in the step "n", Bq or mg

t_n: Duration of the step "n" of the assay, days

V: Specimen volume, cm^3

S: Apparent or geometrical specimen surface, cm^2

- The tests will be performed in High Pressure Reactors of Stainless Steel with Teflon (PTFE) Insert (Figure 4.2) at room temperature. The design of the reactors was developed during the first quarter of 2015 with the Berghof Company. The reactors have been received on 25 June 2015.
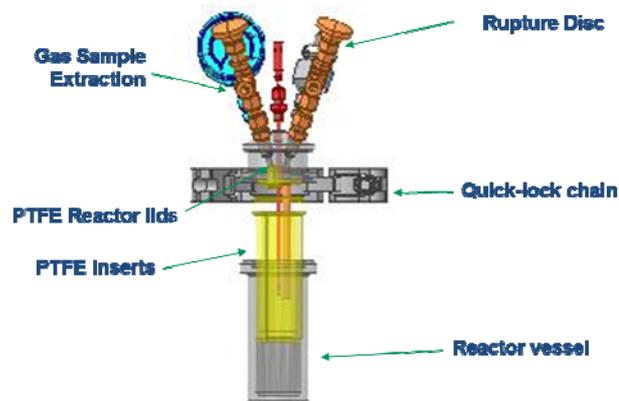
Figure 4.2: Leaching graphite reactors

- The size of specimen used will be approximately 0.5x1x2.5 cm.

- The surface area of specimen will be determined by BET analysis before and after the leaching.

- As leachant a NaOH solution of pH = 12 and an acidic medium will be used.

- A mixture of N_2 and O_2 gas (percentage similar to the content of N_2 and O_2 in air) will be periodically introduced in the container to assure that the leaching process is made in aerobic conditions.

- Both the gas and the leachate will be completely exchanged after: 14, 28, 56, 90, 180 and 360 days from the start of the test. These periods of time may be flexible, especially during the later stages of the experiment.

- First of all the gas will be collected through the gas sample extraction valve (Figure 4.2) and analyzed by GC/MS.

- After completing the previous step, the container will be opened and the volatiles organic compounds in the leachate will be analyzed by GC/MS whereas the species in solution (carboxylic acids) will be analyzed by IC. ^{14}C is measured by Liquid Scintillation Counting (Quantulus equipment).

Both GC/MS and IC have been installed in the laboratories in January 2015. At present, staff are gathering experience with the equipment and learning to interpret the results correctly.

Figure 4.3: Gas Chromatograph coupled to a Mass Spectrometer (left) and Ion Chromatography system (right)

As the steel containers for the leaching tests will be delivered by end of June, the tests are expected to start in October 2015.

5 ENRESA contribution to CAST WP2 Second Annual Report

5.1 *Scope of the test*

The goal of this work is to determine the behaviour of activated stainless steel in standard leaching tests performed at the El Cabril repository. The piece tested is a part of a guide tube of the upper internals of the José Cabrera NPP that is being currently dismantled (see Figure 5.1).

UPPER INTERNALS   GUIDE TUBE   SUPPORT
                         ASSEMBLY   COLUMN
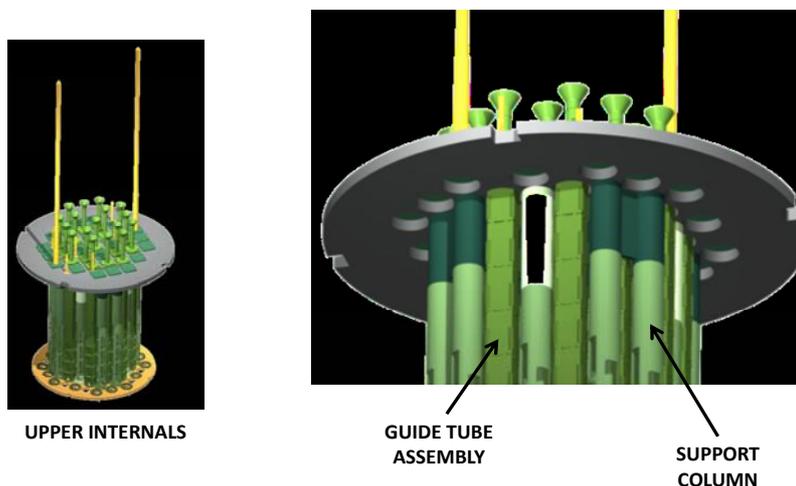
Figure 5.1: Origin of the piece

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.

5.2 *Sample cutting process and piece characteristics*

The cutting of the upper internals was carried out under water on the bottom of the spent fuel pool area in which a turntable was placed, and by using a disc saw and a band saw in a

moving frame. The cutting activities were accomplished in a dynamic and sequential manner (see Figure 5.2).
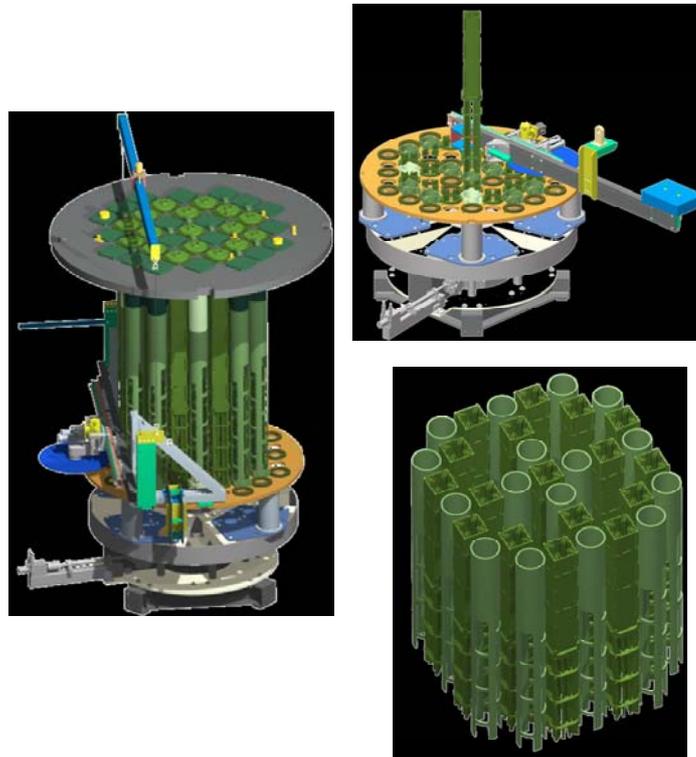
Figure 5.2: Cutting description

Additional detailed cutting was required in order to get a suitable sample for both laboratory management and transport issues (see Figure 5.3).

Figure 5.3: Detailed further cutting activities and final sample (see Tab. 5.1 for scale)

Table 5.1: Sample characteristics

	R-DJ-12-06
	Value
Mass (g)	4352'0
Length (cm)	10
Diameter (cm)	20
Volume (cm^3)	2638'94
Surface (cm^2)	1407'43

The dose rate of the piece at the test date was 1.08E+01 mSv/h.

5.3 Test description

The test is a semi-dynamic leaching process where the piece is immersed in deionized water in 7 consecutive steps of different time in which the activity release is measured. In each step the leachate is replaced with fresh leachant (see Table 5.2).

Table 5.2: Schedule of the test

Leaching step	Step days	Total days	Initial date	Final date
1	14	14	14/02/14	28/02/14
2	14	28	27/02/14	14/03/14
3	28	56	14/03/14	11/04/14
4	35	91	11/04/14	16/05/14
5	84	175	16/05/14	08/08/14
6	189	364	08/08/14	13/02/15
7	91	455	13/02/14	15/05/15

The leachant characteristics are the following (see Table 5.3):

- pH=7±1

- Conductivity σ < 5 μS/cm

- Temperature =20 ± 3 °C

These parameters have been measured in the leachant for every step.

Table 5.3: Leachant characteristics

Leaching Step	$(T_{LF})j$ (°C)	$(\sigma_{LF})j$ (μS.cm^{-1})	$(pH_F)j$
1	1'90 E01	1'56 E01	6'78 E00
2	1'64 E01	9'17 E00	7'02 E00
3	2'15 E01	3'67 E00	6'93 E00
4	2'12 E01	2'18 E00	7'15 E00
5	2'48 E01	2'90 E00	6'50 E00
6	2'47 E01	4'51 E00	6'29 E00
7	2'41 E01	3'59 E00	6'12 E00

5.4 Current results

The test has been performed to measure/estimate the activity of the radionuclides in the list below.

Table 5.4: Initial activity of the piece (MBq total)

ISOTOPE	ID: R-DJ-12-06 (MBq)
Co-60	1'20 E02
Mn-54	5'03 E-01
Cs-137	8'28 E-01
Ag-108m	< 4'09 E-01
Sb-125	< 1'27 E00
Eu-154	< 4'85 E-01
Eu-155	< 4'35 E00
Am-241	< 2'12 E01
C-14	7,72E-02

The $^{14}C/^{60}Co$ ratio has been theoretically determined by means of Origen Scale code, whereas the ^{60}Co and the rest of listed radionuclides have been measured by gamma-ray spectrometry.

A solid fraction in the leachate was observed, and both the leachate and the solid fraction have been measured for the different radionuclides considered.

Table 5.5: Leached activity in addition to the leaching rate for each step and the accumulated activity of ^{60}Co

R-DJ-12-06			A_{0i} (Bq) = 1'20 E08		
Leaching step	Step days	Total days	\multicolumn{4}{c}{Leached activity (Bq)}	$(R_v)_i$	R_k
			\multicolumn{2}{c}{a'_j}	Step Activity	Total Activity	$(cm.d^{-1})$	$(cm.d^{-1})$
			Al	As				
1	14	14	5'20 E04	9'57 E02	5'30 E04	5'30 E04	5'92 E-05	5'92 E-05
2	14	28	2'41 E04	5'22 E02	2'46 E04	7'76 E04	2'75 E-05	4'33 E-05
3	28	56	2'53 E04	1'76 E02	2'55 E04	1'03 E05	1'42 E-05	2'88 E-05
4	35	91	2'03 E04	3'39 E02	2'06 E04	1'24 E05	9'20 E-06	2'12 E-05
5	84	175	2'42 E04	1'38 E02	2'43 E04	1'48 E05	4'52 E-06	1'33 E-05
6	189	364	1'48 E04	6'18 E01	1'49 E04	1'63 E05	1'23 E-06	7'01 E-06
7	91	455	3'70 E03	1'56 E02	3'86 E03	1'67 E05	6'63 E-07	5'73 E-06
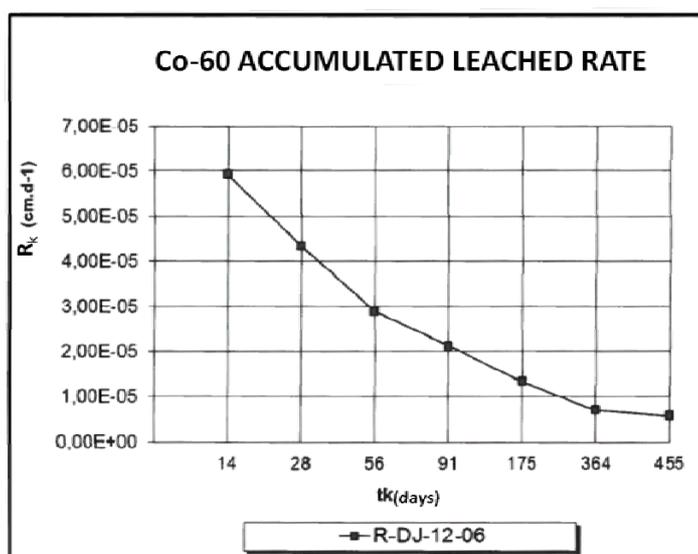
Figure 5.4: Accumulated leaching rate of ^{60}Co

Table 5.6: Leached activity in addition to the leaching rate for each step and the accumulated activity of ^{14}C (measured values)

C-14

			R-DJ-12-06	
Leaching Step	Step days	Total days	Leached Activity Al (Bq)	Accumulated Activity ΣAl (Bq)
1	14	14	< 3'38 E02	< 3'38 E02
2	14	28	< 6'65 E02	< 1'00 E03
3	28	56	< 6'54 E02	< 1'66 E03
4	35	91	< 6'61 E02	< 2'32 E03
5	84	175	< 6'94 E02	< 3'01 E03
6	189	364	< 6'55 E02	< 3'67 E03
7	91	455	< 6'75 E02	< 4'34 E03

A_{oi}:   Initial activity of radionuclide 'i', ^{60}Co in this case.

a'_j: Step activity, it is the activity release in step 'j' for radionuclide 'i', that comprises the solid phase activity, 'As', and the liquid one, 'Al'.

$(R_v)_j$:   Mean release rate for radionuclide 'i' in step 'j'.

R_k: Mean accumulated release rate up to step 'j' for radionuclide 'i'.

Similar behaviour of the mean accumulated release rate is observed for all the gamma isotopes, but no ^{14}C activity has been detected by liquid scintillation counting above detection limit in any steps (between 0.04 and 0.07 Bq/g); therefore further analysis will be performed for this purpose, although it is expected to have a similar mean release rate to the observed for ^{60}Co.

Table 5.7 shows a summary of the following quantities for ^{60}Co measured by gamma-ray spectrometry in the liquid and solid fraction:

- The final percentage of the activity release in relation to the initial activity.

- The Activity Rate Release, R_0, in the conventional units of μm/y (not referring to the corrosion rate).

- The Annual Fraction Release, AFR, a quantity determined from R_0 and also takes into account the geometry of the waste (surface, S, and volume, V) and the time t considered (a year), as described in the relationship AFR= R_0(S/V)t.

Table 5.7: Summary results for ^{60}Co

QUANTITY	^{60}Co
Ratio of the activity release (%)	1,39E-01
Activity Rate Release (μm/y)	6,75E+00
Annual Fraction Release, AFR	3,59E-04

After 455 days test, the piece shows clearly that oxidation processes took place as can be seen in the Figure 5.5.
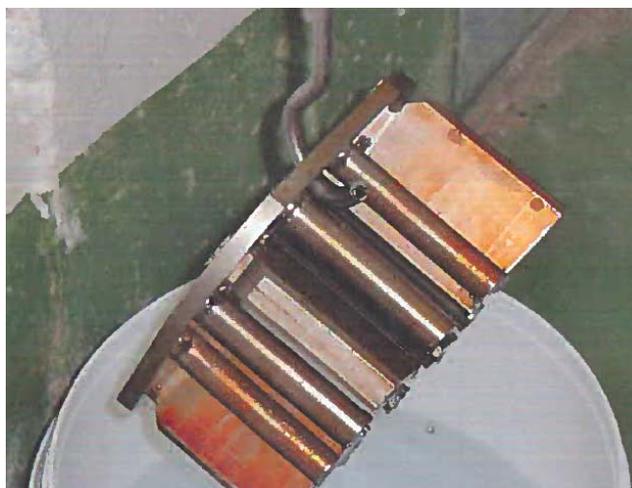
Figure 5.5: Final aspect of the piece after the test

The final part of this work will consist of the measurement of ^{14}C, in the leachate after each step, by means of AMS technique that is currently under development in the National Centre of Accelerators, CNA, in Seville, Spain. The chemical separation of the single compounds will be done in cooperation with Ciemat (see Section 4).

6 JRC-ITU contribution to CAST WP2 Second Annual Report

6.1 *Materials*

6.1.1 Stainless Steel cladding composition and Burn-Up

The cladding test material is documented as a 15Cr-15Ni Ti-stabilized (15-15-Ti (ε)) stainless steel cladding. The cladding comes from a relatively high burn-up mixed (U,Pu) carbide and nitride fuel (NIMPHE 2) with a mean burn-up of 53.8 GW/tU for the nitride and 51.6 GWd/tU for the carbide fuel (~5.8at%). Cutting plans have been prepared and the fuel /blanket pellet interface and the mid-height positions have been cut. The mid-height position will present higher burn-up and ^{14}C content. Non-irradiated samples are available for this cladding and have been submitted for analysis at ITU's analytical chemistry department. Particularly the values for N and C content will be important as estimates of the initial cladding's initial content.

6.1.2 Sample preparation

2 Samples were cut as 7mm long rings or as 10mm long half-rings (1-0.5g) at mid-height (max. power) and at the fuel /blanket interface at the lower end. The second half of the half-ring will be used for metallography (determination of the oxide thickness). The fuel is yet to be removed for the mid-height position; it is planned for September 2015. All the samples will have fuel or blanket pellets mechanically removed (pressed out) but will require fuel dissolution by 7M HNO_3 (or 15% H_2SO_4) followed by cleaning in water and then drying in air. This treatment is expected to remove all fuel but may remove some of the outer oxide, although as an oxidizing acid HNO_3 would also be expected to form/maintain a thin oxide layer.

One blanket/fuel interface sample will be mounted for metallography (determination of oxide thickness); the max. power and blanket position sample has already undergone optical microscopy. Some SEM-EDS data is available on the cladding condition at the max. power condition. Part of the samples from fuel and blanket/fuel interface position will be cut off

and used for total C content (and subsequently total ^{14}C) determination. The remaining samples will be for leach testing in the autoclave. Further cutting of the sample into smaller pieces may be necessary.

6.2 *Autoclave for leach tests*

The ITU autoclave (able to go to 250°C and 150 bar pressure) now has a PEEK lining constructed to replace the Teflon lining that is considered unstable under strong irradiation fields. The autoclave testing parameters will be 80°C and 1-2 bar pressure (slight excess pressure for gas sample extraction) and performed at 2 pH's: alkaline 12.0 (NaOH solution) and neutral 5.5-6 (natural Volvic water). The choice of simple NaOH solution was made at the last annual progress meeting. The use of a natural water for neutral pH was based on the reliability of its composition and that it is typical neutral ground water. However it contains, as is typical for many natural waters, a lot of carbonate/bicarbonate (~100mg/l) which may make the ^{14}C analysis more difficult, thus the choice of Volvic water may be revised.

The autoclave and the PEEK lining are seen in Figure 6.1. An existing heating mantle in the Hot Cell 4 will be used for heating the autoclave.

Figure 6.1: Autoclave with old Teflon (left) and new PEEK linings (right). The autoclave will be used with the more stable PEEK lining. The cladding samples will be placed in small PEEK crucibles with holes to allow the water to drain from the sample.

If time permits the additional test (requested at the last WP2 & 3 meeting) for stainless steel samples at room temperature (30°C) and pH 12 will also be performed.

The adaptations for the hot cell connections to the analytical glove box will be carried out when the glove–box is in position. A gas capsule system has been purchased as an alternative means of transferring the gas samples into the ^{14}C analysis glove box. The cladding corrosion rates will also be assessed by ^{60}Co gamma counting of the solution (following discussions at the last WP2 & 3 meetings).

The first autoclave tests will be expected to start in early 2016 when the glove box commissioning is nearing completion.

Separate gas and liquid samples will be taken at the end of the 3 month leaching experiments, with no intermediate samples.

6.3 *Analysis*

6.3.1   Glove box preparation

A glove box is under construction at ITU main Workshop for collection and analysis of the ^{14}C content of carbon-containing gases and liquids from the autoclave. The glassware has been ordered as well as 2 ovens, a balance and vessel heating plate. The catalysts and chemicals have also been ordered. The construction of the wash bottles and gas lines in the glove box is about to start (Aug. 15). The connection between the autoclave in the hot cell and the glove box will be made during installation of the glove box (this may instead, involve use of gas capsules for gas transfer).

The analytical technique will be as close as possible to that used by KIT-INE. It is intended that ITU and INE will collaborate on the technical construction of the analytical glove box, to optimize the analytical technique and make the best comparison possible (given INE's experience in this field).

A schematic diagram of the analytical glove box layout is shown in Figure 6.2 below.
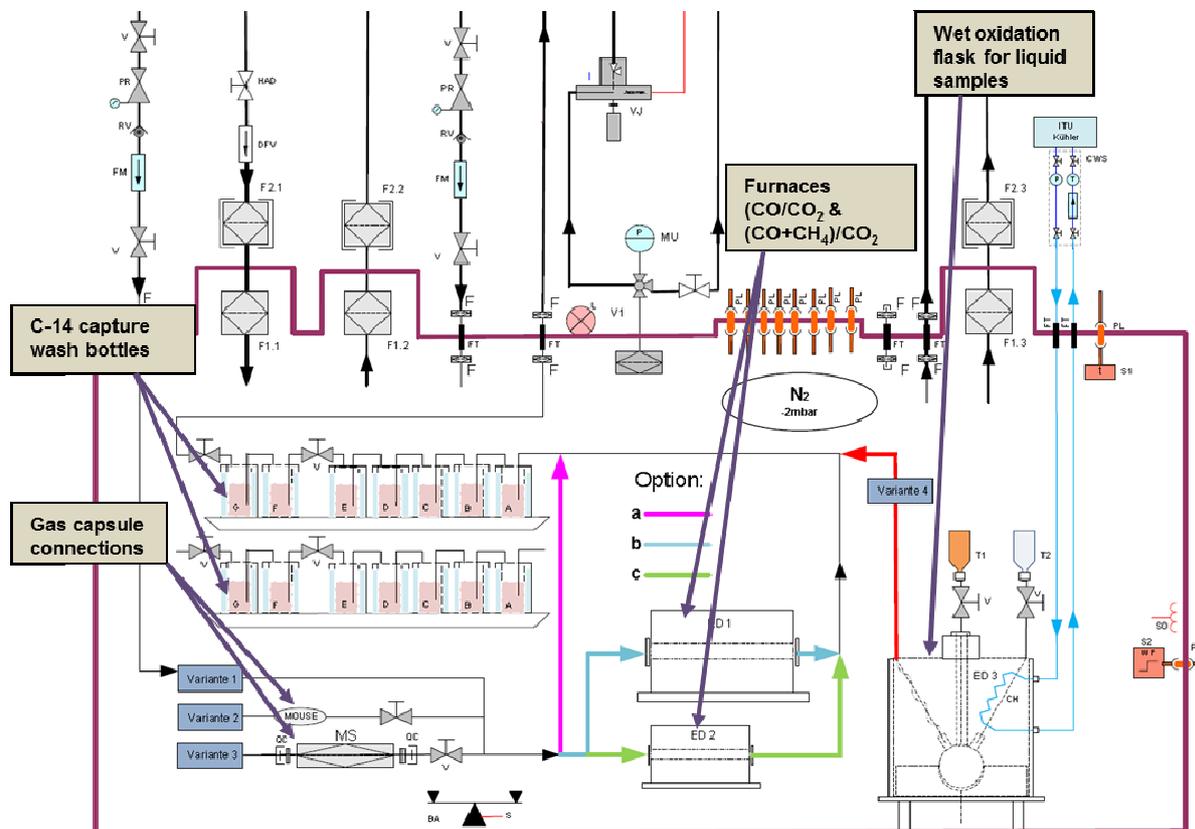
Figure 6.2: Technical drawing of the ITU [14]**C aliquot testing glove box based on the KIT-INE glove box design.**

6.3.2 Device for total C content determination

An ICARUS H4 total inorganic C determination device is currently under construction for installation in the hot cell. It is intended to adapt it to be able to determine directly the ^{14}C content levels of the irradiated fuel and so check the modelling of ^{14}C contents in irradiated cladding. It is assumed that this is all in solid solution and therefore present as inorganic C in the cladding. The device is for determination of total C in irradiated cladding samples (C is converted to CO_2 by burning the sample in O_2 and then measured by IR absorption). A molecular sieve filter in the off-gas line will also be used for collection of the CO_2 gas. This filter can then be transferred to the analytical glove box for analysis and ^{14}C determination by beta-counting. The total C device is undergoing final design alterations, at the manufacturers (Bruker Elemental, Karlsruhe). These alterations relate to separating the

transformer and oscillator from the induction furnace and placing these below the hot cell caisson. This will gain additional space in the caisson. It is expected that the construction will be completed by end October 2015 for works testing. Then installation in the hot cell and cold testing can begin along with the addition of a small glove box to enable exchange the molecular sieve in the return gas line. First tests could be possible for early 2016, with initial samples in the following months (2nd Qtr 2016).

7   KIT-INE contribution to CAST WP2 Second Annual Report

7.1 *Introduction*

In the second year of the CAST project KIT finished the development of the separation, quantification and speciation methods for ^{14}C bearing compounds in aqueous and gaseous samples. Monte Carlo N-particle calculations (MCNP-X) were performed for the irradiated stainless steel taking into account the nominal chemical composition as well as the irradiation characteristics of the fuel rod. In order to trouble-shoot the methodology for the work with the highly activated stainless steel (dose rate (DR) ~1'600 mSv/h), the ^{14}C extraction and analysis method was first applied to an irradiated Zircaloy-4 cladding (DR ~20 mSv/h) as discussed in [HERM *et al.,* 2015]. The lessons learned from the operations with the activated Zircaloy-4 cladding are implemented into the procedures for the operations with the activated stainless steel, e.g. the use of additional H-3 traps in the ^{14}C separation technique. Moreover, non-irradiated steel was used to optimize the digestion of steel in various acid mixtures under argon and air atmospheres and the recovery of ^{14}C from ^{14}C doped samples, treated in the extraction and analysis system was tested. In the following chapters the activation calculation, the model used in these calculations, the dissolution experiments with non-irradiated steel, the recovery tests and preliminary results from the activation calculations are described.

7.2 *Activation calculation and model*

The activation of the stainless steel plenum spring was calculated by means of the Monte Carlo N-particle code (MCNP-X) with its burn-up and activation module CINDER. The nuclear data library that was used was the ENDF/B-VII database [ENDF/B-VII, 2011; MCNP, 2011]. The simulation is based on a fuel subassembly of the PWR Gösgen core in which the experimental fuel rod segment SBS1108–N0204 with its plenum spring is inserted [METZ *et al.*, 2014]. The properties of the plenum spring (mass, density and dimension, see Fig. 7.1 and Fig. 7.2) were accounted for in such a way that will include as much as possible all heterogeneity effects around the fuel rod segment. Thereby the local

neutron flux within the spring could be simulated more accurately. It is important to note that the exact composition of the steel and cladding components used in the fuel rod segment about 25 years ago was not available. Hence, nominal chemical composition data (see table 7.1) were used for simulation of the neutron flux and consequently for the activation calculation. Normative specifications usually indicate a range of composition (for alloying elements) or maximum values (for impurities). Especially the content of the ^{14}C precursor elements ^{14}N, ^{17}O and ^{13}C are important for the ^{14}C inventory. The main contribution to ^{14}C comes from ^{14}N and ^{17}O. Unfortunately the impurity levels of nitrogen and oxygen in the stainless steel spring are both not available. [SAKURAGI *et al.*, 2013] recommend 500 ppm nitrogen impurity for stainless steels. Further, for determining the flux of the core one needs in general the nuclear data of all nuclides. Although the ^{14}C and ^{13}C nuclides have only minor influence on the flux evolution, their appearance is necessary for the CINDER code, in a sense that CINDER considers only the given nuclides for the flux calculation and their first decay daughters. For missing transport nuclear data of nuclides such as ^{14}C and ^{13}C several options were analyzed. The first one was to ignore the missing data in the transport (flux) calculation and to use only the available activation nuclear data in the CINDER package. The second option was to create the ^{14}C and 13C transport data, missing in the ENDF/B-VII library, using the TENDL library [KONING AND ROCHMAN, 2012] (similar to the ENDF/B-VII library) and in this way to test the impact on the flux level. In this case, the module CINDER uses the input data inserted from the TENDL library for the burn-up calculation instead of its own activation library. An additional option was implemented in the MC_CINDER code in which the additional transport data was used only for the flux calculations and for the activation the original CINDER data was used. All those options have shown minor variations in the estimated inventories of the relevant nuclides and by far lower in comparison with the accuracy expected from experimental results.
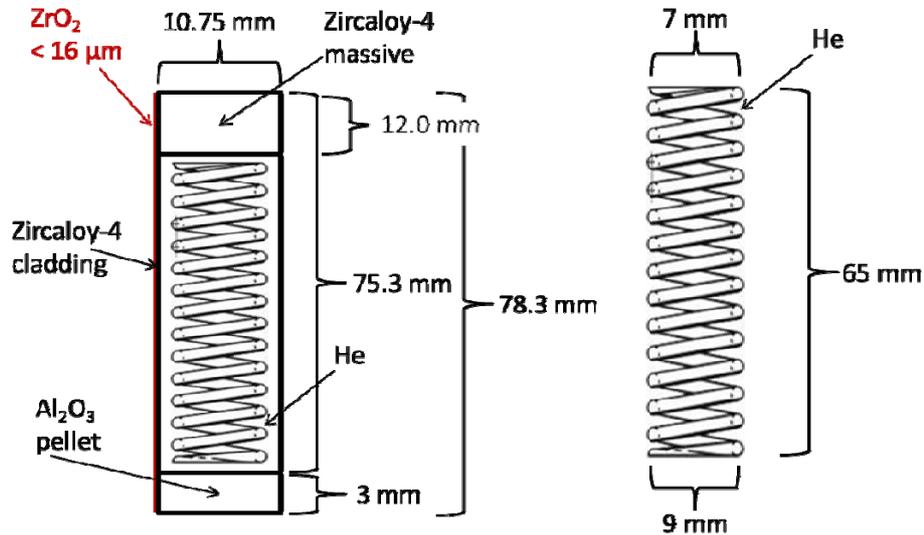
Figure 7.1: Model of the stainless steel plenum spring used for the calculation. The image on the left shows the close surrounding of the spring inside the Zircaloy-4 plenum cladding whereas the image on the right shows details of the dimensions of the spring.

Figure 7.2: Photos of the irradiated stainless steel plenum spring.

Table 7.1: Nominal composition of X7CrNiAl17-7 (1.4568, ASTM A 313 (631), UNS S17700) steel according to DIN EN 10270-3.

	X7CrNiAl17-7 steel [wt.%]	composition used for calculation [wt.%]
Fe	balanced	balanced
Cr	16–18	18
Ni	6.5–7.8	7.8
Al	0.70–1.50	1.50
Mn	≤ 1.00	1.00
Si	≤ 0.70	0.70
C	≤ 0.09	0.09
P	≤ 0.040	0.040
S	≤ 0.015	0.015
N	–	0.05
O	–	–

7.3 *Dissolution experiments with non-irradiated steel*

Digestion experiments were performed with non-irradiated steel (material no. 2.4642, UNS N06690) using various acid mixtures under argon or air atmosphere and room temperature. Table 7.2 summarizes the outcome of the dissolution tests. The non-irradiated steel was digested within a day in 30% HCl and 54.5% H_2SO_4 whereas it was digested within days in dilute sulphuric acid and a 32.5% HNO_3 + 48% H_2SO_4 mixture. In the other digestion tests, no visible dissolution of the sample took place.

Although concentrated hydrochloric acid readily dissolves the steel, chloride containing solvents are inappropriate to the ^{14}C separation and quantification method due to the use of silver nitrate as catalyst during the wet oxidation step and resulting precipitation of silver chloride. Also 54.5% H_2SO_4 is unsuitable since half concentrated sulphuric acid is oxidizing and possibly oxidizes reduced ^{14}C bearing compounds during the digestion leading to an overestimation of inorganic ^{14}C species. The same is true for nitric acid at any concentration. Therefore dilute sulphuric acid or a dilute H_2SO_4/HF mixture, to accelerate the dissolution, will be used in the experiments with the activated stainless steel spring.

Table 7.2: Summary of dissolution experiments conducted with non-irradiated steel and various acid mixtures. A tick (✔) indicates complete digestion of a steel sample (within a day or days) whereas a cross (✖) indicates no visible dissolution of the sample.

solvent	atmosphere		solvent	atmosphere	
30% HCl	air	✔	85% H_3PO_4	air	✖
54.5% H_2SO_4	air/argon	✔	65% HNO_3	argon	✖
20% H_2SO_4	argon	✔	43% HNO_3 + 7% H_2SO_4	argon	✖
32.5% HNO_3 + 48% H_2SO_4	air	✔	43% HNO_3 + 28% H_3PO_4	argon	✖

7.4 *Recovery tests performed with carbon-14 labelled standards*

During the development of the ^{14}C extraction and analysis system ^{14}C labelled sodium carbonate (Na_2CO_3, 200 kBq, Eckert & Ziegler) and sodium acetate (CH_3CO_2Na, 1.85 MBq, PerkinElmer) reference material was used with 10 to 100 Bq for the inorganic as well as the organic compounds respectively. Different activity ratios between the sodium carbonate and acetate were tested too. The recovery tests show that the chemical yield of the separation method is well above 90% for the inorganic (~95%) and the organic (91%) ^{14}C fraction. In addition the efficiency of the catalytic furnace was tested using a 10% methane + 90% argon gas mixture (Air Liquide) with a yield of about 99% for the CH_4 to CO_2 conversion.

7.5 *Preliminary results of the activation calculations*

Table 7.3 shows the five inventory determining radionuclides according to the MCNP-X calculations for the irradiated stainless steel plenum spring. The calculations indicate a ^{14}C inventory of about 851 kBq/(g steel).

Table 7.3: Calculated radionuclide inventory of the irradiated stainless steel plenum spring.

	radionuclide	calculated inventory [Bq/g] [p.w.]
1	^{63}Ni	2.05×10^9
2	^{55}Fe	2.47×10^8
3	^{60}Co	7.78×10^7
4	^{59}Ni	1.60×10^7
5	^{14}C	8.51×10^5

8   NRG contribution to CAST WP2 Second Annual Report

8.1 *Introduction*

Within the CAST EU project, WP2, NRG will 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 realized 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 characterized, detailed information has been presented in the previous Annual Report [MIBUS *et al.,* 2015].

For the experiments with irradiated and un-irradiated 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 are planned to start during spring/summer of 2016. A deliverable related to this work is planned in month 40; in this report the results of the six months sampling will be incorporated. An update of the report will be prepared when all experimented are finished.

8.2 *Progress in the reporting period*

In the second reporting period, no work was scheduled for NRG. In parallel with the CAST project, pre-CAST project is running. This is a cooperation project involving Amec Foster

Wheeler and Radiocarbon Dating Limited; funded by Radioactive Waste Management. In this project all preparations required for the starting of experimental work within CAST are being performed.

This section gives a short overview of the work performed.

8.2.1   Chemical hot cell

The leaching experiment will be performed in the chemical hot cell (see Figure 8.1), this hot cell is commonly used for all chemical work on high active samples; to avoid/minimize the possible cross contamination of the stainless samples, the inbox of the cell has been removed and cleaned by the Decommissioning and Waste Treatment facility of NRG. The inbox is being built in the cell at this moment, waiting on some new crucial spare parts.
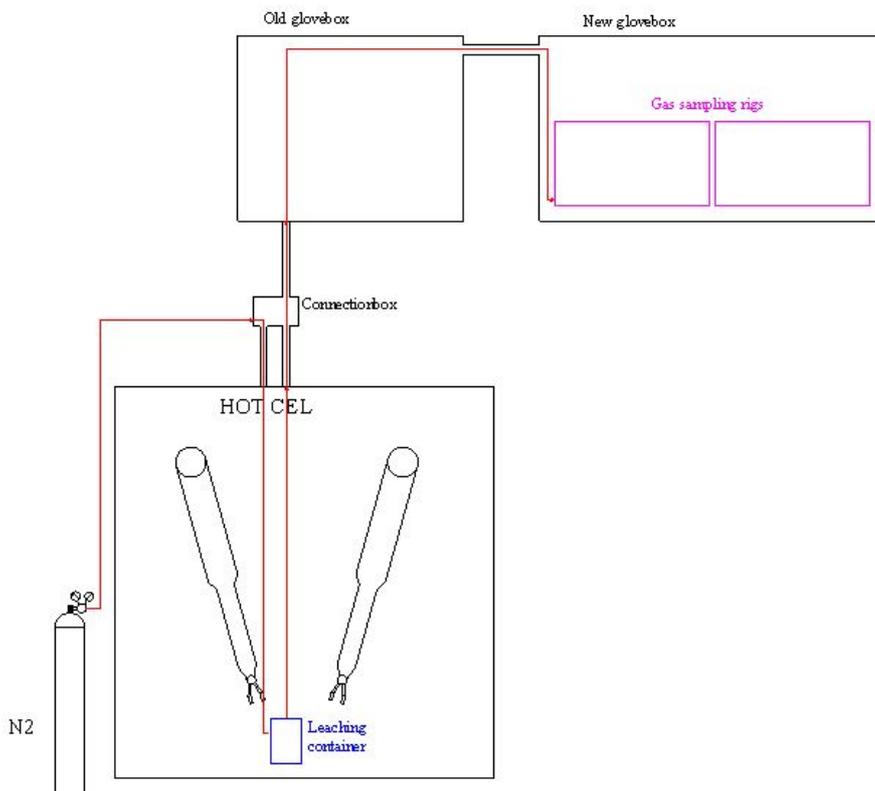
Figure 8.1: Schematic drawing of the leaching experiment in the chemical cell in the HCL

8.2.2   RCD rig and glove box for carbon-14 gas analysis

As mentioned above, the gas samples will be analyzed for presence of ^{14}C. This will be done by using a RCD rig (equipment designed by Radiocarbon Dating Limited (RCD), for details see input Amec Foster Wheeler, Section 2); based on risk assessment (Hazard Identification), this RCD rig has to be placed in a glove box above the chemical cell. A placing of the glove box above the cell and making connection to the cell had to be approved by the Dutch licensing authority; all required documents have been prepared and the permission has been obtained. The glove box has been designed, tailor made, installed and tested; and is ready to be used for its purpose (Figure 8.3). The RCD rig has been delivered to NRG by RCD, tested and is ready for use (Figure 8.2).
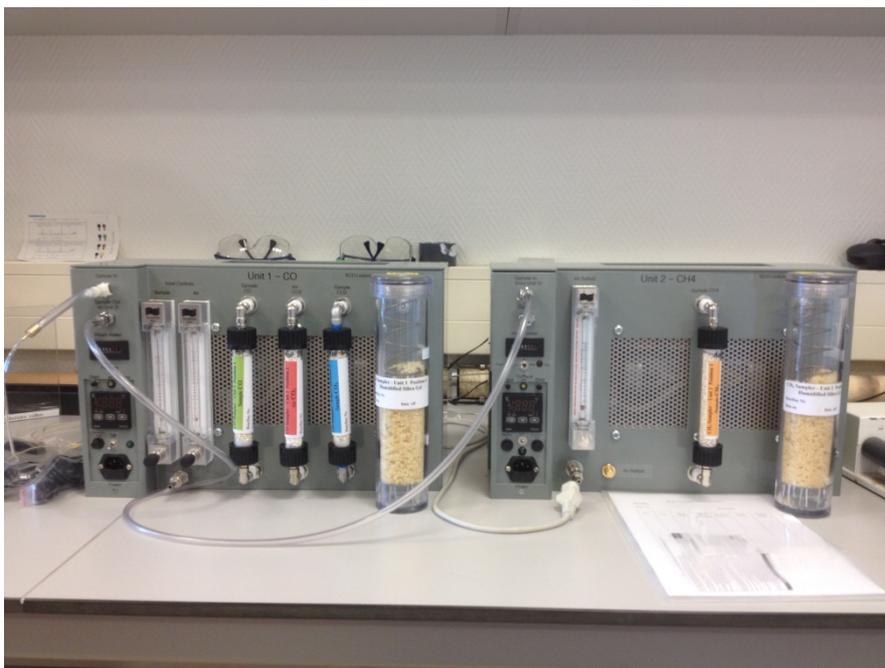
Figure 8.2: A picture of the RCD rig installed in the lab

Figure 8.3: A glove box to be used for placing of RCD rig, installed above the chemical cell

8.2.3   Container design

The leaching experiment will take 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 (RWM) a number of options have been considered. The final container design (Figure 8.4) will consist of an outer vessel with cover, both made from borosilicate glass. An inert zirconia crucible will serve as an insert where the leachant will be 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 AND MERCER, 1995], 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 will be connected to nitrogen source and outlet to the RCD rig. Liquid sampling and leachant addition will be performed via a dip leg (quartz).
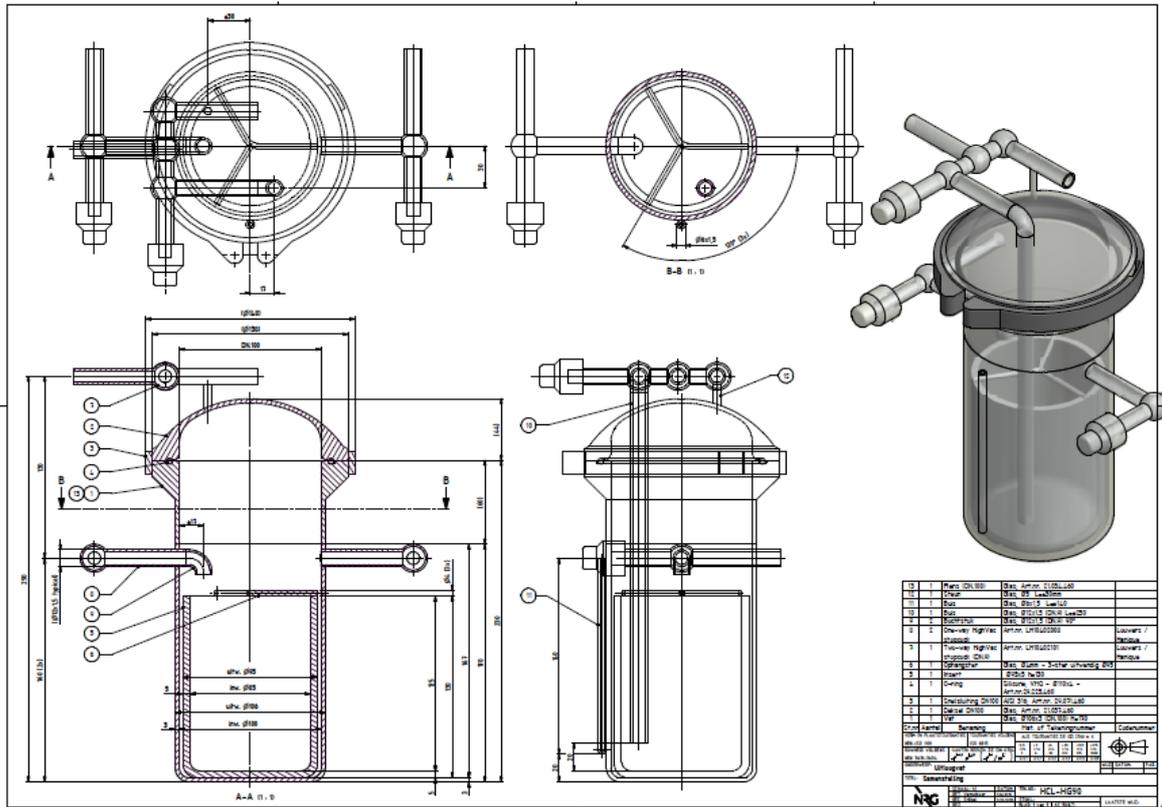
Figure 8.4: Technical drawing of container for leaching experiments

Stainless steel samples will be placed on a triangle, which will be placed on the zirconia insert. The CT samples will be fixed with stainless steel hooks and will be hung from the triangle (see Figure 8.5).
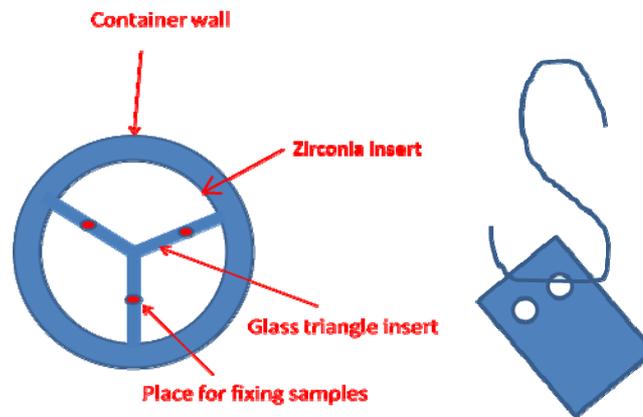
Figure 8.5: A schematic drawing of the triangle insert and fixing the CT samples

First, a prototype of the container will be fabricated and fully tested during the blank tests; based on the results, changes could be made in the design. Finally, three containers will be fabricated for the leaching experiments with irradiated and non-irradiated samples. The prototype is being fabricated during August 2015 and is expected to be ready for testing by end of September 2015.

8.2.4   Leachant addition

As described above, the leachant will be added by the dip leg. The procedure of leachant addition has been setup and tested (Figure 8.6). This procedure will be validated during the blank tests. A known /required amount of the leachant will be put in the feeding vessel and through feeding valve and dip leg added in the container.
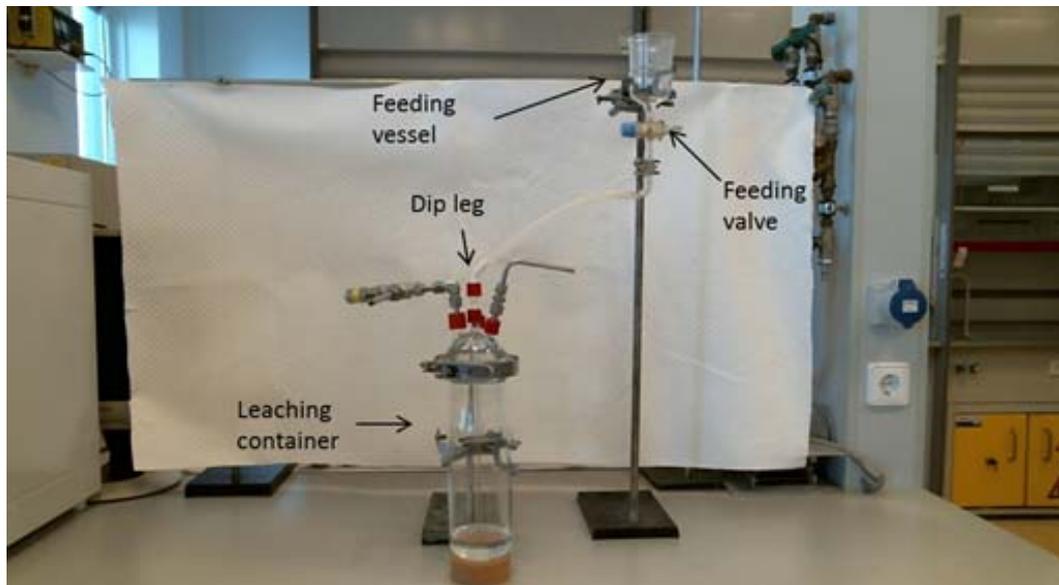
Figure 8.6: A picture of the leachant addition setup

8.2.5   Liquid sampling

The liquid samples have to be taken during the leaching experiments to determine the ^{14}C and ^{60}Co. The liquid sampling procedure has been setup and tested by building a mock up (Figure 8.7). This will be validated during the blank tests in the coming period. The liquid sampling will be done by flushing the dip leg by nitrogen to remove the solution from the dip leg, than the system will be evacuated and after certain period of time a representative sample of the leachant will be taken. Two liquid samples will be taken for each of the three experiments, one sample for ^{60}Co measurements and one for ^{14}C analysis.
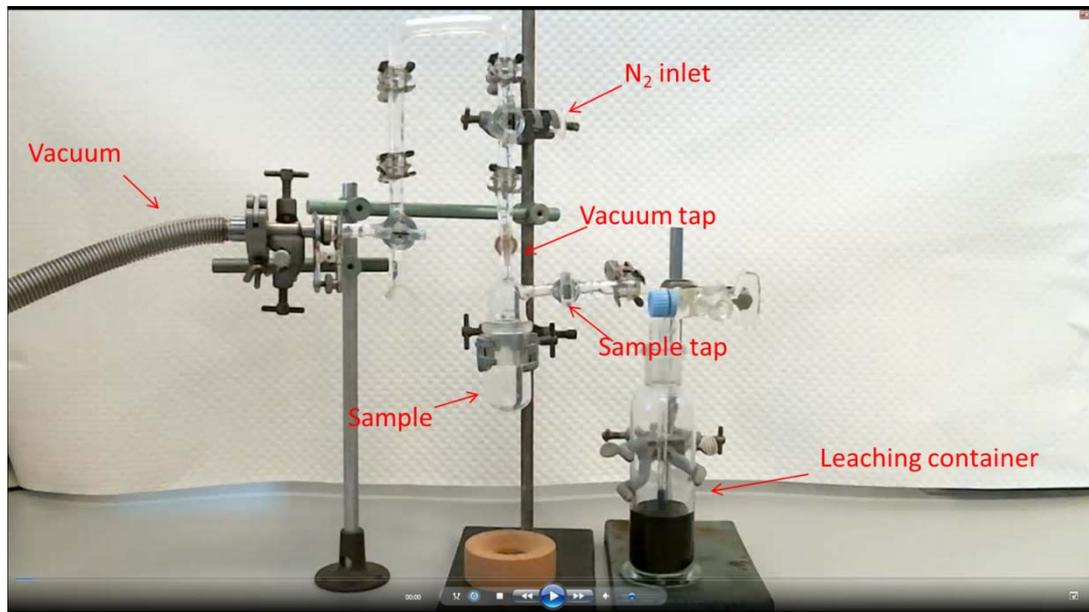
Figure 8.7: A picture of the liquid sampling mock up

8.3 *Milestones & Deliverables*

No milestones or deliverables were scheduled in the second year for NRG.

9   PSI contribution to CAST WP2 Second Annual Report

9.1 *Introduction*

This progress report summarizes the current status of the analytical developments at PSI in conjunction with the identification and quantification of organic compounds generated during the corrosion of activated steel and non-activated iron powders.

9.2 *Development of the Analytical Techniques*

9.2.1   Gas Chromatography (GC)

A gas chromatograph with mass spectrometry detection (GC-MS) was acquired and installed in the hotlaboratory of PSI. The GC-MS system consists of a TRACE™ GC Ultra gas chromatograph (Thermo Fisher Scientific Inc., Waltham, USA) equipped with an ISQ mass spectrometer (Thermo Fisher Scientific Inc., Waltham, USA) with electron ionization (EI). The system is operated with the Thermo Xcalibur 3.0.63 (Thermo Fisher Scientific Inc., Waltham, USA) and the PAL Sample Control (PAL3 System software, CTC Analytics AG, Switzerland) software for data acquisition and processing. The analytical protocols previously developed at the Institute for Chemistry and Bioanalytics (ICB) at the University of Applied Sciences and Arts Northwestern Switzerland (Muttenz, Switzerland) (see [WIELAND AND CVETKOVIC in prep.]) was adapted and optimized for measurements on the new GC-MS equipment.

9.2.2   Headspace Analysis of Hydrocarbons

Headspace analysis was performed using a PAL RTC (CTC Analytics AG, Switzerland) auto sampler. Headspace samples (0.25 - 2 mL) were injected after 30 min incubation at 50 °C under agitation using a heated (85 °C) syringe. The gaseous hydrocarbons were separated using a Restek Rt®-Msieve 5A column (30 m × 0.32 mm with 0.025 mm film) and helium at a constant flow of 2.0 mL/min as carrier gas (Carbagas, AG, Basel, Switzerland, He grade 5.0). The injection was performed in split mode with a split ratio of 1:18. The following oven temperature program was applied: Initial temperature 55 °C

isothermal for 4 min, heating up at a rate of 20 °C/min to 290 °C where temperature was kept constant for 18 min, resulting in an overall run time of 33.75 min.

The MS was operated at standard EI parameters: 70 eV collision energy and 230 °C MS source temperature. The data were acquired in the selected ion monitoring (SIM) mode. Retention times of the compounds and parameters used for the detection of the ions are given in Table 9.1. Nitrogen (Carbagas, AG, Basel, Switzerland, grade 5.0) and a reference gas mixture (Westfalen AG, Münster, Germany) containing 94.8 ppm methane, 98.0 ppm ethane, 94.1 ppm propane, 101.0 ppm n-butane, 98.5 ppm ethane, 98.3 ppm acetylene and 96.2 ppm propene in nitrogen grade 5.0 were used to prepare standards. The reference gas mixture was diluted with nitrogen in headspace vials to prepare calibration standards. These standards were prepared as follows: 5 mL ultra-pure water were transferred into a 20 mL headspace vial (Infochroma, Zug, Switzerland) inside a glove box (nitrogen atmosphere) and closed with a septum cap. A 0.5 L gas bag (SKC Limited, Dorset, UK) was rinsed with nitrogen, evacuated and filled with the 100 ppm reference gas mixture. The sample vial containing ultra-pure water was evacuated and a defined volume of calibration gas was taken from the gas bag and injected into the sample vial through the septum using a gas-tight syringe equipped with a valve (Hamilton Bonaduz AG, Bonaduz, Switzerland). Pressure was compensated in the sample vial by connecting a second gas bag filled with nitrogen for 5 seconds.

For the calibration standards gas volumes of 0.25 mL, 0.5 mL, 1 mL, 2.5 mL, 5 mL, 7.5 mL and 10 mL were transferred into the headspace vial.

A similar procedure was applied to prepare samples from the batch corrosion experiments for GC-MS analysis. These samples were placed on a Neodymium magnet to settle the carbonyl-iron particles used in the batch experiments. Transfer of 5 mL supernatant solution into the prepared headspace vial was accomplished using a 10 mL syringe.

Table 9.1: Technical parameters for quantification of hydrocarbons, alcohols and aldehydes

Compound	Retention Time R_f [min]	m/z
Butane	29.4	43, 58
Ethane	12.1	29, 30
Ethene	16.8	25, 26
Methane	5.4	15, 16
Propane	17.9	29, 43
Propene	25.5	41, 42
Methanol	7.1	29, 31
Ethanol	8.5	31, 45, 46
1-Propanol	11.6	59, 60
2-Propanol	9.5	45, 59
Butanol	14.4	41, 56, 57
Formaldehyde	9.3	75, 76
Acetaldehyde	6.8	29, 43, 44
Propionaldehyde	9.1	57, 58, 59

9.2.3   Headspace Analysis of Alcohols and Aldehydes

Headspace samples (1 mL) were injected into the GC after 30 min incubation at 80 °C under agitation using a heated (85 °C) syringe. The analytes were separated using a ZEBRON™ ZB-624 column (60 m × 0.25 mm with 1.4 µm film) and helium at a constant flow of

1 mL/min as carrier gas. The injection was performed in split mode at a split ratio of 1:20. The temperature program was started at an initial temperature of 40 °C (for 1 minute) followed by two ramps: first 5 °C/min up to 80 °C (for 1 minute) and then 20 °C/min to 200 °C resulting in a run time of 16 min. Retention times of the compounds are listed in Table 9.1.

The MS was operated at standard EI parameters: 70 eV collision energy and 230 °C MS source temperature. The data were acquired in SIM mode. The parameters used for the detection of the ions are listed in Table 9.1. Calibration of the analytes was performed using an analyte mixture, which was obtained by dissolving appropriate amounts of the pure single compounds in Milli-Q water (Milli-Q gradient A10 purification system, Millipore, Bedford, USA). A 20 mL headspace vial (Infochroma, Zug, Switzerland) was filled with 5 mL of the calibration standard and analyzed.

9.2.4   Analysis of Hydrocarbons in Gas Phase

Analysis of the hydrocarbons in the gas phase was performed with the GC-MS previously described in Section 9.2.1 in combination with the programme described in Section 9.2.2. Gas samples were analyzed using a headspace procedure and were injected from headspace vials. At first, the gas samples were released into a gas bag (0.5 L, SKC Limited, Dorset, UK) to achieve ambient pressure. Prior to analysis a headspace vial was twice evacuated and flushed with nitrogen. After the purging procedure 10 mL of the sample were taken from the gas bag and injected into the purged and evacuated 20 mL headspace vial using a gas-tight syringe equipped with a valve (Hamilton Bonaduz AG, Bonaduz, Switzerland). Eventually, a second gas bag filled with nitrogen was connected to the vial for 5 seconds to achieve pressure compensation in the sample vial. For the preparation of the calibration samples a gas bag was filled with the reference gas mixture. Between 0.25 mL and 15 mL volume of the calibration gas was withdrawn (valve equipped gas-tight syringe, Hamilton Bonaduz AG, Bonaduz, Switzerland) and injected into a purged and evacuated 20 mL headspace vial. Prior to the headspace analysis pressure compensation in the vial was achieved using the second gas bag filled with nitrogen, which was connected to the vial for 5 seconds. The calibration curves of an alcohol (ethanol) and a hydrocarbon (propane) are

exemplarily shown in Figure 9.1. Note that the method was also described in detail in [WIELAND AND CVETKOVIC *in prep.*].
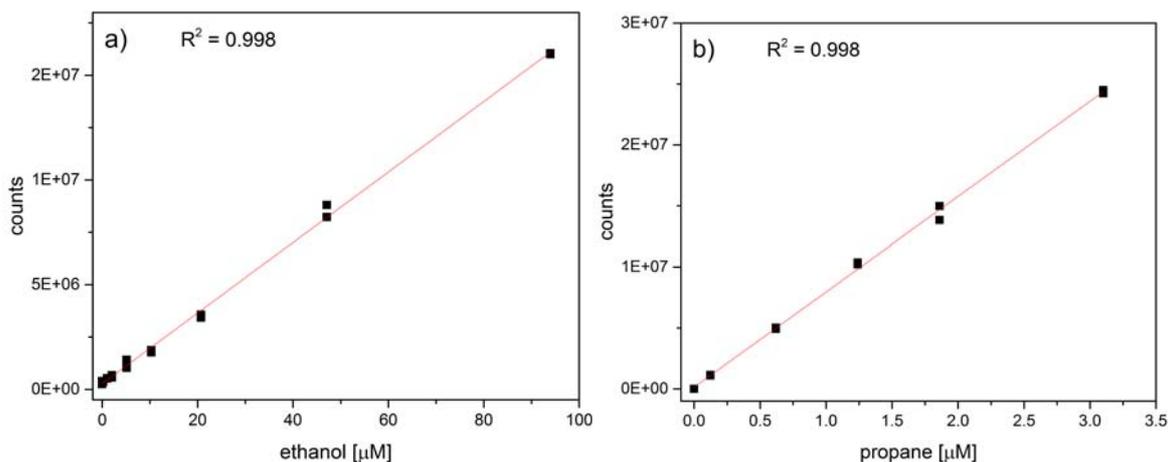
Figure 9.1: Illustration of GC-MS calibrations with standard compounds. a) GC-MS of ethanol, c) GC-MS of propane from gas phase

9.3 *Corrosion Experiments with Non-activated Iron Powders*

Batch-type experiments with non-activated carbon-bearing iron powders were carried out with the aim of further developing and optimizing the analytical protocols (HPIEC-MS, GC-MS) and checking the findings concerning the kind of organic compounds formed in the course of the anoxic corrosion of iron. In particular, the intention was to check whether or not the list of organic compounds reported in the first CAST progress report [MIBUS *et al.*, 2015] and recently published by [WIELAND AND HUMMEL *in prep.*] is complete.

9.3.1 Time-dependent Formation of Organic Compounds

The main findings from the time-dependent corrosion experiments under anoxic alkaline conditions that had been reported in detail in the first CAST progress report [MIBUS *et al.*, 2015] can be summarized as follows: 1) Reduced hydrocarbons (e.g. alkanes and alkenes) as well as oxidized hydrocarbons (e.g. carboxylic acids, alcohols and aldehydes) form during anoxic corrosion of iron powders, 2) fast formation of organic compounds within the first day was observed, 3) long-term production of the organic compounds was significantly slower.

The simultaneous formation of reduced and oxidized hydrocarbons is remarkable as reducing conditions are expected to prevail at the iron-water interface. At present, this finding cannot be explained and prompted us to carry out so-called exchange experiments with the aim of further improving process understanding. In the solution exchange experiments different aliquots of alkaline solution were subsequently added to the same vial containing iron powder (see solution exchange experiments reported in the first CAST progress report [MIBUS *et al.*, 2015] while in the iron exchange experiments described in detail in Section 9.3.3 of this report, the same aliquot of alkaline solution was subsequently added to different vials containing 1g of the same iron powder.

9.3.2   Solution Exchange Experiments

The solution exchange experiments reported in the first CAST progress report [MIBUS *et al.*, 2015] have shown that the concentrations of the organic compounds dropped to a very low level close to the limit of detection already after the first replacement of the solution. No significant increase in the concentrations of carboxylic acids was observed even after a long reaction period of 40 days between two solution replacements, supporting the idea that the corrosion process is very slow under strongly alkaline conditions.

The formation of high concentrations of oxidized hydrocarbons, in particular carboxylic acids, in the initial stage of the corrosion process (i.e. first addition of solution to iron powder) can be explained in two ways: 1) The formation of carboxylic acids (dissolved carbon species) occurs during pre-treatment of the iron powder (oxidizing conditions) and they are accommodated by the oxide layer on the iron particles. Subsequent release to solution is due to fast dissolution of the oxide layer with the first contact with alkaline solution. 2) Presence of residual oxygen in solution gives rise to the oxidation of carbon on the iron particles, a reaction that would occur simultaneously with the reduction of hydrocarbons at the reduced iron surface. Both processes, i.e. the formation of carboxylic acids during pre-treatment and the oxidation of carbon by residual oxygen, allow the presence of high concentrations of oxidized hydrocarbons, in particular carboxylic acids, in the course of the anoxic corrosion of iron powders to be explained.

The two hypotheses were tested on the basis of the following, so-called iron exchange experiments.

9.3.3   Iron Exchange Experiments

In these exchange experiments the alkaline solution was subsequently added to different vials containing the same commercial iron powder such as pre-treated BASF powder, untreated or pre-treated Sigma-Aldrich powder. The experiments were carried out in the glove box under a nitrogen atmosphere (< 2 ppm CO_2, O_2) using degassed solutions in headspace-free gas-tight vials. The solution is representative for cementitious systems, i.e. a solution in equilibrium with calcium silicate hydrate phases with a Ca/Si ratio = 0.8 (pH = 11.0). It is expected that contacting the solution with the iron powder in the first sample will consume residual oxygen. Hence, the solution should be free of residual oxygen in the second and further contacts with different samples with the same type of iron powder.

The results from three replacements (or contacts, respectively) of the same solution (20 mL) in different batches (1 g) of the pre-treated BASF iron powder are shown in Figure 9.2. The linear increase in the concentrations of the main carboxylic acids indicates that the first hypothesis outlined above is true. The second and third replacements clearly show a steady increase in the concentrations of the carboxylic acids which is not attributable to the presence of residual oxygen. It is anticipated that residual oxygen was consumed in the first contact of the solution with the iron powder (exchange I) while the solution is free of oxygen in the following additions to the iron powder (exchanges II and III). Note that the same observation was made for untreated and pre-treated Sigma-Aldrich iron powder. These experiments highlight that the presence of oxidized hydrocarbons in the corrosion studies is most likely attributable to the fast dissolution of the oxide layer formed on the iron particles which accommodates oxidized hydrocarbons. The oxide layer was formed during production of the iron powders and/or during their pre-treatment by an acid wash under ambient conditions. Note that carboxylic acids had been released both from untreated and pretreated Sigma-Aldrich iron powders although concentrations were significantly lower in case of the untreated powder.
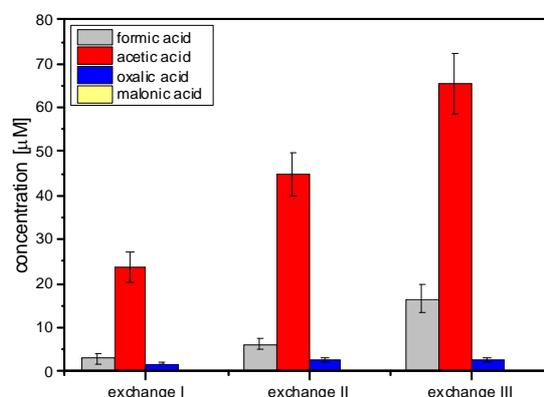
Figure 9.2: Concentrations of carboxylic acids as a function of additions of the same solution to different batches of the pretreated BASF iron powder (exchanges I, II, III) (pH = 11.0)

9.3.4 Organic Compounds Formed during Anoxic Corrosion

In the second year of the project we adjusted the instrumental set-up that had been used to determine carboxylic acids with HPIEC-MS. These adjustments were required after an extensive service of the MS. As a result it was recognized that the sensitivity of the MS had improved after the service modifications which allowed additional carboxylates, in particular lactate, propanoate and butanoate, to be detected at very low concentrations. These compounds will be monitored in future corrosion experiments although the concentrations were found to be only slightly above the detection limit.

9.4 *Coupling Separation Techniques with Accelerator Mass Spectrometry (AMS) for Compound-specific Carbon-14 Analysis*

The ^{14}C concentration for a typical set-up of the planned corrosion experiment with activated steel was estimated using the following parameters: linear corrosion rate under alkaline conditions ~ 50 nm a^{-1}, surface area of the 1 g specimen of activated steel ~ 1 cm^2 and ^{14}C inventory of the activated steel sample ~ 18 kBq g^{-1} [SCHUMANN *et al.*, 2014]. The scoping calculation revealed that the daily production rate of total ^{14}C will be very low, i.e.

$\sim 3 \cdot 10^{-15}$ mol ^{14}C L^{-1} d^{-1}. This corresponds to a released ^{14}C activity of 0.64 µBq L^{-1} d^{-1}. Note that an activity of 0.64 µBq ^{14}C refers to the total activity of ^{14}C released and includes the activity of ^{14}C-labelled gaseous, volatile and dissolved species. Furthermore, additional dilution of about 1:25 to 1:50 has to be taken into account in the course of the chromatographic separation carried out in connection with the compound-specific ^{14}C AMS analytical method. Therefore, it is expected that the ^{14}C activity in the fractionated gas and liquid samples from the corrosion experiment will be well below the detection limit of liquid scintillation counting. To the best of our knowledge ^{14}C AMS is the only suitable technique capable of detecting such a low ^{14}C activity. Note, however, that dealing with such low activities bears the risk of potential contamination effects as ^{14}C is also a naturally occurring radionuclide, which is produced in the upper atmosphere in the form of ^{14}CO$_2$ (activity of 1 m^3 air ~ 53 mBq). In particular, alkaline solutions are commonly known sink for CO$_2$ and thus also for ^{14}CO$_2$. Therefore, the ^{14}C background in the corrosion experiment with activated steel could be affected by an undesirable uptake of ^{14}C from the surrounding atmosphere in any stage of sample preparation and handling.

9.4.1   Determination of the Carbon-14 Background

The ^{14}C background caused by the AMS measurements and by the analytical method (sample preparation, chromatographic separation, sample handling) was determined. The value corresponds to the detection limit and the lower limit of the dynamic range available under the applied conditions.

A cleaning procedure was developed, in a first step, to minimize the background caused by contaminations from the sample vials. Prior to use, the vials were pre-cleaned by repeated rinsing with Milli-Q water over a period of at least 7 days. Within this period the Milli-Q water was replaced daily. The vials were stored in Milli-Q water and dried with pressurized air immediately before use.

Several checks were carried out to assess the most important ^{14}C sources during sample preparation and measurement that are relevant in connection with the ^{14}C background. The effect of the cleaning procedure and sample treatment on the background was tested by

using different sample vials (plastic vs. glass) and water with different purity degrees, such as ultrapure water, untreated, boiled and degassed Milli-Q water (Table 9.2). The results reveal no significant difference in the ^{14}C background for pre-cleaned plastic and glass IC vials. A background of about 0.06 $F^{14}C$ (fraction modern carbon or fm, respectively) was determined for both vials. Furthermore, untreated Milli-Q water does not have a higher background compared to ultrapure or degassed Milli-Q water. However, a significant increase in the fraction modern was observed for a $Ca(OH)_2$ solution with pH 12.5 (0.89 $F^{14}C$). This increase in the ^{14}C background is attributed to the uptake of atmospheric $^{14}CO_2$ during sample preparation, transport to the AMS and during the AMS measurement. This finding shows that alkaline solutions should be neutralized immediately after sampling to minimize/avoid the uptake of $^{14}CO_2$.

In a subsequent experiment the effect of chromatographic separation on the ^{14}C background was tested. To this end, Milli-Q water was injected into the IC and fractions were collected at the retention times corresponding to those of the target carboxylic acids (acetic acid (AA), formic acid (FA), malonic acid (MA) and oxalic acid (OA)). It was notified that various materials (e.g. analytical column, eluent and laboratory atmosphere) interact with the sample during separation/fractionation which might give rise to an enhanced ^{14}C background. Note, however, that the collected fractions are neutralized to a pH ~ 6-7 in the ion suppression unit of the IC during chromatographic separation. Thus, the uptake of $^{14}CO_2$ by these fractions in the course of subsequent sample handling and transfer to the AMS is expected to have only a small effect on the ^{14}C background. All samples subject to AMS measurements were frozen instantaneously after fractionation to avoid any (microbial) degradation of the analytes.

In Table 9.2 the ^{14}C background generated during chromatographic separation is given for the target fractions acetic acid (AA), formic acid (FA), malonic acid (MA) and oxalic acid (OA). The background (0.02 - 0.06 $F^{14}C$) is comparable to 0.06 $F^{14}C$ which is the background determined for cleaned vials and Milli-Q water. Hence, an enhancement in the background was not observed in the course of the chromatographic separation process. This finding clearly shows that the analytical method under development for the AMS based

detection of very low ^{14}C activity is not subject to major ^{14}C contaminations and therefore supposed to be applicable in the framework of the planned experiment with activated steel. To summarize, an average ^{14}C background of 0.06 ± 0.02 F[14]C was determined in the samples after IC separation using pre-cleaned plastic vials for injection and collection.

Table 9.2: Comparison of background (BG) activities (in F[14]C) (see text).

Vial [F[14]C]		Solvent [F[14]C]		IC-fraction [F[14]C]	
Plastic	0.06	BG-Milli-Q	0.06	AA-BG	0.02
Glass	0.07	BG-ultrapure water	0.07	FA-BG	0.04
		BG-degassed-Milli-Q	0.10	MA-BG	0.06
		BG-alkaline (pH 12.5)	0.89	OA-BG	0.02

9.4.2   Dynamic Range of the AMS System and Recovery Tests with Carbon-14 Radiotracer

A second series of experiments was carried out to determine the dynamic range of the AMS system and the recovery of a tracer separated using the IC method. ^{14}C-labelled acetic acid was selected from the list of target carboxylic acids. Solutions with different ^{14}C activities, which corresponded to 10 - 2500 F[14]C (in a matrix of 20 µg ^{12}C), were prepared and injected into the IC system. The fraction corresponding to acetic acid was collected, which was transferred to the AMS facility at the University of Bern and analyzed. The fraction of modern carbon in the fractionated sample (acetic acid fraction) should correspond to 0.2 - 50 F[14]C (in the matrix of 20 µg ^{12}C) due to a 1:50 dilution during IC separation. In Figure 9.3 the experimental scheme (left) and the results of the separation process (right) are shown. The table shows the expected fraction modern (calculated from the ^{14}C activity of the starting solution and taking into account the separation induced dilution factor), the fraction modern measured with AMS as well as the recovery obtained from the ratio of the two values (in %). A rather poor recovery was found for the lowest fraction modern (0.21)

while the average recovery determined from the samples with 0.47 - 49.12 $F^{14}C$ is close to 100 % (93 ± 17 %). It appears that for most samples the measured recovery is systematically lower than the expected value which could be caused by an incorrect window setting during fraction collection. Additional test are ongoing to check and optimize the recovery.

Expected $[F^{14}C]$	Measured $[F^{14}C]$	SD [%]	Recovery [%]
0.21	(0.13)	(2.2)	(64)
0.47	0.59	-	125
0.95	0.91	1.2	96
2.67	2.47	-	93
4.39	(1.80)	-	(41)
11.16	8.50	0.5	76
24.61	17.79	0.5	72
49.12	46.37	1.4	94
		Average:	93 ± 17 %
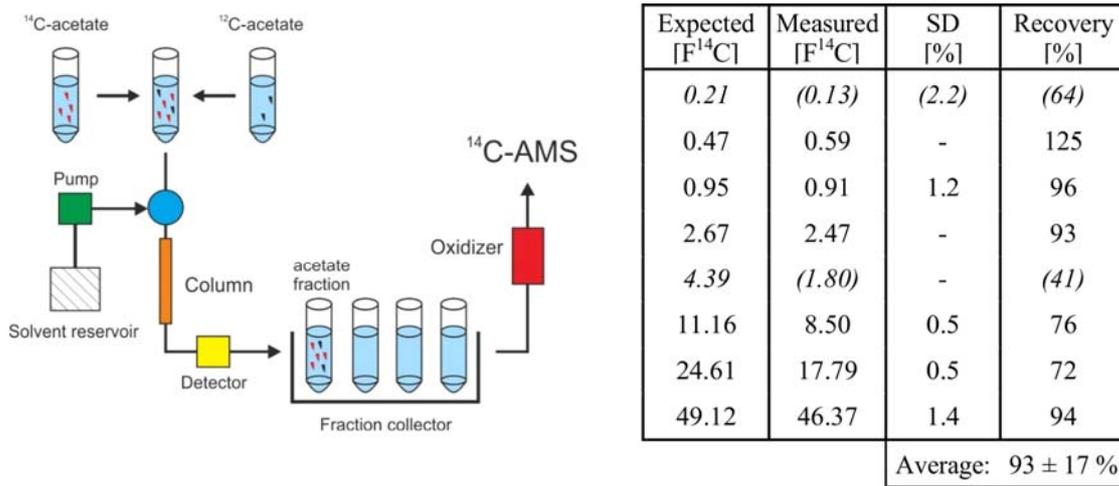
Figure 9.3: Recovery test for the IC separation using ^{14}C-labelled acetic acid. Left: scheme of the experimental setup; right: results obtained from IC separation

The test with ^{14}C-labelled acetic acid further allowed the dynamic range and possible cross contamination between IC samples to be discovered. Even the highest activities gave reproducible results in the AMS measurements, suggesting that cross contamination is not a major problem for these measurements. The dynamic (linear) range of the AMS extends over three orders of a magnitude, i.e. from 0.06 to 50 $F^{14}C$. This wide range opens up sufficient flexibility for sample dilution to achieve ^{14}C contents in the measuring range.

After determination of the ^{14}C background following injection of Milli-Q water chromatographic separation was carried out on an acetate sample with the highest ^{14}C activity (corresponding to 2500 $F^{14}C$ in a matrix of 20 µg ^{12}C). Cross contamination was determined as follows: Milli-Q water was reinjected after the sample with high activity and the acetate fraction was collected (see scheme below):

$$AA\text{-}BG \rightarrow {}^{14}C\text{-}AA\text{-}sample \rightarrow AA\text{-}BG$$

The tests show that samples injected after the highly concentrated ^{14}C standard did not have a ^{14}C content above the ^{14}C background indicating that cross contamination did not occur.

9.4.3 Cross Contamination in AMS Measurements

Cross contamination often occurs when measuring samples with a wide range of concentrations. If the concentration (R_x) and mass (m_x) of the previous "hot sample" is high enough, it is possible that a small fraction (φ) remains inside of the measuring instrument, mixing with the mass (m_s) and concentration (R_s) of the next sample. The mixing will lead to an incorrect measured concentration (R_m). We are considering that cross contamination is constant for the analysis of ^{14}C/^{12}C. Therefore it is possible to subtract and correct the contamination from the measured value. A mass balance analysis of cross contamination is given by:

$$R_m - R_s = \frac{\varphi m_x}{m_s}\left(R_x - R_s\right) \tag{1}$$

The experiment consisted on intercalating injections of ^{14}C-labelled acetic acid (R_x) and ^{14}C-depleted sodium acetate (R_s=0 fm) into the ion chromatograph (IC), collect and analyze the eluate with AMS coupled to an elemental analyzer (EA). The sample mass for both substances was kept constant (m_s=m_x=20 µg). Figure 9.4a shows the plot of R_m vs R_x and the slope corresponds to the cross contamination factor φ=0.45%. Figure 9.4b further shows the ^{14}C/^{12}C ratios given in Figure 9.4a corrected with equation 2:

$$R_m^* = \left(\frac{m_s R_m - \varphi m_x R_x}{m_s - \varphi m_x}\right) \tag{2}$$

The comparison of Table 9.2 and Figure 9.4b shows how the contaminated values of the ^{14}C-depleted substance return to background levels. These results show the fitting of the cross contamination effect and how strong it is.
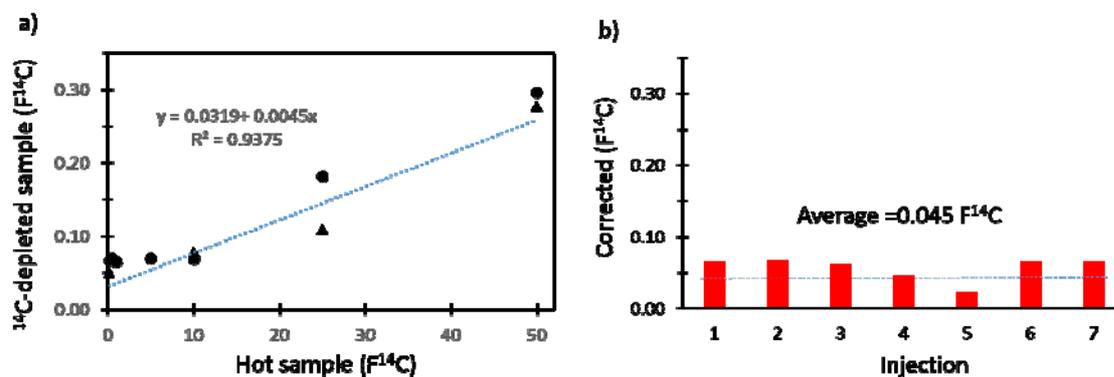
Figure 9.4: a) Cross contamination fitting, b) data corrected from cross contamination

9.4.4   Compound-specific Carbon-14 AMS for Gaseous Species

The corrosion studies with non-activated iron powders revealed that gaseous organic compounds will form during the corrosion of activated steel. The compound-specific ^{14}C AMS analytical method for the determination of low concentrations of ^{14}C-labelled, gaseous compounds will be based on the combination of gas chromatographic separation in combination with ^{14}C detection by AMS. The analytical approach, therefore, is similar for the compound-specific ^{14}C AMS analysis of gaseous (alkane, alkene) and volatile (alcohols, aldehydes) compounds as well dissolved compounds (carboxylic acids). To the best of our knowledge, a methodology for compound-specific ^{14}C AMS of gaseous and volatile compounds has not yet been developed and reported in literature.

Preparation of the gaseous and volatile compounds for compound-specific ^{14}C AMS is novel and therefore requires instrumental developments. The GC system operated at PSI has to be coupled to a combustion reactor and a fraction sampling system for CO_2. The mixture of ^{14}C-labelled, gaseous organic compounds will be separated in the GC and subsequently oxidized to [14]CO_2 by the combustion reactor. Therefore, the fractions collected with the fraction sampler correspond to single ^{14}C-labelled compounds oxidized to [14]CO_2. The modified GC system has been designed and is currently being developed by a private company, Brechbühler AG (Schlieren, Switzerland), the commercial partner involved in this project.

9.5 *Summary and Outlook*

A new GC-MS system has been installed in the PSI hot laboratory, tested and successfully applied for gas phase analyses. The analytical methods for the identification and quantification of gaseous (e.g. alkanes, alkenes) and volatile (e.g. alcohols, aldehydes) organic compounds using the new GC-MS system have been developed and applied in corrosion studies with non-activated iron powders.

The corrosion experiments with non-activated iron powders immersed in cement-type porewater have been drawn to a close. The final experiments comprised a series of so-called iron exchange experiments in which the same alkaline solution was subsequently added to several vials containing fresh iron powder and equilibrated. The aim of these experiments was to distinguish whether residual oxygen causes the formation of oxidized hydrocarbons or the latter compound had formed during pre-treatment of the iron powders and entrapped in the oxide layer which was dissolved in contact with the alkaline solution. The experiments show that the latter process takes place and explains the presence of oxidized hydrocarbons in solution during anoxic corrosion of the iron powders.

Corrosion experiments with non-activated iron powders were further carried out with the aim of critically assessing the kind of organic compounds that could form in the course of the anoxic corrosion of iron and steel. The results from the new corrosion experiments show that, in addition to the list of organic compounds previously reported in the first CAST progress report [MIBUS *et al.*, 2015], lactate, propanoate and butanoate form in iron-water systems. Note, however, that the concentrations of these compounds are close to the detection limit of HPIEC-MS.

Development of the compound-specific ^{14}C AMS analytical method for dissolved species was a major activity in the second year of the project. A great number of measurements and tests have been carried out with the aim of determining the ^{14}C background caused by the developed methodology. These studies provide the fundamental information concerning feasibility of the analytical approach as detection of extremely low concentrations of ^{14}C bearing organic compounds is required in the corrosion experiment with activated steel. The

results show that it is possible to achieve a very low ^{14}C background in the course of the chromatographic separation and subsequent ^{14}C detection by AMS while the dynamic range covers three orders of a magnitude, i.e. from 0.06 to 50 F^{14}C (fraction modern). A first series of tests with ^{14}C-labelled acetic acid further show that recovery is close to 100 % after separation by HPIEC and subsequent ^{14}C detection by AMS.

The experimental programme in the third year of the project will include corrosion experiments with non-activated iron powders immersed in NaOH (pH 11 and pH 12.5). The aim is to assess whether or not the organic compounds produced in cement-type porewater (i.e. highly alkaline, presence of Ca, Si) also form in NaOH. Note that the WP 2&3 consortium has decided to consider a NaOH or a Ca(OH)$_2$ solution (pH 12 or higher) as the common reference solution for the experiments, depending on the conditions.

The recovery tests will be repeated with all main target carboxylic acids, in addition to the tests already carried out with acetic acid. Furthermore, determination of dissolved, ^{14}C-labelled organic compounds in "real" systems, that is activated steel immersed in hyperalkaline solution, is foreseen in the next phase of the project. Eventually, the development of a compound-specific ^{14}C AMS method for gaseous and volatile compounds will be one of the main activities in the year to come.

10   RWMC contribution to CAST WP2 Second Annual Report

10.1 *Long term corrosion test using non-irradiated steel*

10.1.1 Gas flow experimental system

Long-term corrosion tests on stainless steel under simulated geological disposal conditions have been performed by hydrogen measurement. A gas flow system was applied to measure the amount of gaseous hydrogen that evolves from the corrosion reaction over 6 years.

The 18Cr-8Ni austenitic stainless steel with a thickness of 0.1 mm was obtained from Nilaco Corporation (Product No. 753323). The chemical composition is shown in Table 10.1. The stainless steel sheet was polished with 0.02 mm alumina powder and then cut (100 mm×100 mm×0.1 mm). Figure 10.1 shows the surface conditions before the corrosion test.

The experimental setup for the gas flow corrosion system is shown in Figure 10.2. The stainless steel samples (20 sheets, surface area of 0.40 m^2) were immersed in 2.5 dm^3 of deoxygenated dilute NaOH solution (initial pH = 12.5). An argon carrier gas was passed through the inner flask, and the hydrogen concentration in the carrier gas was measured periodically using atmospheric pressure ionization mass spectrometry (API-MS, Hitachi Tokyo Electronics, UG-400). Hydrogen contamination from the atmosphere (approximately 0.5 ppm) was avoided by using a double container system. Three test vessels were prepared for this study: two for stainless steel corrosion and one for a blank run.

Table 10.1: Chemical compositions of 18Cr-8Ni austenitic stainless steel (wt%)

	C	Si	Mn	P	S	Ni	Cr	H(ppm)
Specification	<0.08	<1.00	<2.00	<0.045	<0.030	8.00-10.50	18.00-20.00	n.m.
Specimen	0.07	0.45	0.79	0.028	0.005	8.29	18.14	n.m.

n.m. not measured
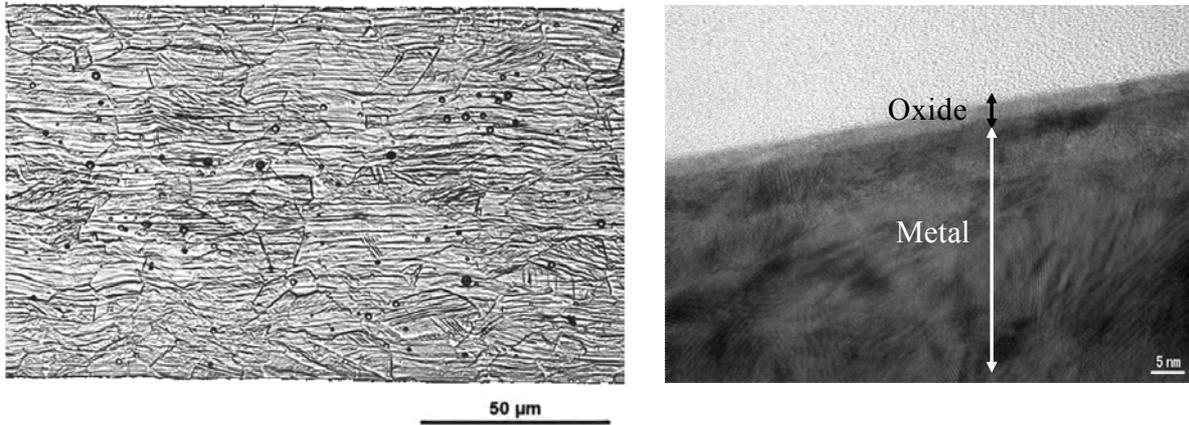
Figure 10.1: Optical micrograph of a chemically etched cross-section of stainless steel (left) and TEM observation of the surface oxide before immersion (right)
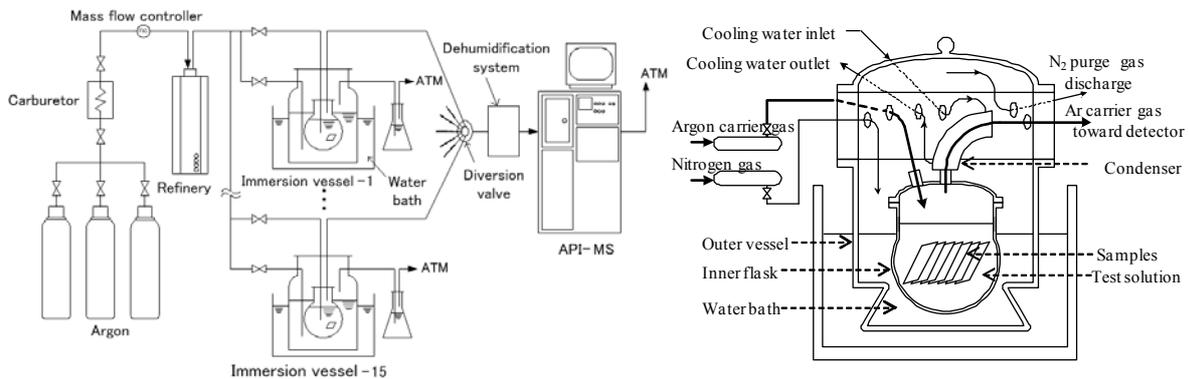
Figure 10.2: Overview of the gas flow experimental system (left) and detailed illustration of the immersion vessel (right)

10.1.2 Hydrogen generation and corrosion rate

The evolved hydrogen concentration in the argon carrier gas decreased over time from 15 to 1.5 ppb in the initial year as shown in Figure 10.3. After that the hydrogen concentration can be considered to be constant: average values of Run 1 and Run 2 are 1.50 ± 0.34 ppb and 1.67 ± 0.42 ppb, respectively. This amount is adequate for the blank test (0.32 ± 0.06 ppb).
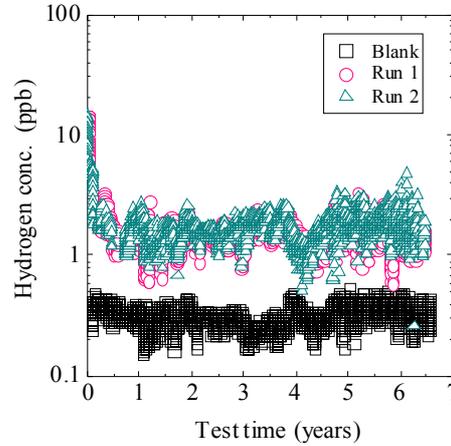
Figure 10.3: Gaseous hydrogen concentration generated from stainless steel

The cumulative atomic molar amount of gaseous hydrogen per unit surface area, A_{gas} (mol/m^2), can be obtained from

$$A_{gas} = \frac{2}{S} \sum \frac{C_{t_i} + C_{t_{i-1}}}{2} \cdot \frac{v}{V^\circ} \cdot (t_i - t_{i-1}),$$

where C_{ti} is the net concentration of H$_2$ gas (ppb) at time t_i, t_{i-1} is one time increment before t_i, v is the gas flow rate (0.9 dm^3/min.), V° is the molar volume of a perfect gas (22.4 dm^3/mol), and S is the surface area (0.4 m^2). As shown in Figure 10.4, the hydrogen gas generation shows a good parabolic relationship with time up to one year. After this first period the kinetics behaviour changes into a linear relationship that holds for time up to 6.5 years. The kinetic behaviour of aqueous corrosion of stainless steel has been discussed by Robertson for high temperatures down to 423 K together with a summary of parabolic corrosion rate constants [ROBERTSON, 1991]. At high temperature, the formation of duplex oxide on a metal surface and the diffusion of Fe ions through the oxide are considered to be rate controlling for the corrosion.
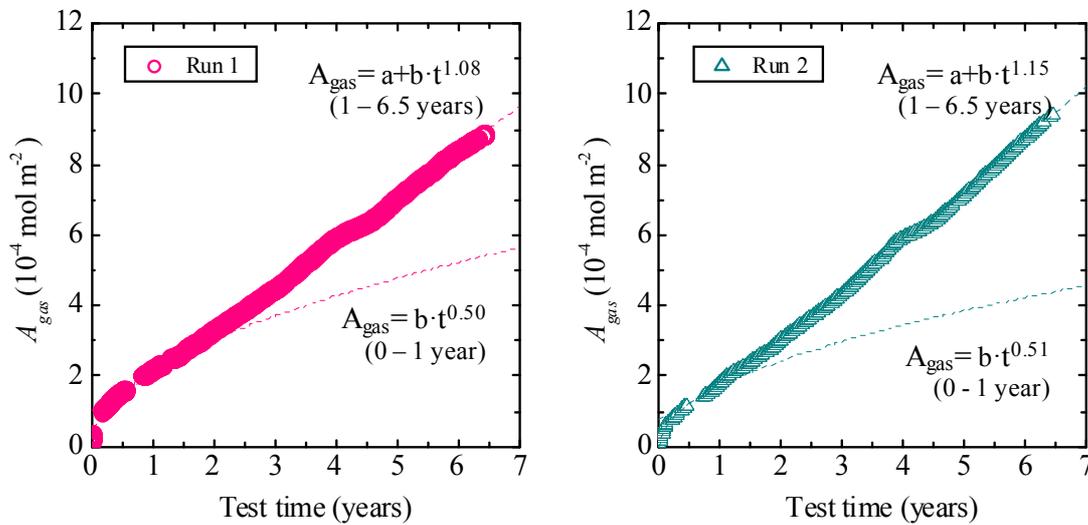
Figure 10.4: Amount of hydrogen as a function of corrosion time. Dashed lines are best fitted curves.

The corrosion rate of the stainless steel can be obtained by assuming the following corrosion reaction:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 8H.$$
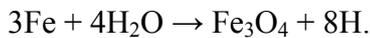
Because hydrogen absorption into the metal is negligible (measured less than 3%), the corrosion rate R_c (μm/year), which represents the amount of iron consumed by oxidation under the stoichiometry in the above reaction, can be obtained from gaseous hydrogen as

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

where M_{Fe} is the molecular weight of iron (55.85 g/mol), ρ is the iron density (7.87×10^6 g/m^3), and t is the test time [years]. The corrosion rate shown in Figure 10.5 decreases with time over the first year and is constant after that, with average values after one year of 3.99×10^{-4} and 3.93×10^{-4} μm/y for the two runs. These corrosion rates are slower at 1/50 times the rate used in the conventional evaluation in Japan ($R_c = 2 \times 10^{-2}$ μm/y) and have an impact on estimation of radionuclide leaching and gas generation in the safety assessment for disposal of stainless steel waste.
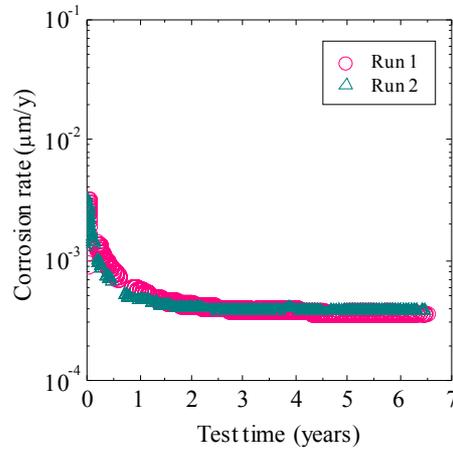
Figure 10.5: Corrosion rate of stainless steel from the gas flow test

10.1.3 Characteristics of surface oxide

Figure 10.6 shows the results of a surface oxide analysis by TEM, EDX, and electron diffraction after two years of corrosion. The cross section image might be constructed in three parts. The outermost surface (Point 1), appearing in heterogeneous light grey, consists of a silicon rich oxide mixture that might be loosely stitched and aggregated onto the surface oxide. The silicate is a dissolution product of the glass vessel. The silicate aggregation is also observed in the elemental distribution by XPS (Figure 10.7). Unless the Si precipitate is compacted, the effect of the loose aggregation on the corrosion resistance is considered to be negligible. The second surface located on the metallic phase (Point 2) is an oxide that is generally referred to as a passive film. The oxide is amorphous and its thickness is approximately 2 nm to 4 nm, which indicates that the oxide does not grow from the initial oxide layer of 3 nm. However, the oxide composition is not clearly determined by XPS in the profile. The detailed characteristics and roles of the passive oxide film are future challenges.
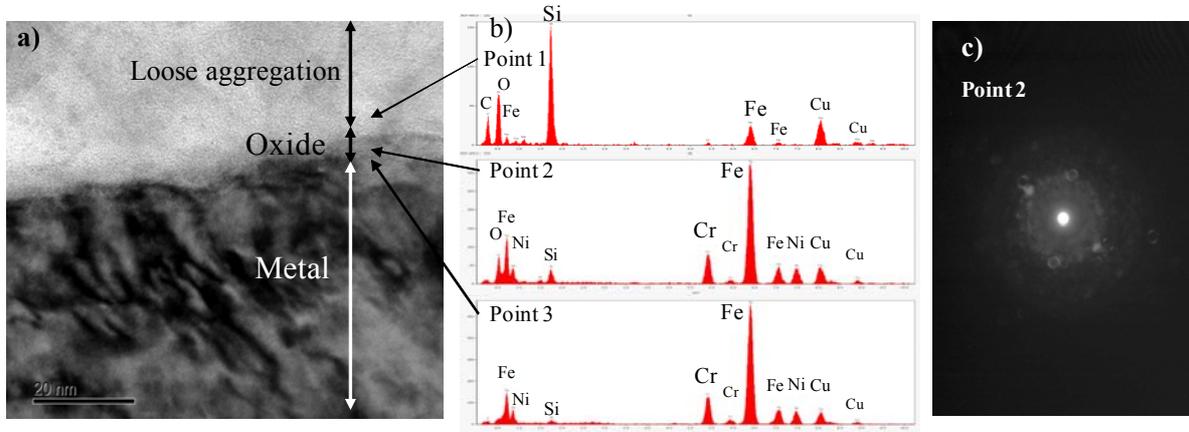
Figure 10.6: TEM observation of the surface oxide after two years of immersion in an ampoule, and the corresponding b) EDX spectra and c) electron diffraction
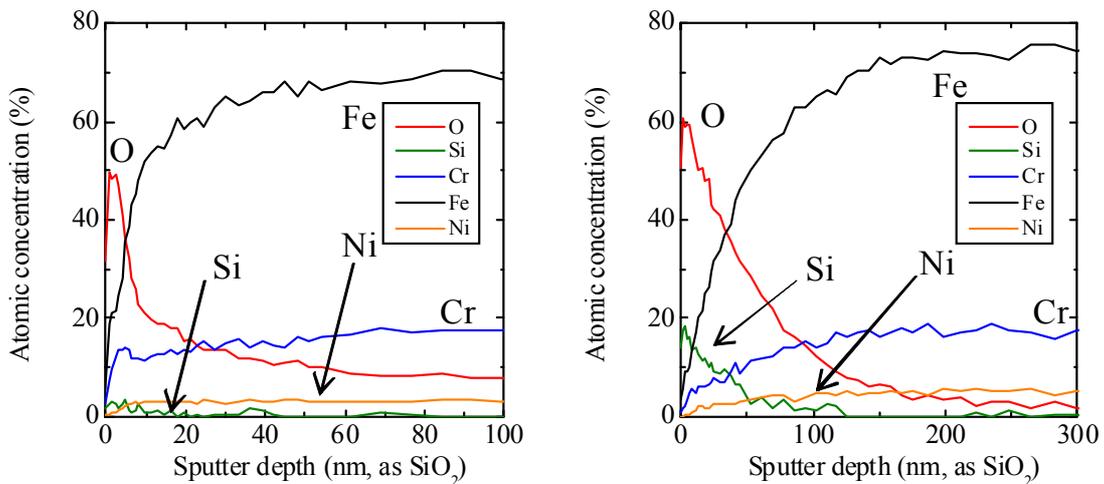
Figure 10.7: Depth profile of elements before (left) and after two years of immersion (right) by XPS measurement

This research is a part of the "Research and development of processing and disposal technique for TRU waste (FY2014)" 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 Second Annual Report

11.1 *Materials*

SCK•CEN has at its disposal both non irradiated and irradiated JRQ (carbon steel) samples. The available irradiated JRQ specimens originate from the SCK•CEN`s BR-2 reactor and are ready for experiments.

11.2 *Methods and experiments*

11.2.1 Nitrogen analysis

Information on the nitrogen content from recent experimental studies and reports were either not available or not presented accurately (i.e. only maximum permitted values). Therefore, the determination of the initial nitrogen content in the metals was required to realistically estimate the ^{14}C production after irradiation campaigns.

The nitrogen content of a JRQ sample was analyzed by an inert gas fusion method. The nitrogen analysis was performed using a LECO TC436 analyzer. The sample was placed inside a graphite crucible and held between the upper and lower electrodes of the impulse furnace. A high current passed through the crucible increasing the temperature inside (> 2500 ºC), eventually melting the sample. Gaseous compounds generated in the furnace were released into the flowing inert gas stream (argon or helium). The gas stream was sent to the appropriate infrared detector: if O as CO_2 was measured, then the thermal conductivity detector measured the nitrogen content. The reported lower limit of detection of the method is approximately 1 ppm for N. Results are presented in Table 11.1.

Table 11.1: Average nitrogen content (N_{avg}) of unirradiated carbon steel samples

Sample ID	material	N_{avg} (ppm)
JRQ	carbon steel	**19 ± 0.4**

It can be concluded that the nitrogen content of this JRQ carbon steel is consistent to the literature values and technical specifications, usually between 20-30 ppm [IAEA, 2009].

11.2.2 Corrosion experiments

Static leaching and accelerated corrosion tests are planned for non-irradiated and irradiated samples.

As it was mentioned during the technical meeting in Switzerland, NaOH is the recommended electrolyte but each participant is allowed to use its own electrolyte. For this reason SCK•CEN reconsidered the original approach and decided to continue its experiments using $Ca(OH)_2$ electrolyte. The main reason is that portlandite is representative to the Belgian national nuclear waste repository situation. The following pore water is planned to be used for the leaching/corrosion tests: de-gassed $Ca(OH)_2$ (pH ~12.5). The pore water will be prepared in a glove box under anaerobic conditions and degassed with (nitrogen or argon) to reduce the risk of any traces of ambient air $^{14}CO_2$ absorbed in the solution.

After consulting with the SCK•CEN`s radiation protection officers on the dose exposure and the associated risks, it was concluded that the experiments can be carried out in glove boxes and fume hoods using plastic glove bags. Hot cells at SCK•CEN may not be available within a reasonable timeframe which is another reason why glove box or glove bag is preferred.

11.2.2.1 Static leaching test

Corrosion test setups are being developed and finalized. The basic design of the setups is left unchanged, only few minor modifications are planned. The first one concerns the test cell volume which is resized from 100 cm^3 to 50 cm^3. The reasons for smaller volume are 1) to reduce the matrix volume i.e. increasing the concentration of produced carbon species; 2) to generate less waste volume which can be significant in case of many replicates.

The liquid phase will occupy 70-80 % of the volume and the rest is for the headspace. Sampling is planned through outlets which enables using gas tight syringe.

11.2.2.2 Accelerated corrosion test

Special glass wares and electrodes have been designed for the accelerated corrosion setup. The inner part of the glass cell will be covered with a PEEK liner to avoid interference due to glass dissolution at high pH.

Gas tightness of the cells is tested on a cell which is identical to the setup selected for the accelerated corrosion experiments. Rubber sealing was used between cell-lid and bottom. The cell was filled with helium and the internal and ambient air pressure together with the ambient temperature were recorded. Pressure in the glass cell was set to 1.1 bar, that is 0.1 bar overpressure comparing to the ambient pressure. The glass cell for the accelerated corrosion experiments is shown in Figure 11.1. The stability of the gas pressure is demonstrated in Figure 11.2.

Figure 11.1: Glass cell for accelerated corrosion test setup
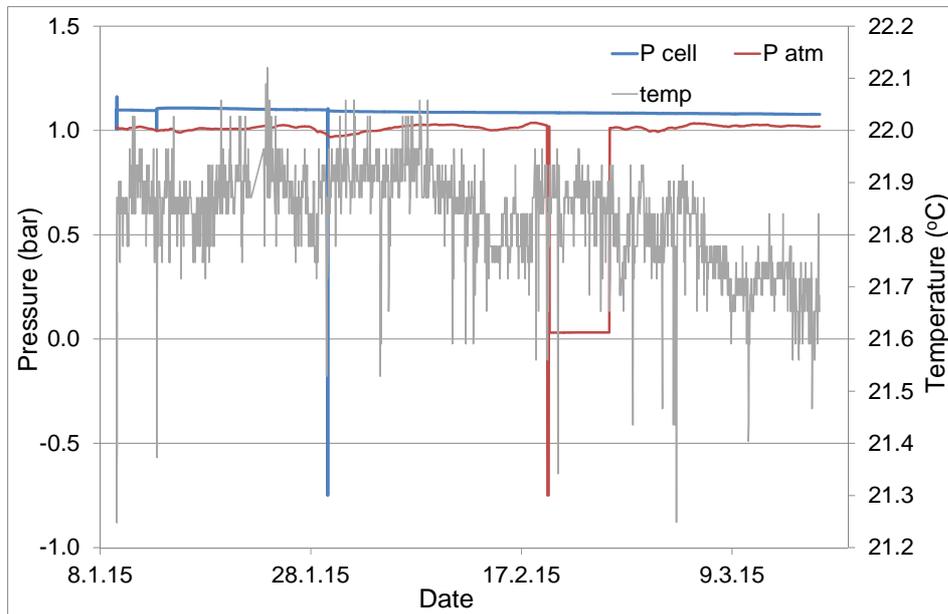
Figure 11.2: Temperature, internal- and external pressure profile during the gas tightness test

The sharp decrease in the temperature and pressure indicate the moment when experiment had to be interrupted or sensors were replaced.

11.2.3 Metallographic analysis

Microstructure analysis of unirradiated metals was performed at the LHMA after the appropriate sample treatment (VAN RENTERGHEM, 2015).

The TEM investigation was done in a JEOL 3010 microscope operating at 300 kV. Bright field, dark field and selected area electron diffraction were used to determine the defect structure and precipitates. Energy dispersive X-ray spectroscopy (EDS) was applied for the qualitative determination of the composition of the precipitates. The grain size of each material was determined from the backscattered electron images (BEC) of the samples after electrochemical polishing for 10 sec. The electrolyte used consisted of 5% perchloric acid and 95% methanol. To polish the carbon steel, the temperature of the electrolyte was reduced to -30 °C and a voltage of 25 V was applied. The grain size is determined in accordance with the ASTM standard E112-95 (ASTM, 2013). The EDS spectrum gives

qualitative information of the composition of the bulk (in blue) and the carbides (in red) in Figure 11.3.
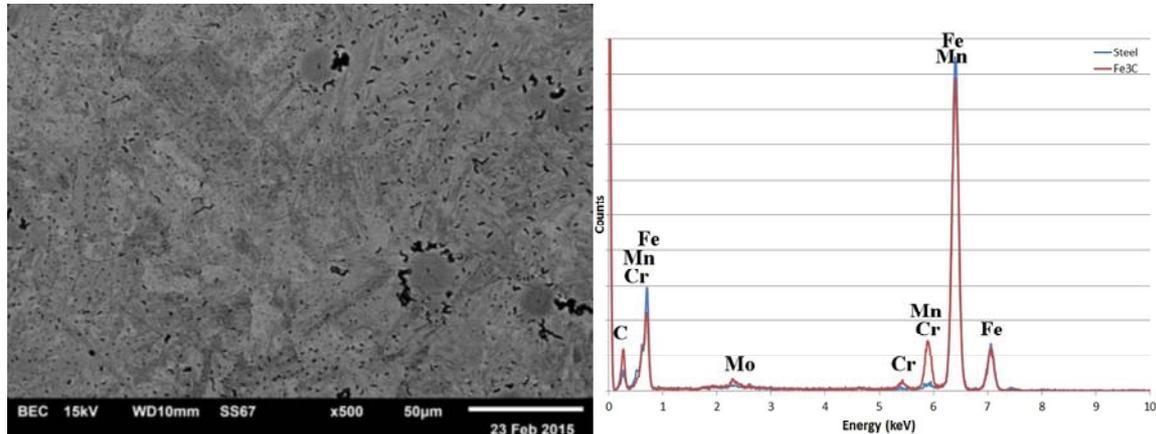
Figure 11.3: Backscattered electron images of a JRQ sample (left); EDX spectrum (right)

The most important findings are the following. No graphite carbon was detected but iron carbide (Fe_3C), which is enriched in Mn, Cr and Mo. The iron carbide has cementite crystal structure and the morphology and size of carbides were found to be inhomogeneous. The grain structure is that of a ferritic-bainitic steel, which is the expected grain structure for a RPV steel. Considering the ferrite grains, the grain size determination gave a grain size number of 8.4, which corresponds to an average grain surface of 380 μm^2 or a grain size of 19.5 μm. The average width of the bainite laths is 2 μm. The carbide morphology changes from almost spherical carbides to elongated, needle shaped structures. The size is on average of the order of a few 100 nm, but the elongated carbides can reach a length of more than 1 μm for a width of about 100 nm. From the carbon release point of view, it is important to mention that carbides were frequently found at the grain boundaries of the bainite laths as well as the ferrite grains, but some are formed in interior of the grain.

The analysis of the irradiated samples has been delayed due to the lack of technical personnel at LHMA. It is likely to be performed in the second half of 2015.

11.2.4 Dose rate and gamma-ray spectrometry analysis

To determine the gamma dose rate from the irradiated carbon steel samples a portable gamma dose rate monitor was used (Automess 6150 AD5 counter). A high purity germanium detector was used for the gamma ray spectrometry analysis to identify the activation products present in the irradiated samples. It has to be mentioned that the analysis was qualitative and semi-quantitative due to the different sample and calibration source geometry. The analysis will be repeated later to get more accurate results. The dose rate and gamma ray spectrometry results are shown in Table 11.2.

Table 11.2: The estimated ^{60}Co, ^{106}Ru activity and the contact dose rate of the irradiated JRQ samples

Sample i.d.	^{60}Co	^{106}Ru	Contact dose rate (mSv/h)
	[kBq]		
16-6-18/2 RA	150	2.4	0.250
16-6-18/2 RB	150	2.6	0.235
16-6-18/2 RC	160	3.0	0.24
16-6-18/1 R	910	33	1.23

It can be concluded that the highest gamma activity contribution in these carbon steel samples is from ^{60}Co and ^{106}Ru also contributes. It is planned to verify the gamma spectrometry results determining the irradiation history with model calculations.

11.2.5 Carbon-14 production estimation

A simple approach using the ORIGEN-ARP tool, which is part of the SCALE-6.1 package, was applied for the ^{14}C production estimation in the irradiated metals. This basic tool has pre-built libraries designed for several commercial assembly types for predicting the spent fuel inventory. In contrast, the input data for the first calculation was based on the initial nitrogen content and neutron fluence data only. The results from the first calculation and the ORIGEN simulation are summarized in Table 11.3.

Table 11.3: Estimated ^{14}C concentration of the irradiated carbon steel sample and its initial nitrogen content

Sample ID	C_N (ppm)	First calculation A_{14C} (Bq/g)	Computer simulation (Bq/g)
JRQ	19 ± 0.4	~ 60	175

Irradiation data: Chivas 0 (Callisto loop); fluence ~3.1 $\times 10^{19}$ n/cm²; temperature 290 °C; in December 1994 in the BR-2 reactor.

The ^{14}C inventory data obtained by the computer simulation will be further refined and compared to experimental ^{14}C measurements.

11.2.6 First carbon speciation experiments

As the first approach, SCK•CEN considered using the available in-house instrumentations to check if carbon species can be detected and quantified. The following techniques are available at SCK•CEN: gas chromatography (GC), high pressure liquid chromatography (HPLC), ion chromatography (IC), total organic analysis (TOC), and for the ^{14}C determination liquid scintillation counting (LSC).

11.2.6.1 Materials and methods

For the preliminary speciation experiments JRQ metal blocks (m $\cong$ 2.3 g, A = 3.2 cm^2) and chips (m $\cong$ 2.0 g) were used. The carbon steel specimens were placed in 20 mL amber coloured vials with a screw cap with septum. For one set of sample a known aliquot of 0.032 M NaOH was added. To another sample de-ionized water was added. Two different electrolytes were used. The first one is identical to the one used for the project experiments (NaOH solution with pH 12-12.5), while the other has a more neutral pH. The reason for using a more neutral pH is to accelerate the corrosion of the metals to increase the carbon species concentration in the solution.

Besides the carbon steel samples, background samples were prepared containing the pure electrolytes only but applying the same type of vials and experimental conditions. We analyzed background solutions prepared and stored in our anaerobic glove boxes and background samples prepared and stored in a regular electrochemical laboratory to see if there is a difference in certain carbon compound levels.

The sample preparation and storage were done in an anaerobic glove box filled with argon and continuous oxygen monitor (MBraun MB 150 B-G, O_2 level < 1 ppm, t~ 25 ^{o}C). Samples were stored for 18 days and then transported for chemical analysis (TOC and IC). The gas phase analysis was not possible due to the unavailability of GC, further maintenance and tests are needed to restart the instrument. The Total Carbon analyzer used was Lachat IL550 TOC-TN with the detection limit of 5 mg/L for carbon.

11.2.6.2 Carbon speciation results

The results from the total organic/inorganic carbon analysis and from the ion chromatographic analysis of the carboxylic acids are presented in Tables 11.4-11.5.

Table 11.4: Results from the total organic and inorganic analysis of the JRQ leachates (mg/L)

Sample ID	Electrolyte/Material	TIC	TOC
BLANK_DW	De-ionized water	< 5	14.1 ± 2.6
BLANK_NaOH	0.032 M NaOH	5.2 ± 2.3	7.6 ± 2.6
BLANK_DW_GB	De-ionized water (glove box)	< 5	< 5
BLANK_NaOH_GB	0.032 M NaOH (glove box)	< 5	< 5
CSP01	Carbon steel (in de-ionized water)	< 5	6.9 ± 2.5
CSP04	Carbon steel (in 0.032 M NaOH)	< 5	8.2 ± 2.5

Table 11.5: Carboxylic acid content of the JRQ leachates and background samples (mg/L)

Sample ID	Electrolyte/Material	acetate	formate	oxalate
CSP01	Carbon steel (in de-ionized water)	**0.36**	**0.13**	< 0.05
CSP04	Carbon steel (in 0.032 M NaOH)	**0.43**	**0.17**	< 0.05
Blank-W-GB	De-ionized water	< 0.025	< 0.05	< 0.05
Blank-S-GB	0.032 M NaOH	0.114	0.075	< 0.05
Blank-W	De-ionized water	3.1	< 0.05	< 0.05
Blank-S	0.032 M NaOH	2.9	3.8	< 0.05

On the basis of the TOC/TIC results it can be seen that some detectable organic carbon was released from the JRQ steel samples at both neutral and alkaline pH. Part of these organic compounds were detected and identified by ionic chromatography as acetate and formate. Analysis of alcohols was planned but the available method did not provide reasonable analytical data yet. In this case method development or refinement is needed.

It has to be mentioned that increased inorganic and organic carbon concentration can be detected in the solutions stored in a regular electrochemical laboratory due to the contamination from the ambient air. Meanwhile solutions prepared and stored in anaerobic atmosphere, values below the detection limits were observed. It shows the importance of electrolyte preparation and storage.

It can be concluded that further method development, system upgrade or investment will be needed to detect more carbon compounds and achieve lower level carbon speciation goals. Some of the concrete steps could be to improve the sample preparation, pre-concentration and detection e.g. using mass spectrometry. Furthermore, if we still fail to detect more carbon species after the improvement, a laboratory with AMS facility will be contacted as a backup option.

11.3 *Meeting participations*

- CAST technical meeting in Brussels-Belgium, (20 October 2014) attended by Viktor Jobbágy; the general assembly meeting in Brussels-Belgium (21 October 2014) attended by Frank Druyts.

- CAST technical meeting and workshop at NAGRA and PSI in Switzerland, (27-29 May 2015) attended by Viktor Jobbágy.

11.4 *Deliverables*

- Contribution to D2.5 (Progress report on year 2).

11.5 *Acknowledgements*

Thanks are due to the following units/people from SCK•CEN for their collaboration:

– Structural Materials: Milan Konstantinovic, Luigi Puzzolante, Rik-Wouter Bosch

– Fuel Materials: Marc Verwerft, Kevin Govers, Rémi Delville

– Microstructural and Non-destructive Analysis: Wouter van Renterghem

– Radiochemical Analysis and Processes: Lesley Adriaensen, Göran Verpoucke, Peter van Bree, Arnaud Campsteyn, Patrick Goethals

– Health Physics: Koen Nijs, Rik Maussen

– R&D Waste Packages: Bruno Kursten, Wim Verwimp, Steven Smets, Ben Gielen and Regina Vercauter

– Mechanical Workshop: Jürgen Verlinden

– Infrastructure Operational Support: Marc Eykmans

– Performance Assessments: Eef Weetjens

– Nuclear Systems Measurements: Antonin Krása

12   VTT contribution to CAST WP2 Second Annual Report

12.1 *Preliminary leaching experiments*

Preliminary leaching experiments with inactive steel materials were finished. The first inactive materials were Loviisa steel, which is identical with the steel components of the core of the Loviisa reactor, and Japanese high carbon steel (see Table 12.). The analyses with optical microscopy and SEM/EDS showed that Loviisa steel has its carbon mainly as interstitial atoms in the austenitic steel lattice. No Fe_3C was observed. In High carbon steel, the main form of carbon is carbide. These two materials were sawed to small fragments with a band saw and purified afterwards with acetone and isopropanol. Simulated groundwater was used as leaching solution in order to simulate the groundwater conditions at the disposal site of Loviisa. The waters included two compositions, with pH of 8.5 and 12.5, respectively. The alkaline pH simulated the effects of cement in the disposal conditions. The batch experiments were conducted in polypropylene vials in a glove box with Ar atmosphere (O_2 less than 1 ppm and low CO_2 content). The ratio of the mass of the solid phase to the volume of the leaching solution was varied. Samples were taken from the leaching solutions after sequential leaching periods for the analyses of the total contents of dissolved organic (DOC) and inorganic carbon (DIC).

Table 12.1: The C and N contents of Loviisa steel and Japanese high carbon steel

	Content (%)	
	C	N_2
Loviisa steel material	0.08	0.008
Japanese high carbon steel	1.2	not analyzed

Relatively high concentrations of dissolved organic carbon (DOC) were measured at the early stages of the experiments (0.9 to 3.3 mmol L^{-1}), see Figure 12.1. Possible contamination of the solid phases by machine oil during the grinding process, or inadequate purification, and their effects on the results could not be excluded. The leachants were replaced with fresh simulated groundwater after the first sampling. Additionally, separate tests revealed that some contamination may originate also from the polycarbonate filtering

medium, which was used in the first sampling. Hence, another filter type (hydrophilic regenerated cellulose) was used in the subsequent samplings. Higher contents were measured for organic than for inorganic carbon in simulated groundwater with both steel materials. The content of inorganic carbon was close to the detection limit in some samples. Due to the uncertainty caused by possible contamination effects, leaching experiments with new solid phases were planned in order to check the results.
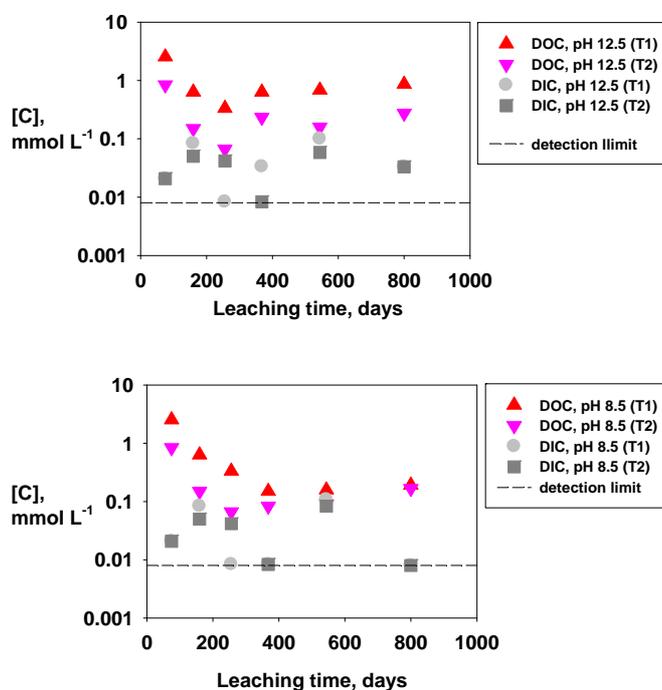
Figure 12.1: Measured contents for dissolved inorganic (DIC) and organic (DOC) carbon in simulated groundwater in the leaching experiments of crushed Loviisa steel (left) and High carbon steel samples (right). T1 represents the tests with m/V=50 g/100 mL and T2 the tests with m/V=25 g/100 mL

12.2 On-going leaching experiments

12.2.1 Steel materials

In on-going leaching experiments unirradiated Fe_3C and AISI316Ti steel powders are being investigated. Because of the difficulties in the grinding process in previous experiments, we decided to prepare the steel powder at VTT. The microstructure of Loviisa steel was

analyzed with optical microscopy, SEM/EDS and XRD and it was shown to be identical with the AISI321 steel (composition reported in [MIBUS *et al.*, 2015], Section 12). The composition of the AISI316Ti steel is otherwise identical except for a lower carbon content. Because of the better availability, AISI316Ti steel powder was acquired as raw material for the preparation of the steel powder. The carbon content was increased using gas atomization method (to 0.3%). The composition and microstructure was checked after atomization and the grain size was adapted to Loviisa steel by heat treatment. A small batch of Fe_3C powder (made from Carajos iron core) was received from a component manufacturer from USA (International Iron Carbide, IIC). Its composition is presented in Table 12.2.

12.2.2 Simulated groundwaters

Simulated groundwaters with similar compositions were used as in earlier leaching experiments (Table 12.3). The basis for the composition was presented in [MIBUS *et al.*, 2015].

12.2.3 Experimental set-up

The experiments with Fe_3C powder as solid phase were started in April 2015 in DURAN® laboratory glass bottles (100, 150 and 250 mL) in the glove box with Ar atmosphere ($O_2 < 1$ ppm, low CO_2). The solid to liquid ratio was varied as follows: 20g/80mL, 50g/100mL and 20g/200mL. The experiments with AISI316Ti powder were started in June 2015. One ratio of solid to liquid (100g/200mL) was applied and three parallel tests were started.

The experiments in anaerobic media bottles (100 mL) with septum stoppers will be started in August 2015. These experiments aim at analyzing the gas and liquid phases to determine the quantity and quality of carbon compounds.

12.2.4 Sampling and carbon-12 analyses

The total amounts of dissolved organic carbon (DOC) and inorganic carbon (DIC) are determined from the solution phase after sequential leaching periods. The first samplings for the Fe_3C experiments were done after the leaching time of 20 days and for the AISI316Ti

experiments after 48 days. The samples were prepared by first rinsing the filters (Whatman® GD/X syringe filters, glass microfiber membrane, pore size 0.45 µm) twice with 10 mL Milli-Q water and then filtering 10 mL of leachate in 50 mL DURAN® glass bottle. Due to the high salinity of the samples they were diluted to a total volume of 50 mL with Milli-Q water. In order to keep a constant m/V ratio in the experiments, 10 mL fresh leaching solution was added to the leaching solutions after the samplings. DIC and DOC analyses were done by Ramboll analytics with a TOC analyzer (Analytika Jena N/C UV HS) as in the preliminary experiments [MIBUS *et al.*, 2015]. Analyses for organic carbon compounds in liquid phase will be done by VTT Expert Services Oy. The aim is to analyze volatile organic compounds (VOCs) with an HS-GC-FID/MS instrument using headspace technique with gas chromatography (flame ionization detector or mass spectrometry). Headspace analysis is a technique to separate and collect volatile compounds (in the gas phase) from different sample matrices such as water. The gas phase is sampled and injected directly into the GC equipment and detected with FID or MS [CAVALCANTE *et al.,* 2010]. ESI-MS/MS (electrospray ionization tandem mass spectrometry) or LC-MS/MS (liquid chromatography tandem mass spectrometry) are used for qualitative analysis of polar molecules sharing similar structures, like different acids.

12.2.5 Results

The total amounts of dissolved organic (DOC) and inorganic carbon (DIC), which were determined in the leaching solutions of Fe_3C (20 days) and of AISI316Ti (48 days) at both pH 8.5 and 12.5, are given in Table 12.4. The results show that the contents of dissolved organic carbon are higher in the leaching solutions in Fe_3C experiments. In AISI316Ti steel tests, the contents of organic and inorganic carbon are rather similar. Compared to the results of the preliminary experiments, the initial contents of organic carbon are lower. This confirms our assumption that the contamination of the samples from the filter material in the first samplings, and/or the contamination of the solid phase from the grinding process have occurred in the preliminary experiments. A higher solid to solution ratio (m/V) results in a higher amount of dissolved carbon, which is expected. The effect of the initial pH of the leaching solutions is minor at the initial stage of the tests.

Table 12.2: Composition of Iron carbide powder

Components	Wt%
Fe_3C	92.4
Fe	3.2
Fe_3O_4	3.4
SiO_2	0.58
Al_2O_3	0.31

Chem analysis: 91.9% Fe, 6.3% C

Table 12.3: Compositions for simulated groundwaters

Solution	*pH*	Na^+	Ca^{2+}	K^+	HCO_3^-	SO_4^{2-}	Cl^-	Br^-
CA85	*8.5*	2680	630	25	-	560	4840	18
CA125	*12.5*	2200	500	25	-	560	4040	18
HC125	*12.5*	3440	-	25	104	560	4840	18

Table 12.4: DOC and DIC results

Solid material		DOC mmol L^{-1}		DIC mmol L^{-1}	
	m/V Ratio (gmL^{-1})	*pH 8.5*	*pH 12.5*	*pH 8.5*	*pH 12.5*
Fe_3C	20/200	0.02	0.03	BDL	BDL
	20/80	0.27	0.36	BDL	BDL
	50/100	0.53	0.90	BDL	0.11
AISI316Ti	100/200	0.14	0.13	BDL	0.05

* Initial pH in the leaching solution

12.3 *Plans for experiments with activated steel*

There are two options:

1. Stainless steel samples from low-active core grid are available from Teollisuuden Voima Oyj. This option needs the arrangements for the transport of the samples from Olkiluoto to VTT's laboratory at Otaniemi, Espoo.

2. Surveillance capsule material seems also to be a suitable steel test material for the experiments. This option emerged since a new capsule chain will arrive late 2015 (or early 2016) to VTT Nuclear Reactor Materials team for testing. It is possible to cut samples for ^{14}C leaching experiments from the capsule material. No separate

Cross-section

SC =surveilance capsule

Radiation specimen chain

A sawed sample for the leaching
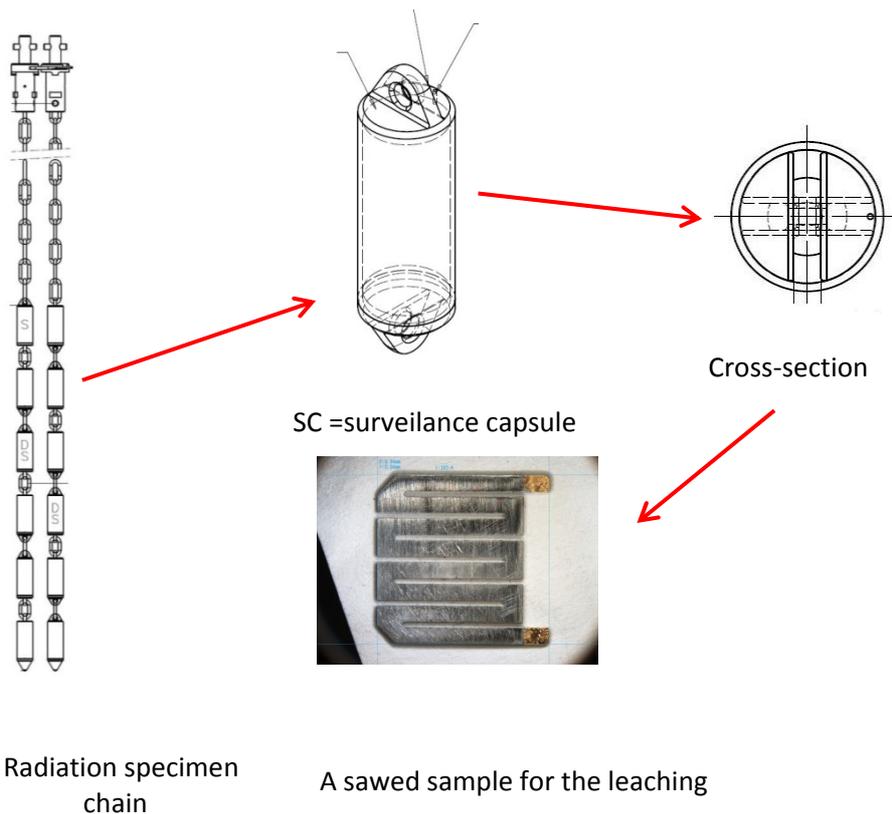
arrangements for transport are needed in this option (Figure 12.2).

Figure 12.2: Schematic drawing of the surveillance capsule (Pictures by Fortum Power and Heat Oy)

These surveillance capsules with the samples of pressure vessel steel and the samples for dosimetry have been used to determine the irradiation embrittlement of the pressure vessel during the operation of the Loviisa reactor. The analytical data for the composition of the capsule material (stainless steel) is available and could be used in our experiments. The nitrogen content will be analyzed for inactive capsule steel. From the initial composition and irradiation history, the theoretical maximum ^{14}C content after exposure can be calculated.

13   Conclusions

In the second project year (October 2014 to September 2015), the development of analytical methods to identify and quantify the speciation of ^{14}C in liquid and gaseous samples at extremely low concentrations has been finalized. It is, however, open to further refinements. In several technical meetings, agreement upon the design of the corrosion experiments and the pre-treatment of the sample material has been achieved. The experimental and analytical equipment are currently being set up and tested in the majority of the laboratories involved. Samples of activated steel are available or, in one case, expected to arrive soon.

In the third project year (October 2015 to September 2016), the corrosion experiments will be launched and the release and speciation of ^{14}C will be measured.

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