CArbon-14 Source Term

CAST

WP2 Annual Progress Report - Year 1 (D2.2)

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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 1 (D2.2)

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 first project year the participants were mainly engaged in Task 2.1 and 2.2 and preparing Task 2.3.

The literature review was carried out by AMEC with support from all participants. It deals with steel corrosion mechanisms and rates as well as the speciation of carbon (stable isotopes and ^{14}C) in iron and steel after release due to corrosion. The review covers the open literature but includes also information from scientific reports especially those provided by the participants. The results of the review, documented in a state-of-the-art report as deliverable D2.1, provide a basis for the experimental design and the interpretation of the results. The review gives a comprehensive compilation of corrosion rates under conditions relevant for a cement-based deep repository. Much less information is available on the speciation of ^{14}C after release from activated steel. Nonetheless, from the possible chemical form of carbon in the steel, a range of aqueous and gaseous compounds can be expected as

^{14}C carrier. However, the results of experiments reported in the literature altogether appear not conclusive.

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 started early in the project as this is an extensive task and the methods to be developed are essential for the further experimental work. This task is done by PSI and Armines in close cooperation with the partners from WP3. In the first project year, experiments with non-irradiated iron samples have been performed to develop analytical strategies for sampling, separation and quantification of possible ^{14}C species. They are complemented by stability tests of organic molecules in highly alkaline solutions. The focus was put on low molecular weight organic substances. For their separation and identification, 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.

Further, the participants involved in the corrosion experiments to measure the release and speciation of ^{14}C started to plan and coordinate the experimental design and the conditions. It is foreseen to use irradiated carbon steel and different grade stainless steel samples, but also non irradiated iron and carbide material. The leaching solution should simulate the expected conditions in a cement based deep repository. A deaerated portlandite ($Ca(OH)_2$) solution of pH 12.5 has been proposed as reference solution. The final composition is, however, subject to further thermodynamic calculations to avoid a potential precipitation of ^{14}C species. In some experiments, pH and oxygen access will be varied to cover a range of conditions and to facilitate process understanding. It has been decided that instead of pre-treating the samples, a thorough characterization of the samples shall document the actual status before and, if possible, after the experiments.

During the first project year, a Technical Meeting was held in the frame of the Kick-off Meeting on 25 – 26 November 2013 in London. A common Technical Meeting with WP3 was organized by Andra on 1 – 2 July 2014 in Paris. Two deliverables were planned in the first project year. An advanced draft of the state-of-the-art report (D2.1) has been available, whereas this annual report (D2.2) was still in progress at the end of the reporting period.

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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 (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. At this point, a comment is placed to avoid any confusion about the leaching solutions. A portlandite ($Ca(OH)_2$) solution of pH ca. 12.5 has been proposed as leachant for the experiments as it is considered relevant for a cement based repository over long time periods. Later thermodynamic calculations showed that the high calcium content might cause the precipitation of solids containing ^{14}C species (e.g., carbonate, oxalate) thus depleting the solution in the species aimed at. Consequently, a NaOH solution of a similar pH was proposed. This change, however, is not reflected in the contributions that were composed earlier.

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 first project year (October 2013 to September 2014). The report is edited by Nagra and contains contributions from all participants. In addition to the authors mentioned, A. Abdelouas, C. Landesman (Armines), E. González-Robles, V. Metz, B. Kienzler (KIT), E. Wieland (PSI), P. Goethals, B. Kursten, F. Druyts (SCK•CEN) and K. Ollila (VTT) made contributions.

2 AMEC contribution to CAST WP2 First Annual Report

2.1 *Introduction*

During Year 1 of the CAST project, AMEC has undertaken a state of the art review of the understanding of steel corrosion rates and carbon-14 releases from irradiated steels under conditions relevant to the storage and long term disposal of radioactive wastes. The overall objective of this task has been to incorporate information available from outside the CAST project into CAST WP2. This information can be used in two ways:

- to support the design of the experimental programme planned under WP2; and
- to support the assessment of the potential radiological impact of carbon-14 released from steel wastes during storage, disposal operations and after closure of a disposal facility (under WP6).

The results of the review have been presented in a project report [SWANTON *et al.* 2015] which forms Deliverable D2.1 of the CAST project. The findings were also presented to WP2 participants at a joint WP2&3 workshop hosted by ANDRA on 1-2 July 2014.

In the following sub-sections, the sources of information drawn upon, and the key findings of the review concerning steel corrosion rates and the release of carbon (stable carbon-12 and carbon-13) and carbon-14 from steels are outlined.

2.2 *Sources of information*

The information provided in the review was drawn from the following main sources:

- an existing data review of carbon steel, stainless steel and Zircaloy corrosion rates that was last updated for NDA RWMD (now RWM) by Serco (now AMEC) in 2006 (and published in 2010) [SMART and HOCH 2010];
- recent reviews on the corrosion behaviour of different types of steels being considered as container materials in national radioactive waste programmes [e.g. SMART 2009];

- a number of recent documents on the topic of carbon-14 from national programmes [JOHNSON and SCHWYN 2008, WIELAND and HUMMEL 2010, NDA 2012, HEIKOLA 2014] and references therein concerned with the chemical forms of carbons in steel and the speciation of carbon and carbon-14 releases;
- an extensive literature search for new corrosion data carried out in two major bibliographic databases: INIS and Corrosion Abstracts for publications from 2006 to early 2014;
- the Dechema corrosion handbooks [DECHEMA 1987-1992] also contained useful bibliographies, as did a number of standard text books and reviews;
- Some additional draft documents and information was provided by partners in WP2 for inclusion in the review.

2.3 *Corrosion rates of steel*

The review of corrosion data has extended a previous compilation of data for carbon and stainless steels, undertaken in 2006/07 [SMART and HOCH 2010], to include new information in the published literature as well as recent information, some of it as yet unpublished, from national programmes supplied by partners in WP2. The review identified the various environments that could be experienced by waste packages containing cement-encapsulated irradiated metal wastes during their long-term management (i.e. during surface storage and transportation, and then in a geological disposal facility (GDF), both before and after resaturation with a groundwater that could have a high chloride concentration). For each environment, relevant corrosion rate data for carbon steel and stainless steels has been compiled and reviewed critically. The literature review has focussed on metal loss and gas generation as a result of general corrosion rather than localized corrosion. The effects of a number of variables (including oxygen concentration, temperature and chloride concentration) on corrosion rates have been considered.

Although, a number of additional datasets have been identified and summarized in this review, in general, they have not changed the view of the likely corrosion rates for carbon steel and stainless steel in the conditions expected during waste disposal, developed previously [i.e. in SMART and HOCH 2010]. However, a recent paper by YOSHIDA *et al.*

[2013] has provided data for the very low corrosion rates experienced by stainless steels under anoxic alkaline conditions, and these results are important in relation to the issue of carbon-14 release from stainless steels in the longer term in the post-closure phase of a GDF. The data are all below 0.01 μmyr^{-1} which was the value recommended as an upper limit in the previous review. The new data indicate a mean anaerobic corrosion rate of 0.0008 μmyr^{-1} for 18/8 stainless steel at 30°C after two years exposure. The Japanese data also show a decrease of the anaerobic corrosion rate under alkaline conditions with time (the significance of which is not yet clear), and a temperature dependence, neither of which could be discriminated previously.

It is noted that all of the corrosion data compiled in this review was obtained for unirradiated materials. It is known that neutron irradiation can change the microstructure of steels, in particular radiation-induced segregation of alloy components can arise at grain boundaries [WAS, 2007]. However, the overall impact of irradiation on the long-term corrosion rates of waste steels is unknown.

2.4 *Carbon and carbon-14 releases from irons and steels*

The current understanding of carbon (stable carbon-12 and carbon-13) and carbon-14 releases from irons and steels can be summarized as follows.

- There is uncertainty concerning speciation of carbon-14 derived from neutron activation compared with carbon in steels and thus uncertainty concerning the speciation (e.g. CH_4, CO_2, CO, C_2H_2) of carbon-14 releases from irradiated materials compared with carbon-12 and carbon-13. It is possible that the carbon-14 may be present as interstitial carbide dissolved in the steel, as distinct metal carbide phases (ionic or intermediate carbides) or as carbonitride phases dependent on the steel composition.
- On the basis of the known information on the reactions of metal carbides and carbonitrides, the following carbon-14 release behaviour might be expected on leaching an irradiated steel. As the steel slowly corrodes, the carbon-14 in its different forms will be exposed to the waste disposal environment. Different forms of carbon-14 may be expected to be released in different ways.

- Ionic and intermediate carbides and interstitial carbon present in the iron phase may be hydrolysed over relatively short time periods to form methane, and other hydrocarbons.
- Intermediate carbonitrides may be hydrolysed at a much slower rate than the equivalent carbides to yield a range of products that may include hydrocarbons and compounds containing C-N bonds such as amines and cyanides.
- Stable carbides and carbonitrides may react only very slowly (if at all) and be released in particulate form.

- There is little published information on the release of stable carbon from irons and steels and some of the findings of studies to date are apparently contradictory.
- Experiments on inactive iron-water systems have shown clear evidence for the release of carbon as hydrocarbon species as a result of the hydrolysis of carbide species in the iron [DENG *et al*. 1997]. A variety of species ranging from C1 to C5 hydrocarbons have been identified in the gas phase in separate studies, and quantitative conversion of carbide carbon to hydrocarbons has been reported. The mechanism of hydrocarbon formation is proposed to occur through processes similar to those that occur in Fischer-Tropsch (FT) synthesis, it is suggested that the carbide species exposed at the iron surface may be similar to the intermediates formed on the surfaces of metal catalysts in the FT synthesis.
- In contrast, in Japanese experiments on inactive carbon steel and iron carbide [KANEKO *et al*. 2003, SASOH 2008], which focussed on releases to the solution phase, carbon releases were presented as arising primarily as water soluble organic species, although some of the carbon in solution was found to be inorganic. A range of low-molecular weight organic species were identified on the basis of HPLC, although these identifications must be treated as tentative. Carbon-14 releases from iron carbide were identified as both inorganic and organic, which appears to be at odds with the results of iron-water studies. These findings remain to be corroborated.
- A proper evaluation of the limited information available on studies of carbon-14 releases from irradiated stainless steels performed in Japan [KOGAWA, 2008, MIYAUCHI *et al*. 2011] is hindered by the lack of reports available in English

providing sufficient details of the materials and the experimental methodologies used. In the most recent experiment reported, a small amount of carbon-14 was reported to be released to the gas phase on leaching irradiated stainless steel in alkaline solution for 42 months; the distribution of the 4.76 Bq released was reported to be 25% to the gas phase with a ratio of organic to inorganic carbon-14 in the solution of nearly one. Dissolved organic species were reported to be predominantly in anionic forms (i.e. carboxylates) rather than neutral species (e.g. alcohols). Again, these findings require corroboration.

- In experiments with irradiated metals (steel, nickel alloy and Zircaloy) where the sample was first acid-cleaned to remove the passivating oxide film, carbon-14 is reported to be released from the irradiated metal into solution at rates that are consistent with metal corrosion rates [KOGAWA, 2008]. Again, these findings require corroboration.

3 Armines contribution to CAST WP2 First Annual Report

The objective of this task is to develop analytical methods to analyze the organic carbon compounds released from irradiated steel containing ^{14}C. It is closely linked with the work in WP3.

3.1 *Materials and methods*

To reach the aim of this work, the definition of the leaching conditions needs to reflect those existing in storage conditions which could be defined as follow (Figure 3.1):

- dissolution of alkali hydroxides, pH ~13.5
- dissolution controlled by the portlandite $Ca(OH)_2$ phase, pH ~12.5
- dissolution of hydrated calcium silicate phases C-S-H, pH from 12.5 to 9
- dissolution of silica

During the kick-off meeting (25-26 Nov 2013), the round table discussion reached to the conclusion that from an analytical point of view and to represent the long term storage of the wastes, the leaching conditions in portlandite water at pH ~12.5 would be used. Moreover, during the meeting of the 1st-2nd of July 2014, the experimental setups (type of samples, type of solution, duration of experiments…) were discussed. At the end of the meeting, the leaching conditions in portlandite were confirmed.

The general procedure to determine the speciation of ^{14}C we propose, is presented in Figure 3.2. The method is based on the measurement of the leaching solution in contact with irradiated steel by gamma spectrometry in order to assess the activity level and to identify the radionuclides. The solution containing inorganic and organic carbon will be separated by acidification. The solution containing only organic compounds will be analyzed by HPLC (or ionic chromatography) and by liquid scintillation.

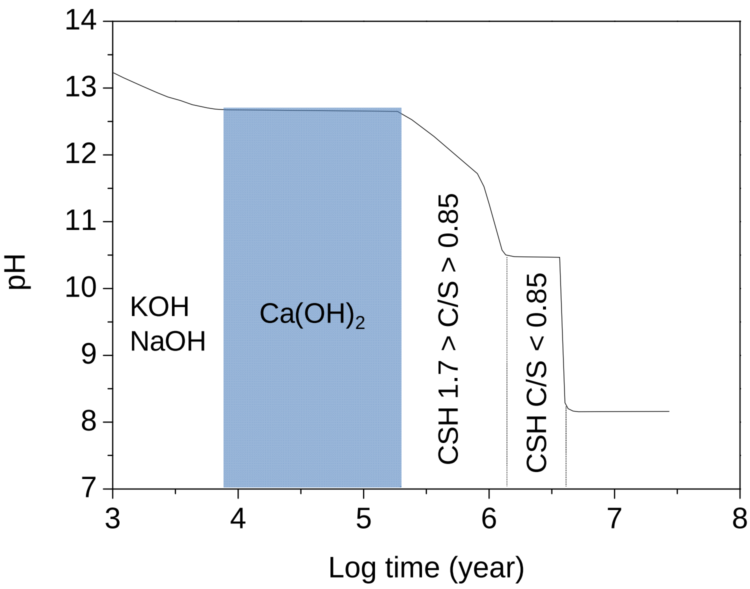


Figure 3.1: Evolution of pH as a function of time in the reference case repository from [Atkinson et al., 1985]

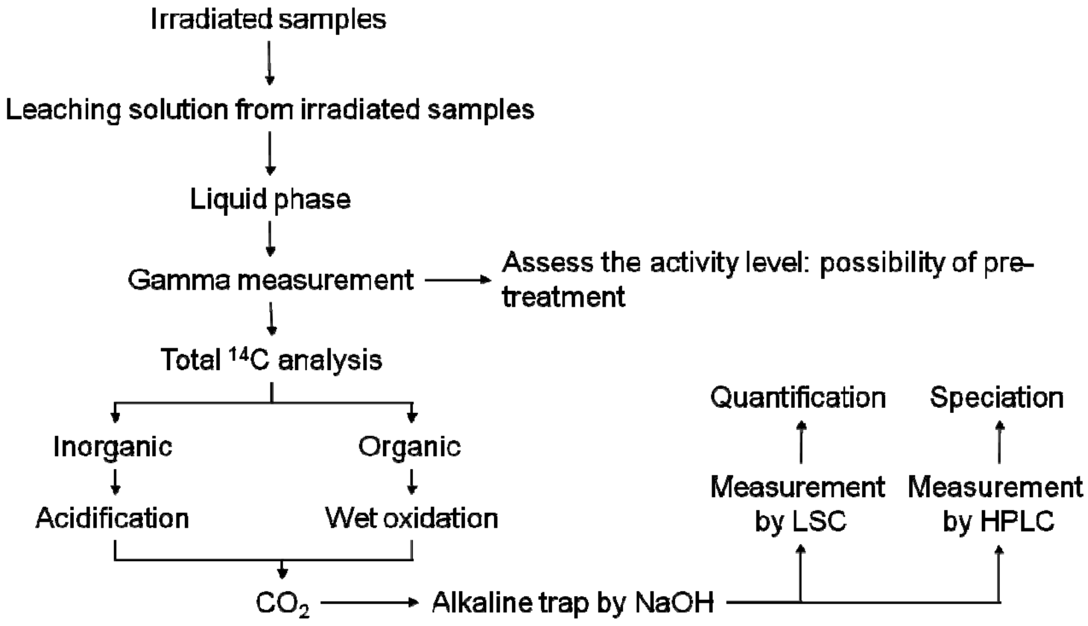


Figure 3.2: Experimental setup for the determination of Carbon-14 species

3.2 First results

An experimental procedure was set up for the speciation of the organic carbon compounds. As very low carbon chains of molecules are expected, six sets of molecules were selected (acetate, formate, propionate, oxalate, valerate and butyrate) and separated with a DIONEX Thermo electron AS11-HC 4 mm-column specifically designed for the separation of inorganic anions and organic acid anions. We used a gradient (1 – 30 mM in 29 min) of KOH eluant to increase the separation of molecules, in particular for the formate and propionate which co-elute.

At this stage, the stability tests of the six sets of organic molecules were prepared in two types of solutions NaOH (pH 12) and $Ca(OH)_2$ (pH 12.5) to assess the effect of pH or the effect of matrix. All experiments were prepared in a glove box (Ar gas). From the first results shown in Figure 3.3 we note that the stability of acetate, formate, propionate and oxalate depends on their concentration and the matrix composition:

- Oxalate is the molecule which is not influenced by their concentration and the matrix composition. It exists under all conditions.
- The presence of acetate and formate depends on their concentration but are not influenced by the matrix composition.
    - Absence of detection for concentration in acetate below 300 ppb.
    - Absence of detection for concentration in formate below 100 ppb.
- The presence of propionate depends on its concentration and the matrix composition.
    - Absence of detection for concentration below 300 ppb in $Ca(OH)_2$ and below 100 ppb in NaOH.

Thus, the results indicate that in portlandite solution oxalate is the most stable molecule and may exist at low concentration.

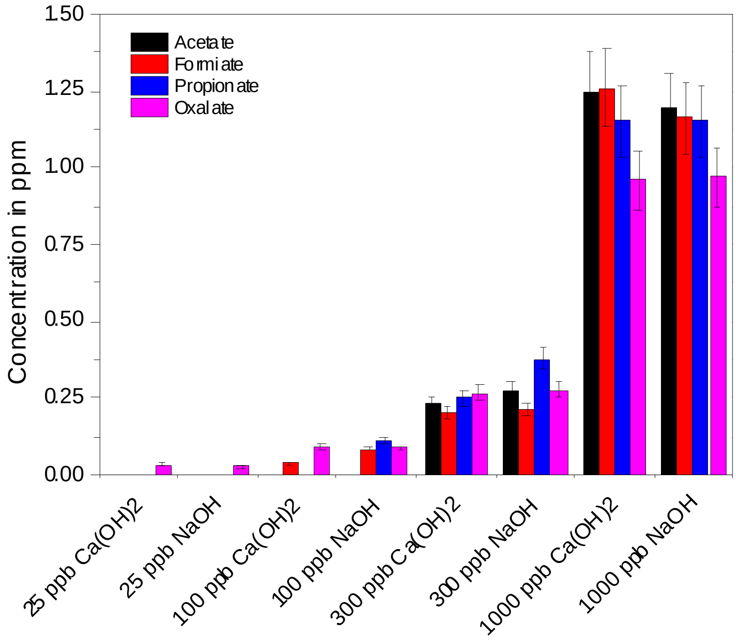


Figure 3.3: Evolution of acetate, formiate, propionate and oxalate at different concentration of $Ca(OH)_2$ and NaOH solutions (25, 100, 300 and 1000 ppb)

Complementary analyses were performed on the stability of these molecules with time. The same set of organic molecules were analyzed after 1 min, 6 hours and 24 hours in $Ca(OH)_2$ solution. The results indicate that only for the case of oxalate, the concentration in solution decreases by a factor of 2 indicating a possible precipitation with calcium. Evolution of organic molecules may occur in solution as it has been observed by Yamashita et al. but these results should be confirmed by complementary analyses [Yamashita et al., 2014].

4 Ciemat contribution to CAST WP2 First Annual Report

From October 2013 until July 2014 different preliminary studies have been performed to prepare the leaching experiments on activated stainless steel from reactor internals of José Cabrera NPP in which CIEMAT is involved.

4.1 *Test material*

Different aspects of material which will be used have been studied.

4.1.1 Chemical composition

The chemical composition of the steel of some pieces that surround the reactor was determined by Enresa. The data obtained are shown in Table 4.1.

Table 4.1: Chemical composition of stainless steel used in NPP

Element	Concentration (% weight)	Absolute Uncertainty	Detection Limit
Si	0.97	0.07	0.07
S	0.22	0.04	0.04
Cr	18.6	0.5	0.03
Mn	2.27	0.11	0.16
Fe	65.4	1.9	0.04
Ni	7.14	0.23	0.02
Cu	0.47	0.04	0.03
Mo	0.45	0.05	0.03

Element	Detection Limit (% weight)
Al	0.13
P	0.14
Ti	0.05
V	0.04
Co	0.3
W	0.2
Pb	0.02

It is assumed that the stainless steel of upper internals, in particular SS 304, has a similar composition. Enresa is trying to prepare a sample from reactor internals to determine its chemical composition. Anyway, the nitrogen content, the main element which produces ^{14}C, of the stainless steel will be very difficult to determine due to the limitations of the technique that is used.

4.1.2 Activation history

The following information has been obtained from the NPP:

1. José Cabrera NPP was operated from 30/06/1968 to 30/04/2006, that means a total of 13818 days, with 29 cycles of operation.
2. The load factor accumulated during the operational life of the plant is the 70.97%.
3. Therefore, the days of irradiation, obtained by multiplying the number of days that the core has been in operation (13818 days) by the load factor, was 9807.
4. The degree of maximum spent fuel burning was 45000 MWd/tU and enrichment at least 3.15% in weight of ^{235}U.
5. Finally, the composition was calculated allowing for decay to a reference date of 01/07/2011.

With this information and using the Origen-S the radiochemical composition of the samples has been obtained. The data, expressed as a fraction of the ^{60}Co content, are shown in Table 4.2.

Table 4.2: Radiochemical composition of stainless steel as a fraction of ^{60}Co (modelled values with Origen-S for reference date 01/07/2011)

Isotope	/^{60}Co	Isotope	/^{60}Co	Isotope	/^{60}Co
^{3}H	1.45E-03	^{154}Eu	1.13E-04	^{93}Mo	1.29E-05
^{36}Cl	6.42E-06	^{178m}Hf	5.87E-25	^{125}Sb	1.85E-08
^{41}Ca	5.56E-08	^{90}Sr	1.59E-06	^{135}Cs	4.09E-11
^{54}Mn	9.39E-03	^{99}Tc	4.64E-07	^{155}Eu	5.14E-06
^{55}Fe	1.13E00	^{133}Ba	2.58E-08	^{233}U	3.25E-15
^{59}Ni	2.36E-03	^{134}Cs	2.21E-04	^{238}Pu	1.95E-09
^{60}Co	1.00E00	^{137}Cs	1.89E-06	^{239}Pu	1.50E-07
^{63}Ni	2.57E-01	^{151}Sm	5.92E-06	^{214}Am	1.43E-09
^{94}Nb	9.13E-06	^{166m}Ho	2.92E-06	^{244}Cm	8.10E-14
^{110m}Ag	1.82E-05	**^{14}C**	**6.77E-04**		
^{152}Eu	2.66E-04	^{39}Ar	1.39E-06		

The theoretical value corresponding to ^{14}C has been highlighted. These values will be compared with the experimental results.

4.2 Sample preparation

At present, the method of cutting the pieces from upper internals, prepared by Enresa, is being defined. In particular the guide tubes and support column will be cut to use them for the leaching tests.

The pieces (5 cm x 20 cm), which arrived on April 9, 2014 to our laboratories, are shown in Figure 4.1.

Figure 4.1: Cut out pieces (size 5 x 20 cm) from upper internal (guide tubes and support column)

Although these samples are stored properly in CIEMAT, due to its activity and as consequence of the dose rate limitations in our facilities (not exceeding 0.01 mSv/h in working areas), the samples are not in our laboratories. The radiological data of the samples are indicated in Table 4.3.

Table 4.3: Radiological data of the samples from upper internals

SAMPLES	Contact Dose Rate (mSv/h)	1 Meter Dose Rate (mSv/h)	Co-60 (MBq)
Sample 1 (Guide Tube)	2.12	0.24	7.1
Sample 2 (Guide Tube)	**6.6**	0.59	**22.0**
Sample 3 (Guide Tube)	2.5	0.23	8.3
Sample 4 (Support Column)	1.1	0.10	3.7

Therefore, in order to work with these pieces, the samples must be cut into smaller pieces. In order to do that, a cutting machine has been acquired by our group. The procedure for cutting and transferring the samples to our laboratories was finished at the end of September 2014. The cutting of samples of stainless steel will be performed once the procedure for cutting is accepted by the Safety Department of CIEMAT.

4.3 Characterization of initial sample

In order to carry out the characterization of initial sample, a process based on the dissolution of the stainless steel by HCl and HNO_3 is going to be developed during the next months.

The gaseous phase (CO_2) formed will be trapped with $Ba(OH)_2$ and measured by Liquid Scintillation Counters (LSC) (Quantulus). The liquid phase (CO_3^{2-}) will be acidified and gas formed trapped with $Ba(OH)_2$ and measured by LSC (Quantulus).

If it was not possible to determine ^{14}C by LSC, the samples will be sent to the National Center of Accelerators, located in Seville, to be analyzed by Accelerator Mass Spectrometry (AMS).

4.4 Leaching process and speciation

During the next three months the leaching experiments which permit to analyze gas and liquid phase will be designed.

Regarding these experiments, finally it was decided to carry out the aerobic leaching tests in the following media:

- $Ca(OH)_2$ solution at pH 12.5
- Acid medium

From leaching process two phases (liquid and gaseous) will be obtained. In these phases ^{14}C will be analyzed (by LSC or by AMS) and different organic and inorganic carbon compounds which are formed as a consequence of the presence of carbides in the steel. The reaction of some carbides with water can lead to the formation of volatile species such as methane, ethane, propane and dissolved species such as carboxylic acids and carbonates.

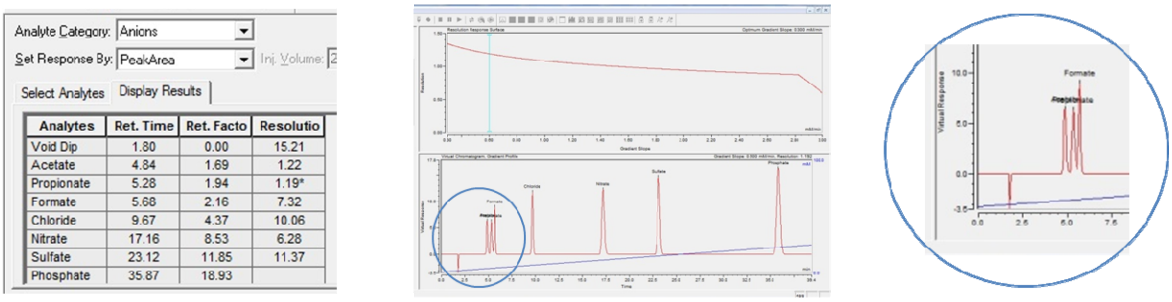
The volatile species will be measured with Gas Chromatography coupled with Mass Spectrometry and the dissolved species, in particular carboxylic acids by ion chromatography. The way of performing the analysis of carbonates is under study.

For the analysis of volatile species, at present, all necessary equipment is purchased such as the GCMS 7890B (Figure 4.2). It is foreseen that at the end of 2014 or in the first trimester of 2015 it may be possible to work with the equipment.

Figure 4.2: GCMS 7890B equipment

If the instrument is not in our laboratories or it has been not possible to make the set-up of the equipment, Ciemat will contact the Mass Spectrometry Center of Complutense University to make use of the equipment.

For the analysis in the dissolved species of carboxylic acids by ion chromatography it is necessary to adapt the ion chromatograph available in our laboratories by adding a device named "Reagent Free Controller (RFC)" which permits bringing gradient capabilities to the isocratic system. In this way it is possible to analyze short chain carboxylic acids with the AS11-HC column. In Figure 4.3 an example of the detection of some carboxylic acids by ion chromatography is shown.



Analyte Category: Anions
Set Response By: PeakArea
Inj. Volume:

Analytes	Ret. Time	Ret. Facto	Resolutio
Void Dip	1.80	0.00	15.21
Acetate	4.84	1.69	1.22
Propionate	5.28	1.94	1.19*
Formate	5.68	2.16	7.32
Chloride	9.67	4.37	10.06
Nitrate	17.16	8.53	6.28
Sulfate	23.12	11.85	11.37
Phosphate	35.87	18.93	

Figure 4.3: Carboxylic acids Chromatogram

The documentation to carry out this adaptation has been prepared and it is foreseen that the new equipment is available for the end of 2014.

5 ENRESA contribution to CAST WP2 First Annual Report

5.1 *Scope of the test*

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

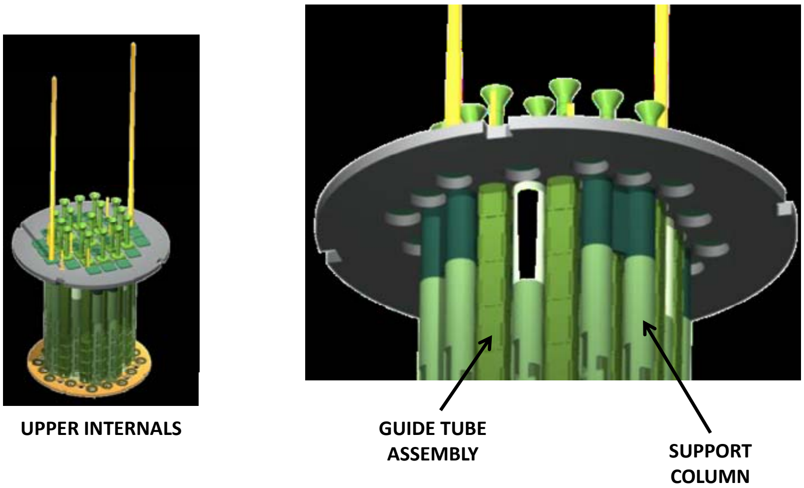


Figure 5.1: Origin of the piece

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 upper internal cutting process 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.

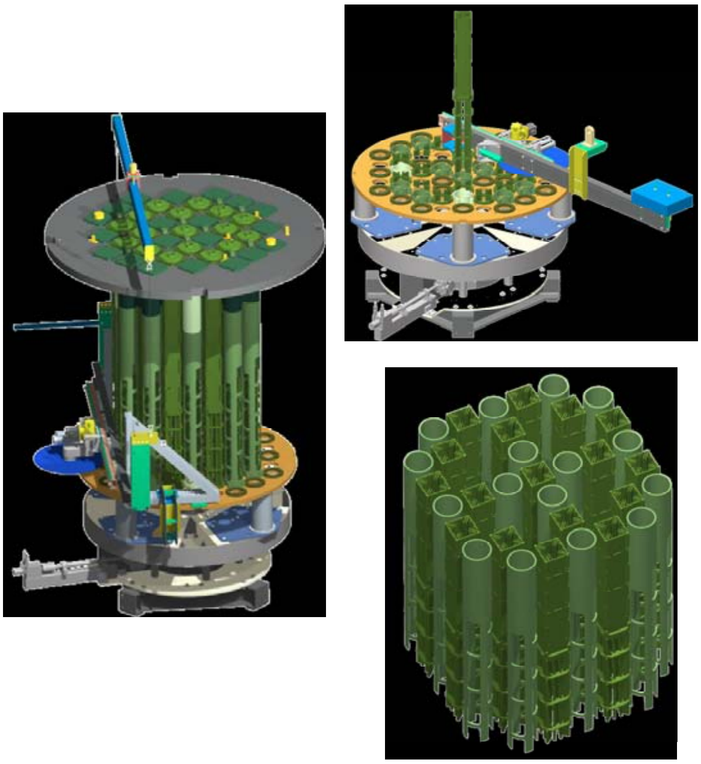
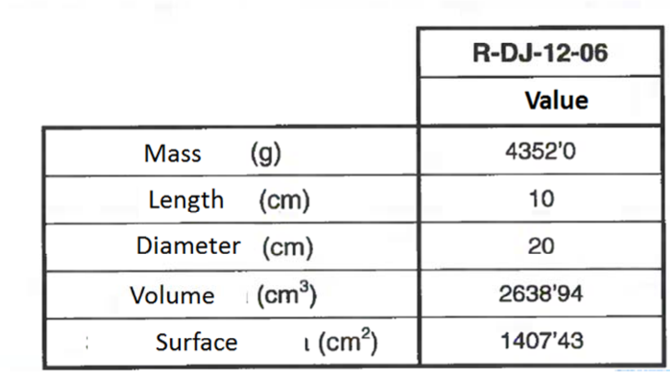


Figure 5.2: Cutting description

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

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

Table 5.1: Sample characteristics

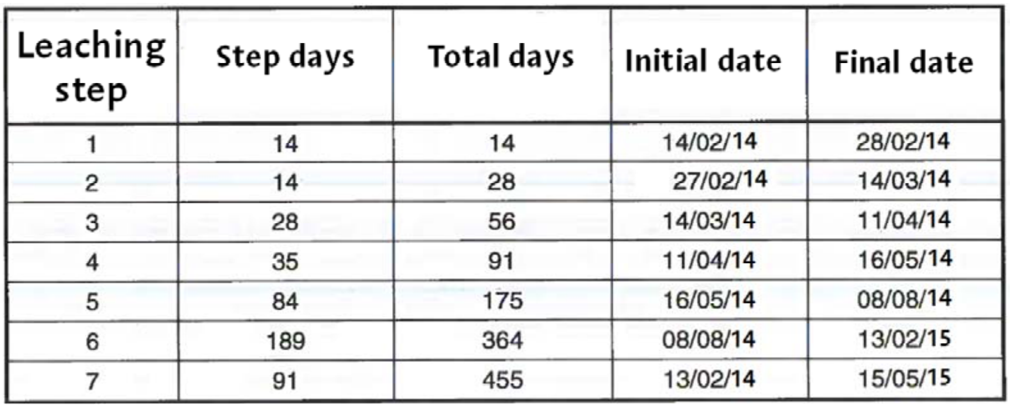


	R-DJ-12-06
	Value
Mass (g)	4352'0
Length (cm)	10
Diameter (cm)	20
Volume (cm^3)	2638'94
Surface (cm^2)	1407'43

5.3 *Test description*

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

Table 5.2: Planned 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

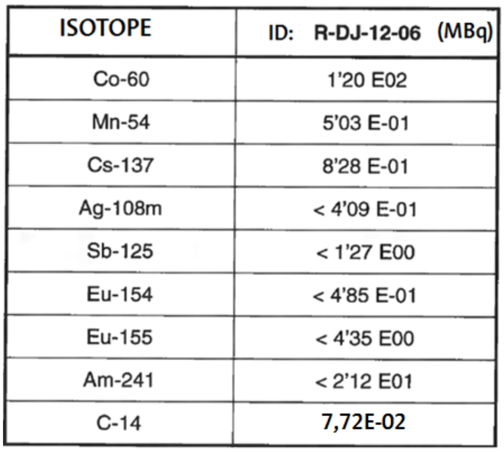
The leachant characteristics are the following:

- pH=7±1
- TOC < 3 ppm
- Conductivity σ < 5 µS/cm
- Temperature =20 ± 3 °C

5.4 Preliminary results

Up to now four steps have been finalized, the transitory period of 91 days, after which the leaching rate is normally calculated.

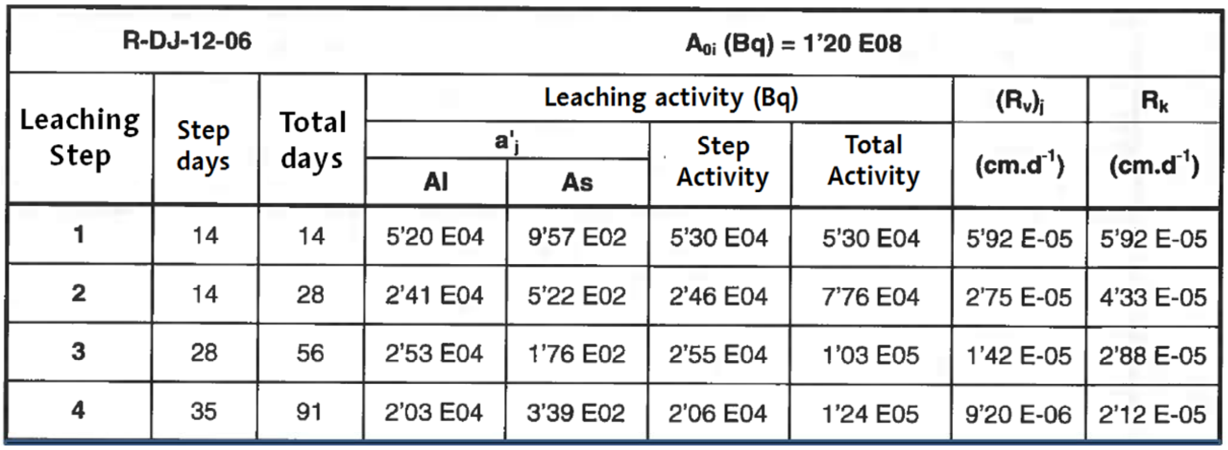
Table 5.3: Initial activity of the piece



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**

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

Table 5.4: Leached activity in addition to the leaching rate for each step and the accumulated one for ^{60}Co



R-DJ-12-06			A_{0i} (Bq) = 1'20 E08					
Leaching Step	Step days	Total days	Leaching activity (Bq)				$(R_v)_j$	R_k
			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

Aoi: 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', which comprises of the solid phase activity, 'As', and the liquid one, 'Al'

$(R_v)_j$: Mean speed of release for radionuclide 'i' in step 'j'

R_k: Mean accumulated speed of release up to step 'j' for radionuclide 'i'

Total activity is the released, accumulated activity up to step 'j'.

Similar behaviour of the release trend has been observed for other activated isotopes, but no ^{14}C activity has been detected above detection limit ranging between 0.03 and 0.06 Bq/g, therefore further AMS analysis will be performed in the current and future steps of the test.

The test will finalize in the first half of 2015, and a completed and detailed report will be developed for the next summary period report of 2015.

6 JRC-ITU contribution to CAST WP2 First Annual Report

6.1 *Selection & preparation of cladding samples*

The steel cladding material is 15-15-Ti stainless steel cladding from a breeder reactor fuel project NIMPHE-2, a (U,Pu)C fuel with approx. 25%Pu content and 55GWd/tHM burn-up. The fuel was irradiated in Phenix reactor. Samples will be 5mm rings or half-rings of the cladding taken from the upper end of the fuel column: some samples will also be cut from the maximum power position close the centre of the pin. The samples containing fuel will have the fuel removed by pressing out followed by HNO_3 dissolution for removal of the remaining fuel and try to determine the ^{14}C content in both metal and oxide. The cladding rings may also be treated to see if it is possible to remove the oxide layers. Cutting plans have been prepared and the cutting was completed in early 2015. Some metallography of NIMPHE 2 cladding is available from previous studies.

One sample will be mounted for metallography, other samples will be used for total C content determination. The remainder will go for leach testing in the autoclave. Any excess samples will be retained for future repeat testing.

6.2 *Preparation of equipment*

6.2.1 Total C content determination

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

concentration is then measured directly by IR absorption for known sample weight. This yields the total C concentration. The induction heating furnace will be sited in the hot cell, while the analytical section will be located in an airtight unit attached next to the hot cell. The purge gas carrying the CO_2 from the oxidized sample will be passed over the measurement IR spectroscopy for on-line and accumulated CO_2 content, before passing back to the hot cells. It is intended to install a unit for a molecular sieve capsule, which can then absorb this CO_2 content. This can then be taken from this unit for transfer to the analytical glove box for purging with N_2 into an alkaline scintillation cocktail for ^{14}C measurement.

6.2.2 Autoclave for leach tests

ITU already had an unused 150ml autoclave with a Teflon lining that is available for the cladding testing. An additional heating jacket was purchased (Feb. 2014) for enabling temperatures to go to 250°C and 150 bar pressure. In fact the autoclave testing parameters will be 30°C & 80°C and 1-2 bar pressure (the slight pressure can aid the gas sample extraction). The autoclave and the heating mantle are seen in Figure 6.1. The temperature stability of the heating mantle was found to be too slow in its reaction. It is intended to use an existing heating mantle in the Hot Cell 4 instead for the few elevated temperature tests (80°C) that will be necessary. This hot cell will need adaptations for detachable connectors to the gas and liquid sampling lines of the autoclave. This will enable gas (and possibly liquid) sample extraction directly to the analytical glove box that is being constructed (see below). A small cylindrical volume has also been purchased for connection to the autoclave and which can act as an alternative gas and liquid sampling system (sample mouse). Ceramic (Al_2O_3) sample holders also need to be made by the workshops for installation in the autoclave. A PEEK lining has been made for testing the stainless steel cladding at acid pH, if this proves necessary. Introduction of the autoclave is intended for the 2nd Quarter 2015, in parallel with advances in the analytical glove box construction. It is intended that the first autoclave test will be approaching completion as the commissioning of the glove box & its analytical techniques are ready.

For the stainless steel cladding samples (WP 2) the pH will be 6-7 (bottled Volvic water) and ~pH12 (using a simple NaOH solution) at just one (80°C) test temperature (for the Zircaloy cladding (WP3) it will be just one pH: ~12 (NaOH solution), but at two test temperatures: 30& 80°C). Separate gas and liquid samples will be taken at the end of the 3month leaching experiments, with no intermediate samples.

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

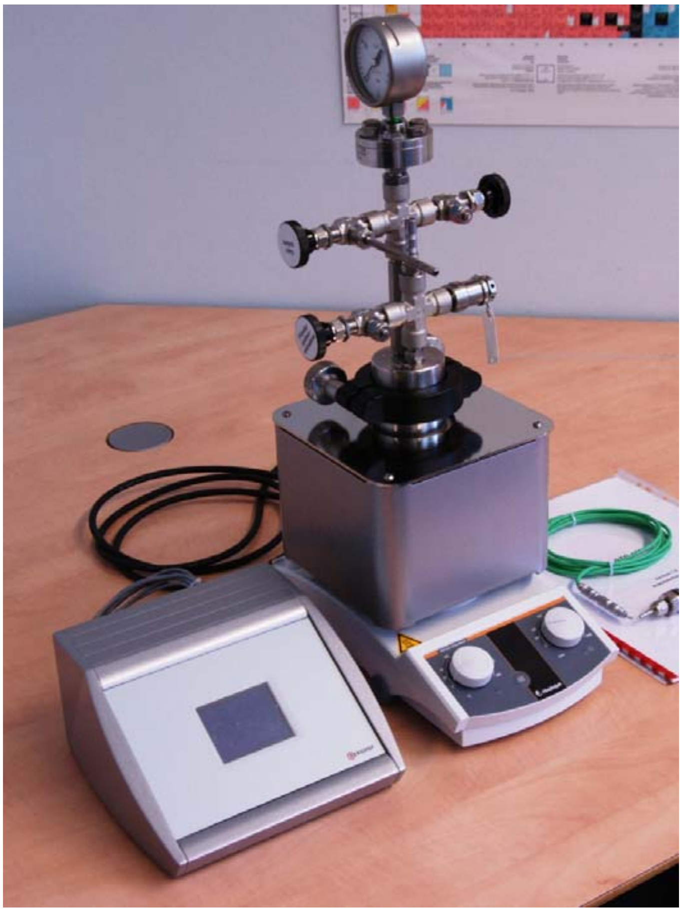


Figure 6.1: Autoclave with heating mantle and hot plate for assuring a constant temperature during the leach tests

6.3 *Preparation of the analysis of the leaching aliquots*

6.3.1 Glove box preparation

A glove box will be required to collect and analyze the carbon-containing gases and liquids from the autoclave. The gases will be transferred under a high purity N_2 gas purge of the autoclave to the glove box the gas purge lines will be passed over wash bottles for ^3H (5% H_2SO_4) and for I removal (4% $AgNO_3$) before being passed through an alkaline solution (2M NaOH) with scintillator (Carbosorb-absorber + Permaflor-scintillator- Perkin Elmer) for collection and subsequent LSC counting for ^{14}C determination in CO_2. There are also 2 switches in the gas line: a) one to enable the gas purge to pass over a furnace with CuO catalyst at 300-350°C to convert CO to CO_2 before collection & LSC counting and so determine the total ^{14}C content in CO & CO_2 forms; b) a second to route the gas purge through a second furnace at 750°C with CuO/ Pt on Al catalyst to convert CH_4/CO to CO_2 before capturing in the alkaline scintillation cocktail for counting & determination of total ^{14}C in $CH_4/CO/CO_2$ forms. In addition there is still the possibility of residual contamination from other radio-active fission products from the hot cells. In this case it may be necessary in addition to capture the CO_2 content on a molecular sieve in an ampoule (CARBOSPHERE® carbon molecular sieve (60/80 Mesh) [Berg and Fonnesbeck, 2001]. before performing the ^{14}C analysis. The ampoule will then be switched to a second high purity N_2 gas line which can purge the CO_2 captured on the sieve and collect it in a liquid with a scintillator ready for counting by LSC.

The liquid phase in the autoclave will be pumped from the autoclave directly into a bottle in the Hot Cell for direct transfer to an analytical glove box where the liquid will be acidified and heated and the gas flow passed through an alkaline collection bottle with scintillation chemicals so that the liquid aliquot would be ready for scintillation counting.

The ^{14}C analyses will be performed by existing beta (scintillation) counting equipment already present in a specific spectroscopy laboratory in ITU.

The analytical technique will be as close as possible to that used by KIT-INE. It is intended that ITU and INE will collaborate on the technical construction of the analytical glove box, firstly as to provide as similar and as optimum an analytical technique as possible (given INE's experience in this field) but also to enable the best possible comparison between the results from the two Hot Labs.

The draft design of the glove box and the necessary chemical glassware and ampoules have been submitted to the workshop. The design has been modified and accepted by the drawing office and a schedule was drawn up in early September 2014. The schedule foresees the main construction will be finished by June 2015. Some items of chemical equipment (e.g. wash-bottles, 3-neck vessel and reflux columns and glass connectors) will be purchased shortly (March/April 2015) either directly from INE or from identical suppliers as will the analytical chemicals for LSC absorption & scintillation. The carbon molecular sieve (Carbosorb-Perkin Elmer) as well as the certified standards of ^{14}C (e.g. NIST traceable standards: stainless steel (# 493-12-2), high purity N_2 gas) will also be ordered at the same time. A vacuum pump with adjustable valve will also be purchased to ensure a constant, controlled gas flow in under-pressure for efficient transfer of the C-containing gases to the absorbant solution (NaOH) for measurement and avoid any unnecessary contamination of the glove box.

Some cold testing will be necessary of the glove box before it can be used on actual test aliquots; optimally this will be done in parallel with starting the first autoclave test so that it is available for the first sample after 3 months.

7 KIT-INE contribution to CAST WP2 First Annual Report

7.1 *Irradiated material*

KIT-INE developed a method that allows the separation and quantification of inorganic and organic/CO ^{14}C species in gaseous and aqueous samples taken from dissolution experiments with irradiated steel. The used stainless steel spring is taken from the plenum of a UO_2 fuel rod segment, which was irradiated in the pressurized water reactor Gösgen, Switzerland (Figure 7.1). Relevant characteristic parameters of the irradiated steel are given in Table 7.1 and dimensions are given in Figure 7.2. Due to the γ-dose rate of the plenum steel spring (1.6 Sv/h at surface), small steel specimens of the spring are used in dissolution experiments, which are conducted in the shielded box-line of KIT-INE.

Table 7.1: Features of stainless steel specimen studied by KIT-INE

Reactor	**type: PWR** **fuel type: UO_2** **thermal power: 3002 MW**
Plenum spring data	material: X7CrNiAl17-7 weight: 10.4 g nominal N conc.: 500 ppm [Sakuragi et al., 2013]
Cladding data	material: Zircaloy-4 rod diameter: 10.75 mm wall thickness: 0.725 mm
Irradiation data	average burn-up: 50.4 GWd/t_{HM} number of cycles: 4 average linear power rate: 260 W/cm maximal linear power rate: 340 W/cm calculated neutron flux: 9.3×10^{13} cm^{-2} s^{-1} date of discharge: 27 May 1989 irradiation duration: 1226 days

Figure 7.1: Irradiated stainless steel plenum spring used for the dissolution experiments

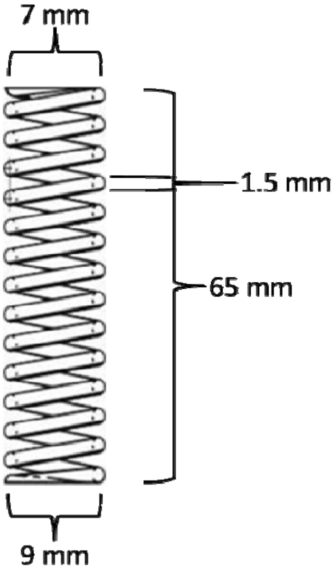


Figure 7.2: Scheme of the stainless steel plenum spring with dimensions

7.2 Experimental procedure for quantification of ^{14}C of irradiated steel specimens

For determining the inventory/chemical form of ^{14}C, dissolution experiments with specimens of the plenum steel spring are going to be performed in autoclaves under reducing conditions at ambient temperature using a dilute HF/H_2SO_4 mixture. An overview on the experimental program including extraction and analytical techniques is outlined in Figure 7.3.

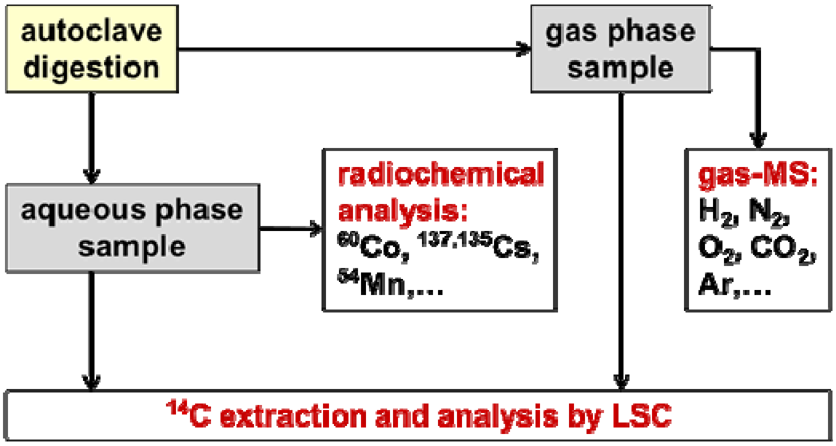


Figure 7.3: Scheme of the experimental procedure for quantification of ^{14}C species of stainless steel specimens

The analytical ^{14}C separation procedure, shown in Figure 7.4 is based on a method developed for determining ^{14}C in spent ion exchange resins and process water from nuclear reactors ([Magnusson and Stenstroem, 2005], [Magnusson, 2007] and [Magnusson et al., 2008]). The procedure involves several steps (i.e. acid stripping and wet oxidation) during which the inorganic and organic/CO fractions are extracted and converted into CO_2 which is then absorbed in washing bottles containing 2 M NaOH. A catalytic furnace between the two sets of washing bottles (first set with bottles #2 and #3, second set with bottles #4 and #5, Figure 7.4) ensures oxidation of reduced compounds like CO or methane. The content of ^{14}C in the NaOH solution is finally determined by liquid scintillation counting (LSC).

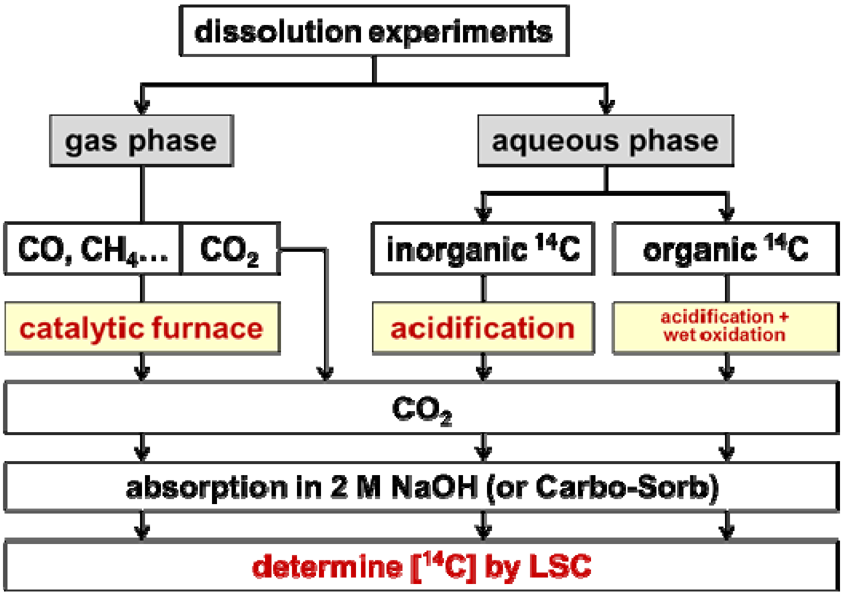


Figure 7.4: Scheme of ^{14}C extraction procedure for gaseous and dissolved aliquots of experiments with stainless steel specimens

The experimental design outlined in Figure 7.5 consists either of a 500 mL three-neck flask with gas-inlet, 120 mL dropping funnel and cooler for aqueous samples or a gas collecting with two valves for gaseous sample samples, connected to the CO_2 gas absorption system.

The CO_2 gas absorption system consists of in total five customized washing bottles filled with 50 mL 2 M NaOH respectively, except bottle #1, which is the ^{3}H trap and contains 50 mL 5% H_2SO_4. The catalytic furnace consists of a tube furnace operated at 750°C, holding a quartz glass tube which is filled with the catalyst mixture (30 wt.% Pt on Al and 70 wt.% copper oxide wire). The system is interconnected by silicon tubing. Nitrogen, supplied by a gas bottle connected through a buffer volume is used as carrier gas with a flow rate of ~250 mL/min. To prevent the loss of CO_2 gas in the case of a leakage, the system is operated under subatmospheric pressure (−0.2 bar) by means of a diaphragm vacuum pump with fine-adjustment valve and manometer.

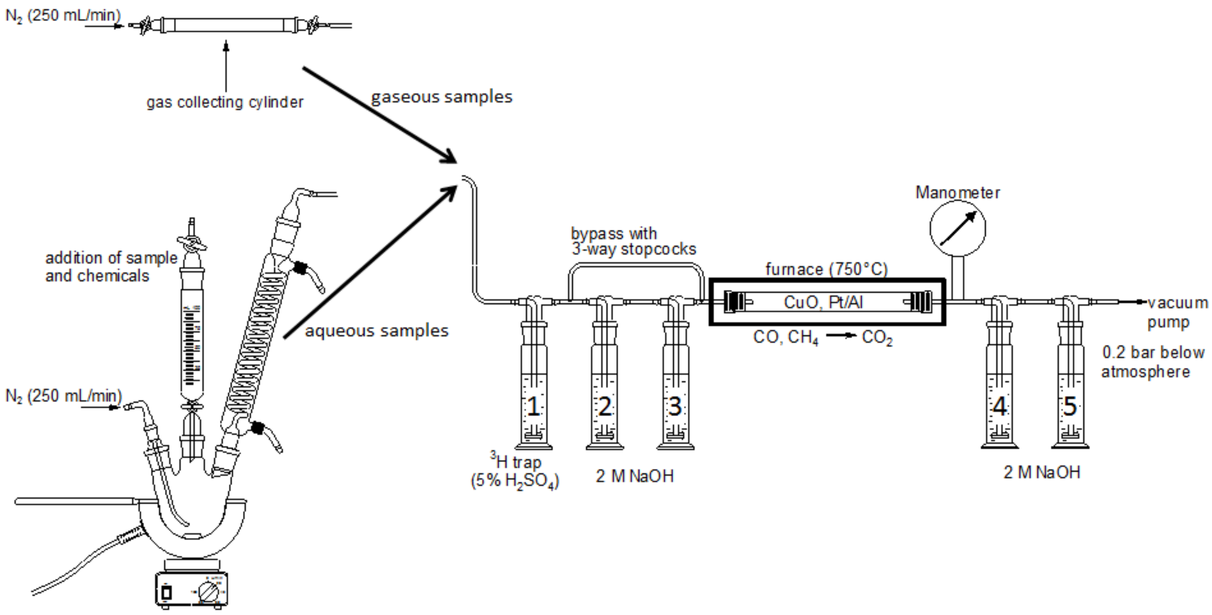


Figure 7.5: Experimental design for ^{14}C extraction of gaseous and dissolved aliquots of experiments with stainless steel specimens

Aqueous sample treatment procedure: Aqueous aliquots, which are sampled from the dissolution experiments, are introduced in the dropping funnel (100 mL) and the system is evacuated to 0.2 bar below atmosphere. Subsequently the nitrogen carrier gas flow rate is set to 250 mL/min. The sample solution is added slowly to the three-neck flask containing a volume of 50 mL 8 M H_2SO_4. The solution is purged and stirred for two hours, during which the inorganic fraction is released as CO_2 and absorbed in the washing bottle #2 (Figure 7.5). Reduced carbon compounds like CO, released during the acid stripping, are oxidized in the catalytic furnace and absorbed in washing bottle #4. Prior to the wet oxidation step, washing bottles #2 and #3 are disconnected from the system using the three-way stopcocks. The remaining carbon compounds in the sample solution (organic fraction) are oxidized by a strong oxidant ($K_2S_2O_8$), catalyst ($AgNO_3$), heat and magnetic stirring. Consecutively 50 mL 5% potassium peroxodisulfate solution and 5 mL 4% $AgNO_3$ solution are added immediately to the sample container through the dropping funnel under simultaneous heating (~95°C). After one hour the same amounts of potassium peroxodisulfate and silver nitrate are added to the flask and the mixture is purged, heated and stirred for another hour. After in total four hours samples are collected from the washing bottles for LSC measurements.

Gaseous sample treatment procedure: The gas collecting cylinder with two valves is connected to the first washing bottle of the CO_2 gas absorption system and the nitrogen gas bottle as shown in Figure 7. 5. The pressure in the system is lowered to about 0.2 bar below atmosphere and the N_2 gas flow rate is set to 250 mL/min. The content of the gas collecting cylinder is flushed into the CO_2 gas absorption system, where carbon dioxide released from inorganic carbon compounds during the dissolution experiments is absorbed in washing bottle #2. Reduced carbon compounds like CO or CH_4 will be oxidized in the catalytic furnace to CO_2 and absorbed in washing bottle #4. After in total one hour samples are collected from the washing bottles for LSC measurements.

8 NRG contribution to CAST WP2 First 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 (see Figure 8.1). The leaching experiment will be realized in 0.1M NaOH (pH 13) under anaerobic conditions 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.

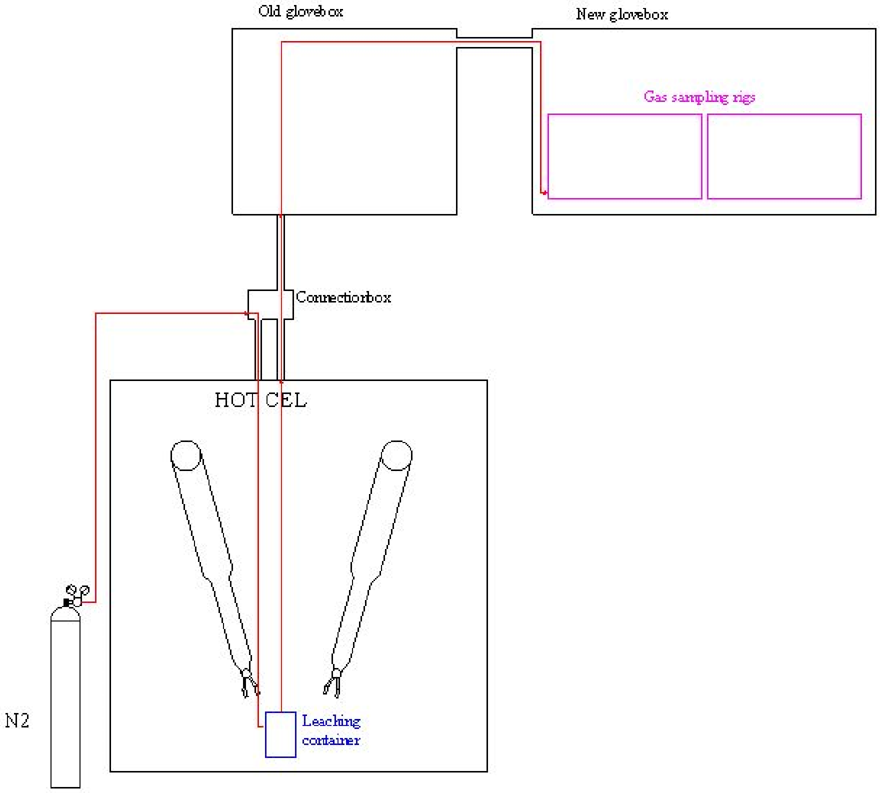


Figure 8.4: Schematic drawing of the leaching experiment in the G1 cell in the HCL

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. Gas samples will be taken to determine ^{14}C.

8.2 *Stainless steel samples*

Stainless steel samples from the irradiation experiment R268-7 (SIWAS 07) have been chosen as suitable candidates for this experiment. The specimen holder R268-07 (SIWAS), for testing the mechanical properties of different types of steel has been irradiated in the HFR Petten up to a nominal target dose level of 2 displacements per atom (dpa) at a target temperature of 80 °C. The specimens were in direct contact with the HFR core cooling water. The irradiation took 5 cycles (28 days per cycle) in the year 1996-1997.

For all cold and hot tests the same composition (the same batch) samples will be used. The composition of the used sampled is listed below in Table 8.1.

Table 8.1: Composition of the used stainless steel samples (wt.%, Fe - balance)

Steel	C	N	Mn	Si	Cr	Ni	Mo	Cu	Co	Ti	S	P
316L(N)	0.02	0.08	1.8	0.4	17.2	12.2	2.4	0.1	0.08	--	--	0.02

The acquired samples for this project are so called CT (Compact tension) specimens shown in Figure 8.2 that are used for material properties tests.

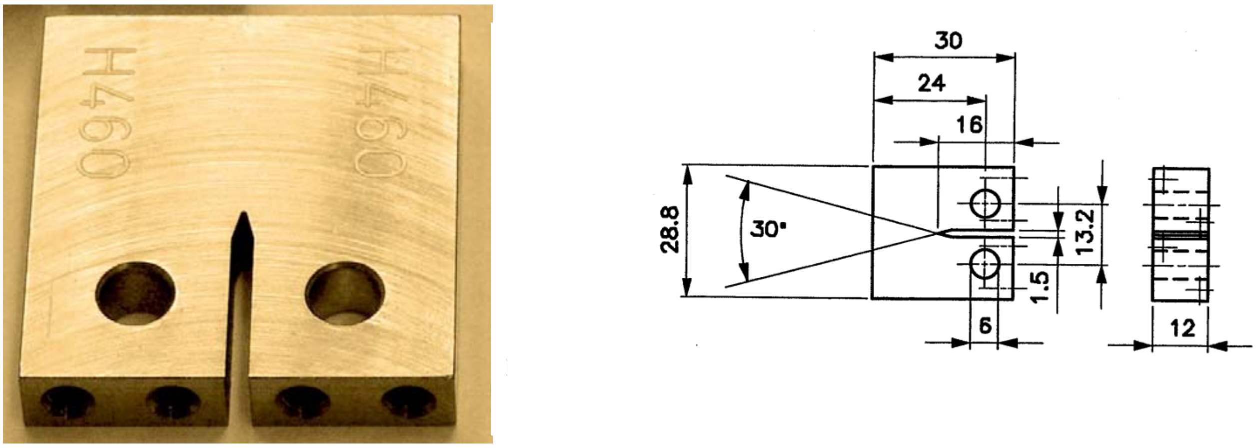


Figure 8.5: CT specimen photo (left) and technical drawing (right)

In previous projects, a characterization of the samples took place. Polarization measurements on non-irradiated samples were performed to estimate the corrosion rate of the samples. These measurements have indicated that the corrosion rate is expected to be about 0.6 µm/year. In order to be conservative and considering the expected ^{14}C levels, a surface area to be leached of 100 cm^2 has been chosen. This chosen leaching area should lead to by analytical methods detectable ^{14}C release.

The amount of ^{14}C (and other radionuclides) in the stainless steel sample has been calculated from the irradiation history of the acquired samples, by means of ORIGEN computational code. The calculated activities of ^{14}C for the acquired samples are 155 to 287 kBq/g steel. The acquired samples will be put in the containers in the way that the total ^{14}C activity in each container will be similar. The calculated activities for ^{60}Co are in the range from 155 to 283 MBq/g steel.

One of the stainless steel samples has been characterized by gamma spectroscopy. A scan of the sample of all gamma emitters has been done and the ^{60}Co amount has been determined. The ^{60}Co specific activity was $1.48 \cdot 10^8$ Bq/g.

8.3 *Progress in the reporting period*

In the first reporting period, no work was scheduled for NRG under CAST WP2 (the design and commissioning of the experimental equipment is being funded by Radioactive Waste Management outside the scope of CAST).

8.4 *Milestones & Deliverables*

No milestones or deliverables were scheduled in the first reporting period.

9 PSI contribution to CAST WP2 First Annual Report

9.1 *Development of the analytical techniques*

Prior to starting the current experimental programme, we carried out an extensive literature survey with the aim of evaluating and identifying the target organic compounds that might be monitored during steel and iron corrosion (Table 9.1).

According to this literature survey [Deng et al., 1997; Agrawal et al., 2002; Seewald, 2001; Yamaguchi et al., 1999; Kani et al., 2008; Schumann et al., 2014], the organic compounds expected to be produced during steel and iron corrosion, can be roughly divided into three groups: a) gaseous (alkanes/alkenes) b) volatile (alcohols/aldehydes), and c) dissolved compounds (carboxylic acids/carbonate). In general, all these corrosion-derived products are low molecular weight (LMW) organic compounds containing ≤ 5 carbon atoms.

Table 9.1: Carbon species expected to be formed as a result of steel corrosion as reported in literature (all table entries) and subsequently identified at PSI in corrosion experiments with non-activated iron powders (highlighted in bold)

Alkane/alkene	**Alcohols/aldehydes**	**Carboxylic acids**	**Carbonate**
Methane (CH_4) **Ethane** (C_2H_6) **Ethene** (C_2H_4) **Propane** (C_3H_8) **Propene** (C_3H_6) **Butane** (C_4H_{10}) Butylene (C_4H_8) Pentene (C_5H_{10})	**Methanol** (CH_3OH) **Ethanol** (C_2H_5OH) **Formaldehyde** (CH_2O) **Acetaldehyde** (C_2H_4O) **Propionaldehyde** (C_3H_6O)	**Formate** ($HCOO^-$) **Acetate** (CH_3COO^-) Propanoate ($C_2H_5COO^-$) Butanoate ($C_3H_7COO^-$) **Malonate** ($CH_2(COO^-)_2$) **Oxalate** ($C_2O_4^{2-}$)	CO_2 CO_3^{2-} (CO)

The analytical strategy developed in the framework of this project is outlined as follows: Gas chromatography (GC) coupled to mass spectrometry (MS) is being used for the identification and quantification of gaseous and volatile compounds for which two different analytical protocols, that is one for the polar alcohols/aldehydes and one for the nonpolar alkanes/alkenes, were developed. High performance ion-exclusion chromatography (HPIEC) coupled to conductivity detection (CD) and mass spectrometry (MS) is being used for the identification and quantification of dissolved compounds. These analytical techniques allow the target compounds listed in Table 9.1 to be detected in the low micro-molar concentration range (see next section).

9.2 *Corrosion experiments with non-activated iron powders*

Batch-type experiments with non-activated carbon-bearing iron powders were carried out with the aim of developing and optimizing the analytical protocols (HPIEC/MS, GC/MS) to identify and quantify the organic compounds listed in Table 9.1 in corrosion studies and further assessing whether or not the above list of organic compounds formed during steel corrosion is complete. The experiments were carried out using two different commercially available carbon-containing iron-powders (Sigma and BASF), either pre-treated [Deng et al., 1997] or untreated, and exposing them to conditions relevant to a cement-based repository, i.e. anoxic conditions and different solution compositions (Opalinus Clay pore water with pH = 7.6, equilibrium pore water of calcium silicate hydrate phases with pH = 11.5, a portlandite-saturated solution with pH = 12.5). 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. Pre-treatment of the iron powders aimed at removing the residues remaining from the manufacturing process by an acid wash. The different solutions and materials used in this study enable us to assess the influence of material properties and solution conditions on corrosion.

9.2.1 Time-dependent formation of organic compounds

In the first series of batch-type corrosion experiments, the formation of organic compounds was monitored up to 35 days. As an example, Figure 9.1 displays measurements of the carboxylic acids formed during the corrosion of BASF pre-treated (Figure 9.1A) and Sigma untreated (Figure 9.1B) carbonyl iron powders in alkaline pore water solution (pH = 12.5). In general up to four different carboxylic acids (formic-, acetic-, oxalic- and malonic acid) could be identified during the corrosion process. After a fast, initial increase in the concentrations, especially in case of the pre-treated powders, the concentrations remained constant over time ranging between a few up to about fifty micro-molar. In particular the concentrations of acetic- and formic acids were high (35 µM and 10 µM, respectively) in the experiments with pre-treated iron powders. In contrast, the concentration of the acids was typically less than five micro-molar in the experiments with the untreated iron powders thus indicating almost insignificant formation of carboxylic acids in these samples. In all corrosion samples acetic acid was the predominantly formed carboxylic acid. Note that propanoate and butanoate (Table 9.1) could not be identified in the present study.

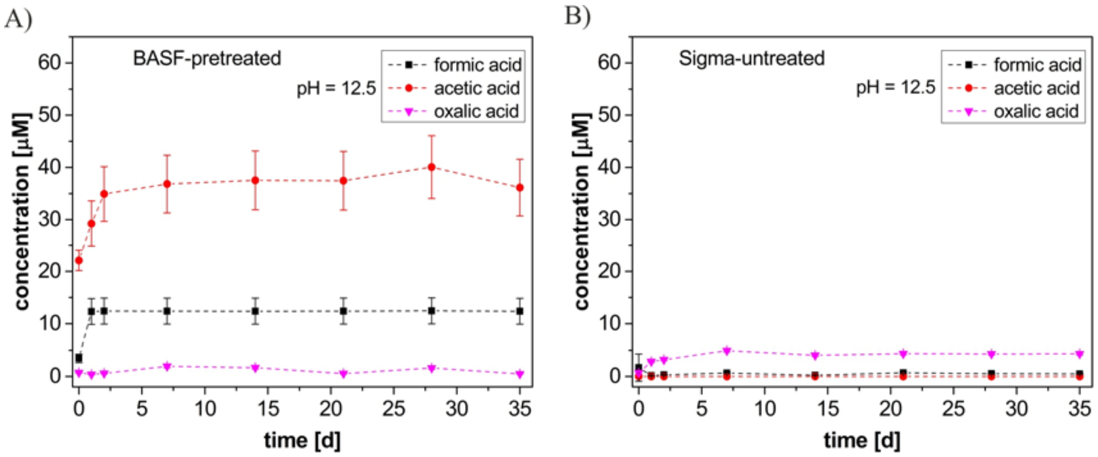


Figure 9.1: Time dependence of the concentrations of carboxylic acids during the anoxic corrosion of two different iron powders at pH = 12.5

The following gaseous organic compounds were identified in the experiments: methane, ethane, ethane, propane, propene, and butane. As an example, Figure 9.2 shows the time-dependent formation of hydrocarbons during iron corrosion in two different pore water solutions (pH = 12.5 and 7.6). Again, in agreement with the compounds reported in the literature (Table 9.1), only LMW carbon species were detected. Methane was found to be the compound with the highest concentration. In general, the concentrations of the identified compounds decreased with increasing carbon content of the gaseous species, i.e. a decrease of the concentration from methane to butane was observed. In the experiments performed at high pH (e.g. at pH = 12.5 in Figure 9.2A), the same pattern of time-dependent concentration changes was observed as for the carboxylic acids. An initially strong increase in the concentrations (within about 1 day) was followed by virtually constant concentrations over the remaining experimental period. Thus, we infer that, under strongly alkaline conditions and after the initially fast corrosion of the iron powders, the corrosion process is very slow. At a pH of 7.6 (Figure 9.2B), however, a significant increase in the hydrocarbon concentrations was observed with time in agreement with higher corrosion rates reported at lower pH values.

Polar volatile compounds are the third group of compounds that have been detected (Table 9.1). However, their concentration was found to be close to the limit of detection of the analytical methods and therefore, no clear trend in concentration and behaviour can be deduced.

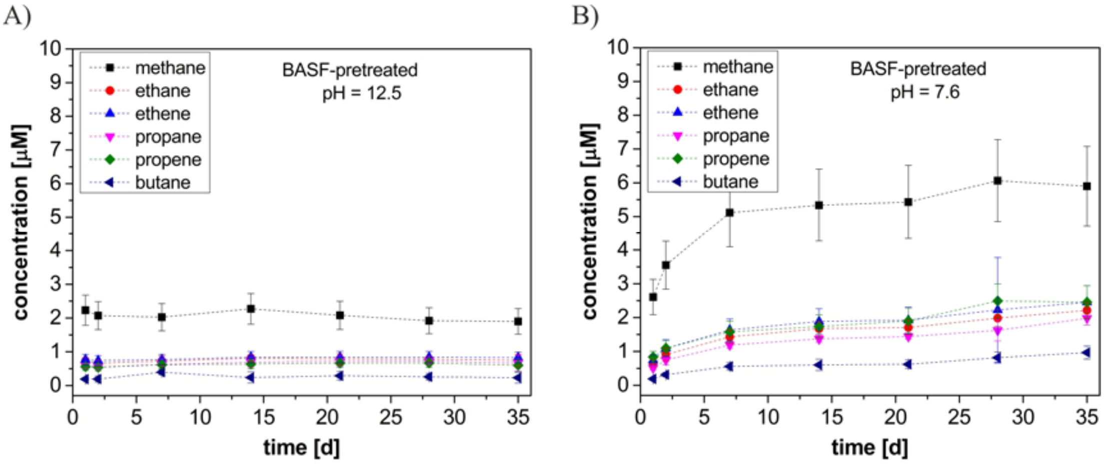


Figure 9.2: Time dependence of the hydrocarbon concentrations during the anoxic corrosion of pre-treated BASF iron powder at pH = 12.5 (A) and pH = 7.6 (B)

9.2.2 Initial stage of iron corrosion

The main findings from the time-dependent corrosion experiments under alkaline conditions can be summarized as follows: 1) A fast formation of organic compounds within the first day was observed, and 2) a large difference in the concentrations of organic compounds between the experiments with pre-treated and untreated iron powders was noticed. In order to illustrate the rapid formation of organic compounds in the initial stage of the corrosion process, a series of corrosion experiments were carried out in which the pore water solution was replaced with fresh solution after 3, 6, 9 and 49 days (Figure 9.3). After the first replacement of the solution, the concentrations of the organic compounds clearly dropped to a very low level close to the limit of detection. Even after a long period of 40 days between exchange III and exchange IV (Figure 9.3) no significant increase in the concentrations of carboxylic acids was observed, supporting the fact that the corrosion process is usually very slow under strongly alkaline conditions.

Two possibilities for the fast formation of organic compounds in the initial stage of the corrosion process can be envisaged: 1) the high starting concentrations of carboxylic acids (dissolved carbon species) could be caused by a contamination generated during the pre-treatment process, or 2) carboxylic acids are formed rapidly and simultaneously with the reduced carbon species due to the presence of residual oxygen in solution. At the present time additional experiments are being carried out with the aim of testing the two hypotheses.

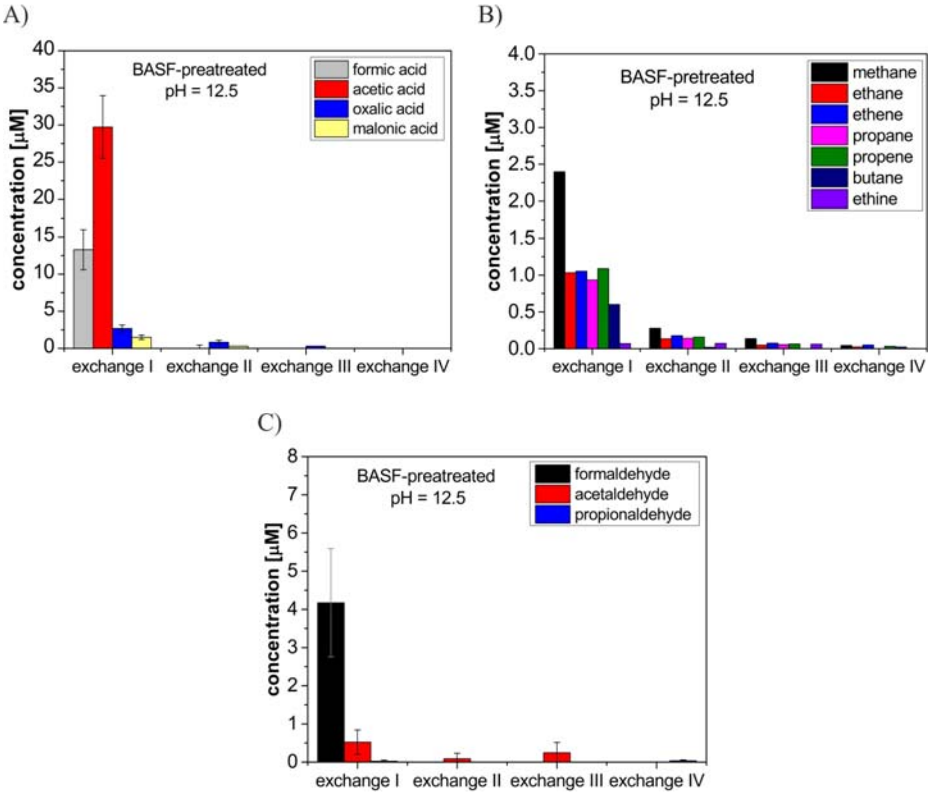


Figure 9.3: Concentrations of carboxylic acids (a), gaseous hydrocarbons (b) and aldehydes (c) as a function of solution replacements (pH = 12.5)

9.3 Coupling separation techniques with accelerator mass spectrometry (AMS) for compound-specific 14C analysis

Preliminary calculations of the concentrations of ^{14}C bearing organic compounds expected to be determined in a corrosion experiment with the available activated steel sample [Schumann et al., 2014] revealed that these concentrations will be extremely low and therefore, a highly sensitive analytical method for the detection of ^{14}C has to be coupled to standard separation techniques (GC, HPIEC) to detect the ^{14}C-bearing single compounds. Estimates using typically measured corrosion rates under alkaline conditions (50 nm a^{-1}), the known surface area and activity of the activated steel sample (1 g material with surface area of ~ 1 cm^2 g^{-1} and ~ 18 kBq g^{-1} ^{14}C [Schumann et al., 2014]) showed that the ^{14}C production rate will amount to ~ $3{\cdot}10^{-15}$ mol L^{-1} d^{-1}. The ^{14}C quantity to be determined will be further reduced due to the application of chromatographic separation into single ^{14}C bearing compounds. To the best of our knowledge, accelerator mass spectrometry (AMS) is the only suitable technique capable of detecting such small ^{14}C concentrations.

The general scheme as shown in Figure 9.4 illustrates the compound-specific ^{14}C AMS approach currently being developed by coupling chromatographic separation to ^{14}C detection using AMS. After the chromatographic separation, the different species have to be collected in separate fractions and transferred to the AMS system. For the ^{14}C measurements with AMS, various aspects have to be taken into account, in particular the required concentrations of ^{12}C, ^{14}C and the ratio of $^{14}C/^{12}C$. Theoretical calculations were performed in order to assess the procedure for sample preparation on the basis of the required $^{14}C/^{12}C$ ratio for ^{14}C AMS. The calculations show that the compound-specific ^{14}C AMS approach should be feasible.

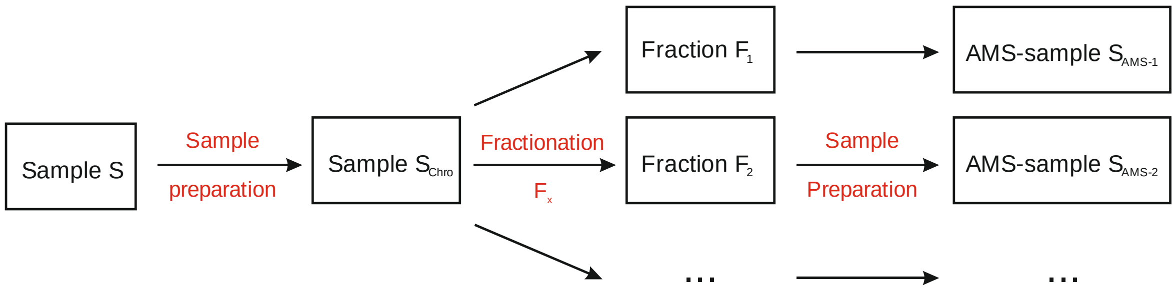


Figure 9.4: Simplified flow chart of the chromatographic separation of 14C bearing organic compounds coupled to 14C detection by AMS

First steps have been taken towards the development of the compound-specific ^{14}C AMS method. Chromatographic separation of the carboxylic acids and fractionation of the samples was optimized and quantified. Known concentrations of carboxylic acid standards (single compounds) were injected to optimize the fractionation parameters and to determine the recovery (Table 9.2). Recoveries ranging from 95 to 110 % were determined, which highlights the efficiency and reproducibility of fractionation by HPIEC.

Table 9.2: Recoveries of the carboxylic acids after fractionation by HPIEC

Substance	Recovery [%]	SD [%]
Acetic acid	107	7
Formic acid	95	6
Valeric acid	100	2
Malonic acid	104	15
Oxalic acid	101	1

9.4 *Summary and outlook*

Corrosion experiments with non-activated iron powders enabled us to determine of organic compounds that might form during the corrosion of activated steel. The compounds were identified using ion and gas chromatography. The experimental protocols for the identification and quantification of dissolved organic compounds (carboxylic acids), gaseous hydrocarbons and polar, volatile compounds (alcohols, aldehydes) have been developed.

The corrosion experiments with non-activated iron powders carried out under conditions relevant to a cement-based repository (i.e. anoxic conditions in cement-type pore waters) showed high initial concentrations of the organic compounds generated in the very early stage of the corrosion process (within one day) while the concentrations remained constant during the remaining time period of the experiments (up to 35 days). The reason for the high starting concentrations of oxidized organic compounds (i.e. carboxylic acids, alcohols and aldehydes) is currently being investigated.

First steps have been taken towards the development of the compound-specific ^{14}C AMS technique required to detect the extremely low concentrations of ^{14}C bearing organic compounds expected to form in a corrosion experiment with activated steel. The conceptual framework of the technique has been developed and predictive calculations were carried out to assess whether or not the selected approach is feasible. Fractionation of carboxylic acids by HPIEC was established and optimized. In the next phase, ^{14}C free organic compounds have to be identified, which will be used as ^{12}C carriers in the course of sample preparation for compound-specific ^{14}C AMS and further, the ^{14}C background in samples subjected to fractionation has to be determined. Eventually, a series of tests with ^{14}C labelled carboxylic acids will be carried out with the aim of determining the recovery for the compound-specific ^{14}C AMS method.

10 RWMC contribution to CAST WP2 First Annual Report

10.1 *Experimental setup*

Evaluation of the long-term corrosion of stainless steel under geological disposal condition is performed according to Figure 10.1. It is judged whether localized corrosion occurs under the disposal condition by literature survey and preliminary test. If the literature research and the test corroborate localized corrosion being an issue in a disposal environment, it will be studied under several conditions to assess the corrosion volume including localized corrosion. About uniform corrosion, a corrosion test is done under pure water conditions, and a long-term corrosion rate is evaluated. In order to evaluate the acceleration influence of material and environment, the corrosion tests are carried out with a parameter of temperature, pH, ionic species (Na^+, K^+, Ca^{2+}, Cl^-, SO_4^{2-}), irradiation etc.

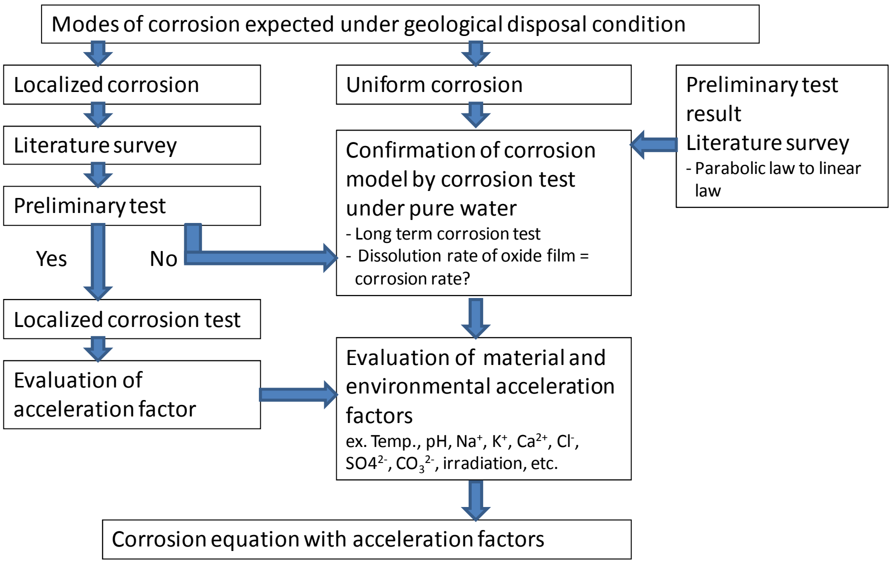


Figure 10.1: Method to evaluate corrosion expected under geological disposal condition

10.1.1 Specimen pre-treatment

Specimens

The chemical compositions of 18-8 SS are presented in Table 10.1. Two kinds of specimens were prepared. Specimen A was used to measure hydrogen released to the gaseous phase, specimen B was used to measure hydrogen absorbed in the SS. Specimen B was specially prepared to lower the analysis limit for the quantity of hydrogen absorption by thinning. Specimens were cut to the sizes of 3 mm × 90 mm × 0.1 mm^t (A) and 3 mm × 90 mm × 0.02 mm^t (B), and polished with emery paper up to grade 800. Before being supplied for the corrosion tests, the specimens were washed with acetone and stored in a vacuumed desiccator. The oxide film was analyzed using TEM-EDX (JEM-2010F). A thin oxide film of approximately 3 nm was observed.

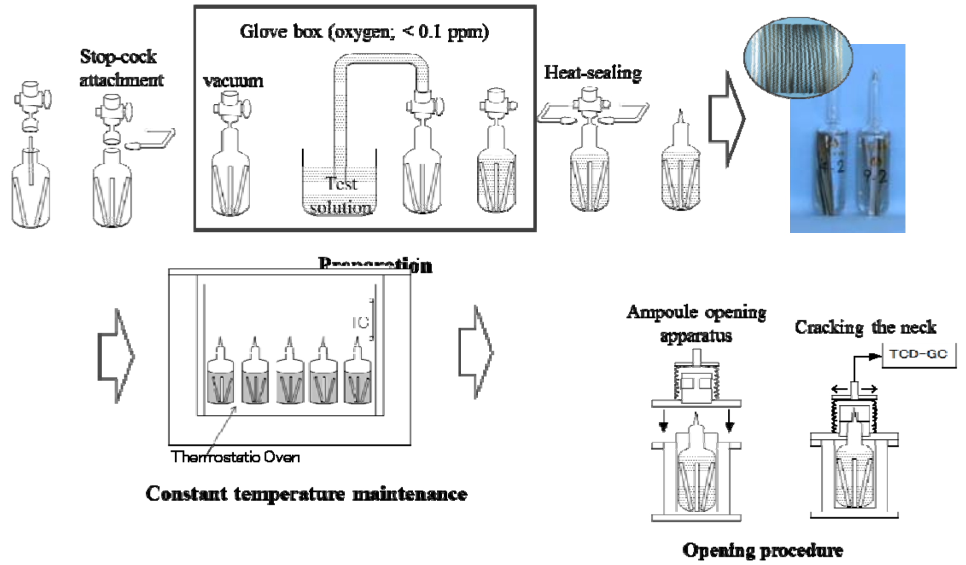
Table 10.1: Chemical compositions of 18Cr-8Ni austenitic stainless steels (wt%)

	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	-
Specimen A	0.07	0.45	0.79	0.028	0.005	8.29	18.14	-
Specimen B	0.05	0.76	0.97	0.029	0.001	8.05	18.17	1.5

10.1.2 Experiment for uniform corrosion

Procedure

An ampoule batch test was performed according to the methods developed by Honda et al. [Honda, 1999], and test procedure is presented Figure 10.2.



Hydrogen analysis method

Gas phase

- **Released Hydrogen Gas : Gas chromatography ((TCD-GC)**

Test Specimen

- **Absorbed hydrogen: Inert gas melting system* coupled with gas chromatography**
- **Characteristics of oxide film: TEM-EDX, Electron diffraction, XPS**

* high-frequency induction heating ～2000℃

Figure 10.2: Corrosion test and hydrogen measurement procedure of SS

In the corrosion test procedure to measure released hydrogen, specimen A (22 pieces, surface area 1.2×10^{-2} m^2) was placed in a glass ampoule. A stop-cock was attached, the ampoule was filled with NaOH solution (pH 12.5), and the stop-cock was closed. The test solution was deoxidized in advance. This enclosure procedure was performed in a glove box that had been purged by nitrogen gas with oxygen concentration below 0.1 ppm. The ampoule was moved outside the glove box and sealed by heating the top part of the ampoule. The test periods were set to 90, 120, 360 and 720 days, with temperatures of 303 K, 323 K, and 353 K. After a setup period at setup temperature, the ampoule was set in a vacuum gas collecting system connected with a gas chromatograph, and the hydrogen gas was measured.

Hydrogen absorbed in specimen is measured with an inert gas melting system coupled with gas chromatography. The oxide layers after the test were analyzed with TEM, EDX, and XPS.

10.1.3 Experiment for Crevice corrosion

(1) Measurement of corrosion potential

A flat surface specimen was immersed into an NaCl solution and the corrosion potential (E_{corr}) was measured when localized corrosion did not occur. E_{corr} was measured until potential was stabile (about 7 days), and the value at this time was set as spontaneous potential (E_{sp}).

(2) Measurement of repassivation potential for crevice corrosion

Repassivation potential for crevice corrosion ($E_{\text{R,CREV}}$) was measured according to the Japanese industrial standard method (JIS G 0529). The test sample is shown in Figure 10.3. Two 18-8SS plates formed a crevice by tightening the titanium bolt and nut. The bolt shaft was covered with silicone tube in order to insulate bolt, nut and test sample. The tightening force was controlled from 0.1 to 0.3 kg·m by a torque wrench. As pretreatment, cathodic reduction treatment was performed to remove surface film made after polishing at 1V, for 300sec.

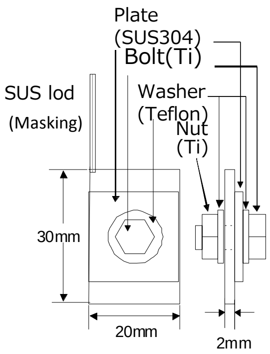


Figure 10.3: Test specimen for measurement of repassivation potential for crevice corrosion (ER,CREV)

The potential and current were controlled (Figure 10.4). The current was varied from 0.2 to 10 mA, hold time was also varied from 0.5min to 3 hour. When the current rise stopped, the potential at that time was set to $E_{\mathrm{R,CREV}}$.

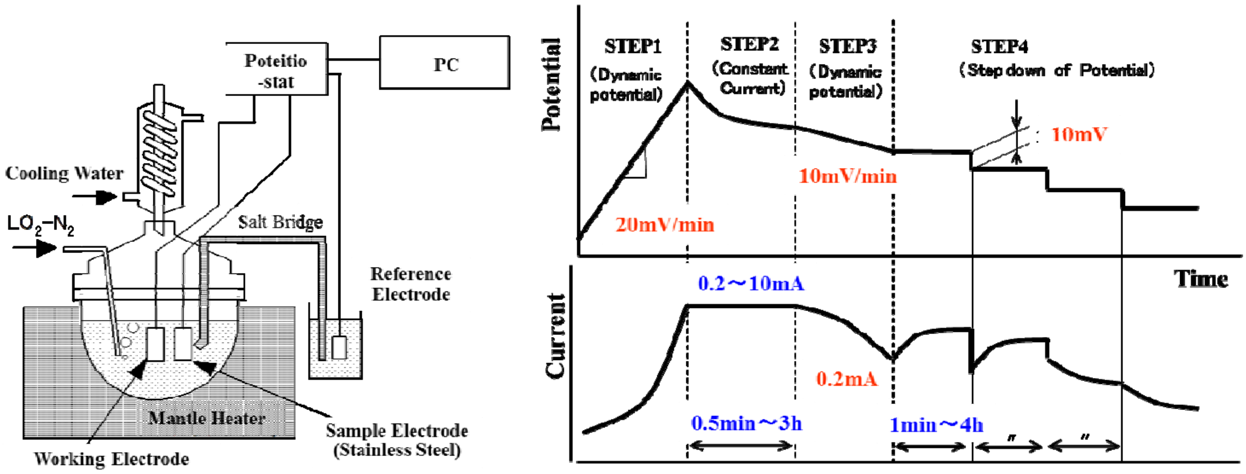


Figure 10.4: Apparatus and measurement method of repassivation potential for crevice corrosion (ER,CREV)

10.2 *Experimental condition*

The corrosion mode and test conditions for corrosion evaluation of stainless steel are shown in Table 10.2.

Table 10.2: Corrosion test conditions planned and ongoing

Corrosion mode	Test Conditions				
	Temp.	Soln.	pH	Ion Spices	Period
Uniform Corrosion					
1) Confirmation of corrosion model by corrosion test under pure water	303K~353K,	Pure Water	7~8	-	Long term ~5y
2) Evaluation of material and environmental acceleration factors	303K~353K	Alcaline Solution etc.	7~13.5	Na^+, K^+, Ca^{2+}, Cl^-, SO_4^{2-}	
Local Corrosion	~353K	NaCl Solution	7~13.5	Cl^- (~19000ppm)	

10.3 *Analytical procedure*

10.3.1 Hydrogen measurement technique

a. Released hydrogen

After corrosion test, the ampoule was set in a vacuum gas collecting system connected with a gas chromatograph, and the hydrogen gas was measured.

b. Absorbed hydrogen

Specimen B (22 pieces; surface area 1.2×10^{-2} m^2) was used to measure the absorbed hydrogen in the above procedure. The test period was 90 days at a temperature of 353 K. After the test, the hydrogen content absorbed into the specimen was determined by the inert gas melting system coupled with gas chromatography (LECO RH-404).

10.3.2 Calculation of equivalent corrosion rate

The main components in SS are Fe, Cr, and Ni, but authors supposed only Fe influenced the corrosion reaction. However, as described below, the elements in the corrosion reaction are not an equal composition of metals; the majority is Fe. To simplify the discussion, the anaerobic corrosion reaction is assumed as shown in equation (10.1). The corrosion rate is calculated by the equation (10.2).

$$3\mathrm{Fe} + 4\mathrm{H_2O} \rightarrow \mathrm{Fe_3O_4} + 4\mathrm{H_2}\uparrow \qquad (10.1)$$

$$R_{gas} = \frac{3 \times V \times 10^{-3} \times M \times 365}{4 \times 22.4 \times S \times \rho \times T} \qquad (10.2)$$

where,

R_{gas} [mol/m^2]	Generated hydrogen volume (released)
V [cm^3]	Volume of released hydrogen gas
M [g/mol]	Atomic weight (= 55.85 g/mol)
S [m^2]	Specimen surface area

ρ [g/m^2]	Density (= 7.87 × 10^6 g/m^2)
T [day]	Corrosion period

10.3.3 Characteristics of oxide

The oxide layers after the test were analyzed with TEM (Transmission Electron Microscope), EDX (Energy Dispersive X-ray spectrometer), and XPS (X-ray Photoelectron Spectrometer). To view cross sections of the oxide layer thickness, TEM samples were prepared from the specimen by FIB (Focused Ion Beam) processing. XPS was applied to analyze the elemental concentration distribution in the depth profile of the oxide layer. Analytical instruments and analysis conditions are shown below.

TEM: JEOL JEM-2010F
    Accelerating Voltage:200KeV
EDX: Noran Vantage EDX
FIB: Hitachi FB2000A
    Beam Ion:Ga$^+$, Accelerating Voltage:30KeV
XPS: Physical Electronics Quantera SXM
    X-ray: Al $K\alpha$, Beam Diameter: 0.2mm, X-ray Power:25W, Sputtering: Ar$^+$(1kev)

10.3.4 Crevice corrosion possibility

In order to judge whether localized corrosion occurs under an expected disposal condition in Table 10.2, it is necessary to evaluate whether crevice corrosion takes place. When E_{sp} potential is higher than $E_{R,CREV}$, crevice corrosion will take place. $E_{R,CREV}$ is the critical potential whether crevice corrosion occurs or not. If E_{sp} is much lower than $E_{R,CREV}$ under most unfavourable conditions, it is not necessary to take crevice corrosion into consideration any more.

Therefore, comparative evaluation of E_{sp} and the $E_{R,CREV}$ has to be measured and carried out under most unfavourable conditions (temperature:353K, Cl$^-$:19000ppm).

10.4 *Results*

Corrosion rate in an NaOH solution (pH 12.5)

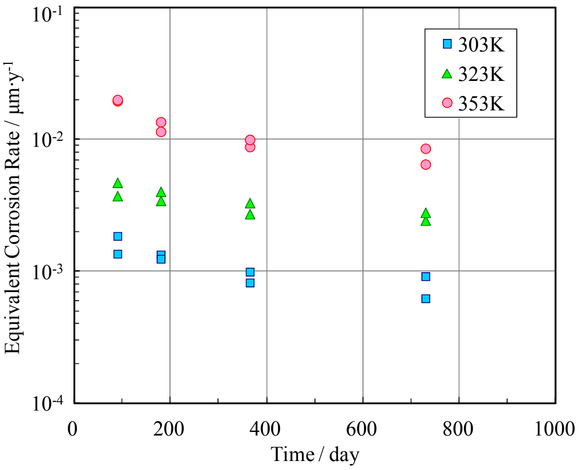
The results are shown in Table 10.3. The absorbed hydrogen pick-up ratios obtained in abs-1 and abs-2 were 1.2 and 2.9%, respectively. Because of the small pick-up ratios, the absorbed hydrogen was ignored and released hydrogen volume data was used to calculate equivalent corrosion thickness by equation (10.2).

Table 10.3: Corrosion test data

Sample	Temp.	Corrosion period	Generated hydrogen volume /mol·m^{-2}			Equivalent corrosion thickness	Corrosion rate
No.	/K	/day	Released	Absorbed	Pick-up Ratio/%	/µm	/µm·y^{-1}
abs.-1	353	90	2.00×10^{-3}	2.40×10^{-5}	1.2	-	-
abs.-2	353	90	2.20×10^{-3}	6.70×10^{-5}	2.9	-	-
1-1	303	90	0.017	-	-	3.3×10^{-4}	1.4×10^{-3}
1-2	303	90	0.02	-	-	4.6×10^{-4}	1.9×10^{-3}
2-1	323	90	0.05	-	-	9.2×10^{-4}	3.7×10^{-3}
2-2	323	90	0.06	-	-	1.2×10^{-3}	4.7×10^{-3}
3-1	353	90	0.242	-	-	4.8×10^{-3}	2.0×10^{-2}
3-2	353	90	0.25	-	-	4.9×10^{-3}	2.0×10^{-2}
4-1	303	180	0.033	-	-	6.6×10^{-4}	1.3×10^{-2}
4-2	303	180	0.031	-	-	6.1×10^{-4}	1.2×10^{-3}
5-1	323	180	0.099	-	-	2.0×10^{-3}	4.0×10^{-3}
5-2	323	180	0.085	-	-	1.7×10^{-3}	3.4×10^{-3}
6-1	353	180	0.335	-	-	6.7×10^{-3}	1.4×10^{-2}

Sample	Temp.	Corrosion period	Generated hydrogen volume	Equivalent corrosion thickness	Corrosion rate
No.	/K	/day	Released /mol·m-2	/µm	/µm·y^{-1}
6-2	353	180	0.283	5.7×10^{-3}	1.1×10^{-2}
7-1	303	360	0.05	9.9×10^{-4}	9.9×10^{-4}
7-2	303	360	0.041	8.2×10^{-4}	8.2×10^{-4}
8-1	323	360	0.136	2.7×10^{-3}	2.7×10^{-3}
8-2	323	360	0.165	3.3×10^{-3}	3.3×10^{-3}
9-1	353	360	0.441	8.8×10^{-3}	8.8×10^{-3}
9-2	353	360	0.499	1.0×10^{-2}	1.0×10^{-2}
10-1	303	720	0.062	1.2×10^{-3}	6.2×10^{-4}
10-2	303	720	0.092	1.8×10^{-3}	9.2×10^{-4}
11-1	323	720	0.244	4.9×10^{-3}	2.4×10^{-2}
11-2	323	720	0.28	5.6×10^{-3}	2.8×10^{-3}
12-1	353	720	0.648	1.3×10^{-2}	6.5×10^{-3}
12-2	353	720	0.855	1.7×10^{-2}	8.6×10^{-3}

The average corrosion rate decreased as the corrosion period increased and as temperature decreased. At 720 days, the average corrosion rates at 303, 323 and 353 K were 7.7×10^{-4}, 2.6×10^{-3} and 7.5×10^{-3} µm/y, respectively (Figure 10.5). Data fitting was performed using the power-law ($\Delta W = a \times t^{b}$), and a multiplier change (b) was evaluated for test period. The result is shown in Figure 10.6. At the higher temperature of 353 K, b appears to be close to 0.5.



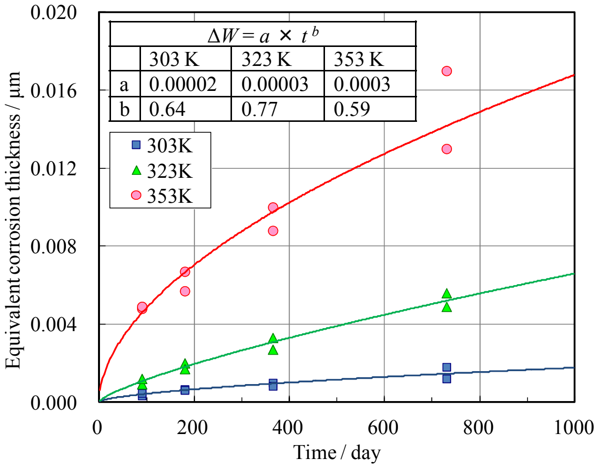
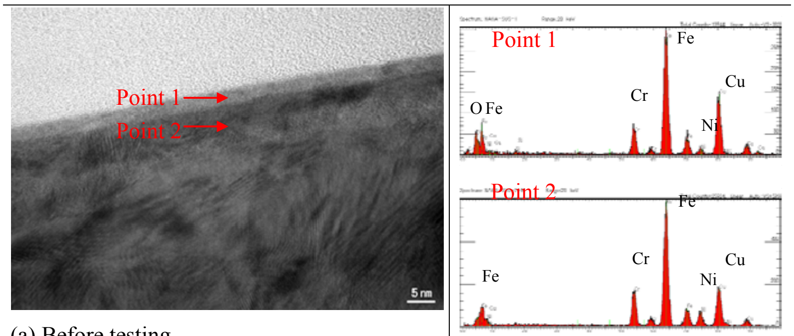


Figure 10.5: Equivalent SS corrosion rate **Figure 10.6: SS loss of**

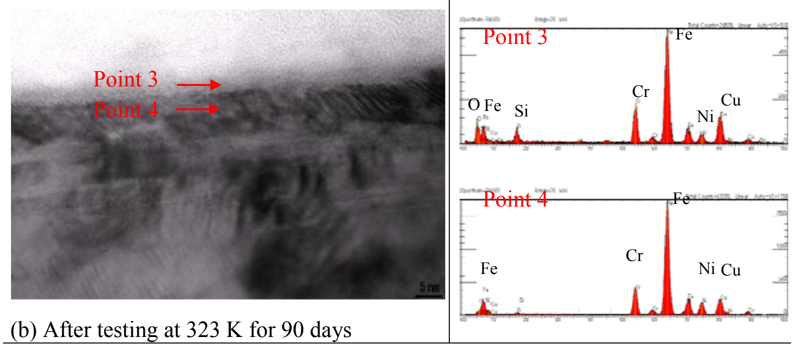
thickness

Observation of oxide layer and depth profile

The surface layer TEM images and EDX spectrum are given in Figure 10.7.



(a) Before testing



(b) After testing at 323 K for 90 days

Figure 10.7: TEM and EDX spectra of surface layer

The thickness of the oxide layer before and after the test for 90 days at 323 K was approximately 3 nm. No clear growth of the oxide layer was observed in this period. The equivalent thickness of the oxide layers was measured with the hydrogen measurement technique for Specimens abs-1 and abs-2 and was found to be 0.9 nm and 1.2 nm, respectively. The TEM picture of oxide surface layer after 90 days test was of low contrast, and it appeared that some metal elements were eluted into solution.

The depth profile of the oxide surface layer in XPS analysis with the same specimen is shown in Figure 10.8. The oxide layer near the outer surface contained Fe and Cr, while the oxide layer near the metal-oxide interface contained rich Cr, which supported the TEM-EDX results. SiO_2 was observed on the outermost oxide surface, but it is thought to have come from adherence through elution from the glass.

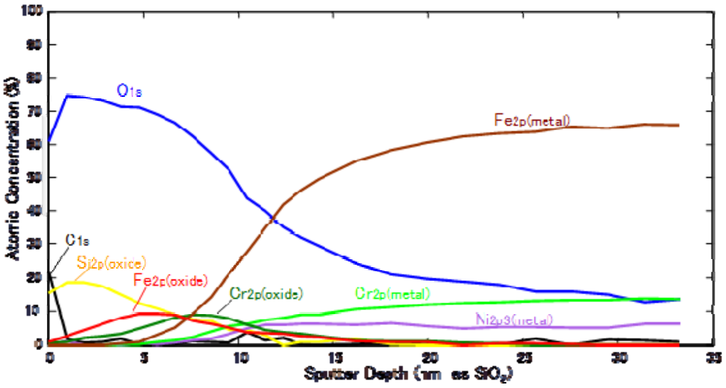


Figure 10.8: Depth profile of SS surface layer after 90-day test through XPS analysis

This research is part of “Research and development of processing and disposal technique for TRU waste (FY2013)” financed by the Agency of Natural Resources and Energy of the Ministry of Economy, Trade and Industry of Japan.

11 SCK•CEN contribution to CAST WP2 First Annual Report

11.1 *Materials*

Reactor pressure vessel carbon steel material will be used for our experiments. There are two candidates for the corrosion tests, a JRQ (ASTM A533 grade B class 1 steel) and a welding steel. The material with higher initial nitrogen content will be selected for the carbon speciation analysis. These samples are from two of SCK•CEN`s facilities, BR-2 (Belgian research reactor) and LHMA (Laboratory of high and intermediate activity). The advantage of analyzing these materials is that they are readily available on the SCK•CEN site in the original non-irradiated and irradiated forms too. Furthermore, they are well characterized samples with known chemical composition and irradiation history which represent end-of-life conditions in Belgian nuclear power plants.

A non-irradiated JRQ sample is available so far in a form of broken Charpy V specimen with the following dimensions: ⌀ = 10 mm; l ≅ 60 mm (depicted in Figure 11.1). The other sample (welding) is under arrangement.

Figure 11.1. A non-irradiated JRQ steel Charpy V test specimen before (left) and after (right) slicing for further tests

Table 11.1: Typical chemical composition of a non-irradiated JRQ steel sample [Lucon et al., 2008].

	C	P	Mn	Si	Ni	Mo	Cr	Cu	Fe
wt %	0.18	0.017	1.42	0.24	0.84	0.51	0.14	0.14	Bal.

11.2 *Methods and experiments*

11.2.1 Nitrogen analysis

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

The initial nitrogen content of each steel sample will be analyzed by a state of the art method (inert gas fusion). One batch of samples is being analyzed by an external laboratory and preliminary results are available. These results will be published later together with the results from the material characterization experiments. At SCK•CEN there is a nitrogen analyzer available but it is broken at the moment. There is an intention to get it repaired in 2014 and later performing nitrogen analysis using our own instrument. With the instrument at SCK•CEN it would be possible to analyze active samples as well since the instrument is inside the controlled area.

11.2.2 Corrosion experiments

Static leaching and accelerated corrosion tests are planned for non-irradiated and irradiated samples. The layout of the corrosion tests are presented in Figures 11.2 and 11.3. Experiments will be done in an airtight small volume (≤ 100 cm^3) container with possibilities for sampling without opening the vials. The released ^{14}C and stable carbon will be measured by using the developed analytical techniques and the organic/inorganic ratio determined if amounts are sufficient. The cell will be equipped with a gas inlet for the purging gas (argon), a gas outlet for the GC system and an outlet for the liquid phase sampling which is connected to a GC or ion chromatography (e.g. HPLC) unit.

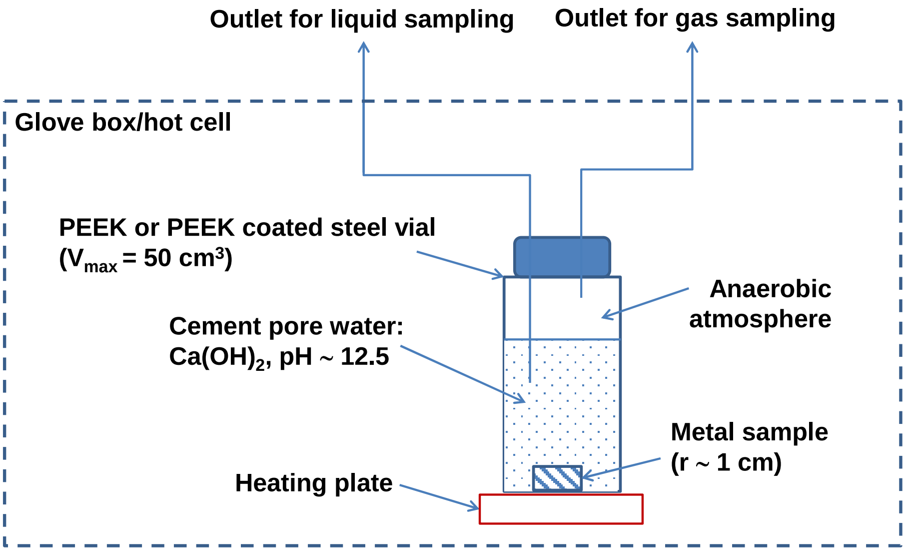


Figure 11.2: Proposed layout of the static leaching test setup in glove box/hot cell under reducing atmosphere

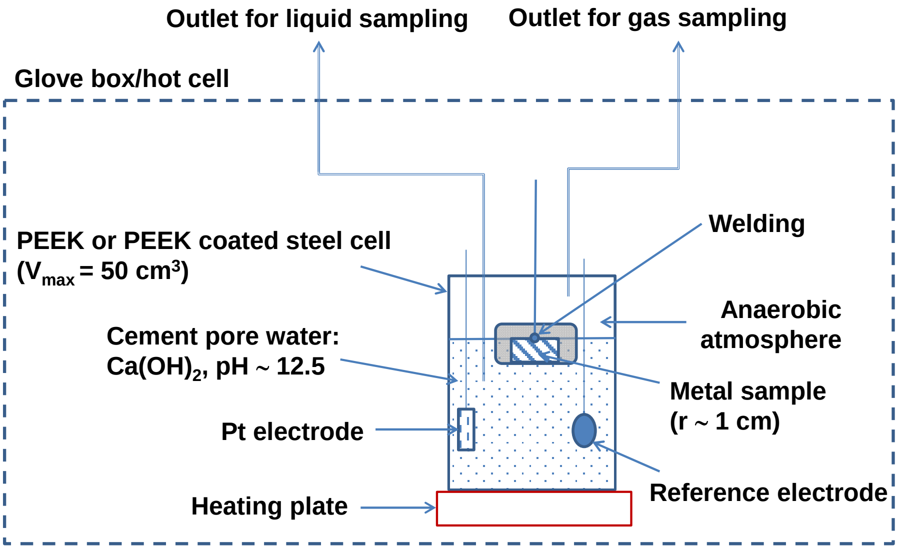


Figure 11.3: Proposed layout of the accelerated leaching test setup in glove box/hot cell under reducing atmosphere

In the long term safety case the most representative temperature is between 20-30 °C [Weetjens, 2009; Kursten et al., 2013], therefore this will be applied for our experiments. 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 environmental origin $^{14}CO_2$ absorbed in the solution.

11.2.2.1 Static leaching test

Before starting the experiment, the glove box/hot cell will be flushed with argon to exclude oxygen from the system, eventually obtaining anaerobic condition. During the static leaching test, irradiated samples (approximately 0.5 cm thick) will be placed in a test cell filled with saturated Portlandite electrolyte. It has to be noted that the mode of sample introduction is not fixed yet. The easiest way of sample introduction is to place the sample at the bottom of the vial but then not the whole surface is in contact with the pore water (e.g. where the sample touches the cell). We consider applying another arrangement where the sample is placed in a chemically resistant sample holder and immerse them together into the solution.

The cell will be closed gas tight with a screw cap having two outlets, one for gas sampling and another is for liquid sampling. Sampling will be done from the gas and liquid phase only once at the end of the experiment. The leaching test would last one year as it was recommended during the work package meeting in Paris [Necib et al., 2014]. The carbon components are accumulated in the test cell and transferred to the analytical instrument through their corresponding outlets. One dedicated cell will be used for the frequent sampling and the other cells won`t be disturbed during the experimental period.

11.2.2.2 Accelerated corrosion test

The accelerated corrosion tests would consist of imposing a pre-determined potential in the transpassive domain that would result in accelerated corrosion of the sample. To determine this potential, polarization measurements should be performed to determine the E-i behaviour of the sample in the tested environment. Depending on the active corrosion rate, a single accelerated experiment can last from few days till some weeks.

The metal samples are first polished and then either embedded in a radiation resistant resin or simply immersed into the electrolyte after point welding a wire to the back of the sample which serves as an electric connection. Silver reference and platinum counter electrodes will be used. The electrodes will be introduced through the cell cap but these holes will be made gas tight by adding resin or glue into them. The experiment will be stopped after dissolving sufficient material. For the accelerated leaching test, one sample will be taken at the end of the experiment. After disassembling of the test cell, another sampling will be done and the liquid and solid radioactive waste will be collected separately.

11.2.3 Metallographic analysis

A metallographic examination of the material could be beneficial for determining e.g. the grain size, grain orientation, different phases which play a role in the carbon release process. We focus on the carbide phases since they are the reactive carbon compounds in the metal material. Scanning electron microscopic and optical microscopic analyses are planned. These analyses are scheduled for the first available irradiated samples in September 2014. As soon as we have the rest of the samples they will be analyzed too. However, there can be a delay due to the heavy workload of the staff and other high priority samples from the Belgian nuclear power plants.

11.2.4 Gamma-ray spectrometry analysis

Before the ^{14}C analysis, samples will be analyzed by gamma-ray spectrometry to quantify the activation products in the metal samples. High purity germanium detector will be used for this analysis. On the basis of the gamma-ray spectrometry results and the model calculation of activation products production we can estimate the possible interference of activation products on the ^{14}C analysis.

11.2.5 Analytical methods for ^{14}C and carbon analysis

A brief report has been drafted about the possible options for carbon speciation and ^{14}C analysis at SCK•CEN [Jobbágy, 2014]. This report concludes that due to the very low concentration of organic compounds that is foreseen, a pre-concentration step (solid phase micro extraction) and application of coupled techniques (gas chromatography - mass spectrometry) for the speciation analysis are desirable. The pre-concentration step is based on solid phase micro extraction where the organic carbon species are extracted to. These carbon species can be quantified by chromatographic techniques (gas chromatography or high performance liquid chromatography) coupled to mass spectrometry or a sample collector followed by liquid scintillation counter for ^{14}C measurement.

The proposed analytical techniques are listed in order of preference:

a) Gas phase analysis
1. GC-MS,
2. GC-LSC.

b) Liquid phase analysis
1. SPME - HPLC - non-destructive detection-fraction collection – LSC,
2. SPME – HPLC – MS,
3. SPME – GC - MS/LSC.

List of available instruments with their detection limits (if available) at SCK•CEN:

- Total Carbon analyzer:
  - Lachat IL550 TOC-TN (LD: 0.2 ppm)
- Chromatographs:
  - Thermo GC ultra GC (LD: ppb level),
  - HPLC (Shimadzu Prominence modular)
- Liquid scintillation counters:
  - Packard TriCarb 2800 TR (LD: 1-2 Bq),
  - Quantulus 1220 (LD: mBq level).

The sequence of the proposed analytical steps is presented in Figure 11.4. The report contains a proposal for the scenario when these conventional techniques fail to detect carbon species due to extremely low concentrations (e.g. not sensitive enough). In this case samples have to be sent to a laboratory having accelerator mass spectrometry (either a project partner or external laboratory).

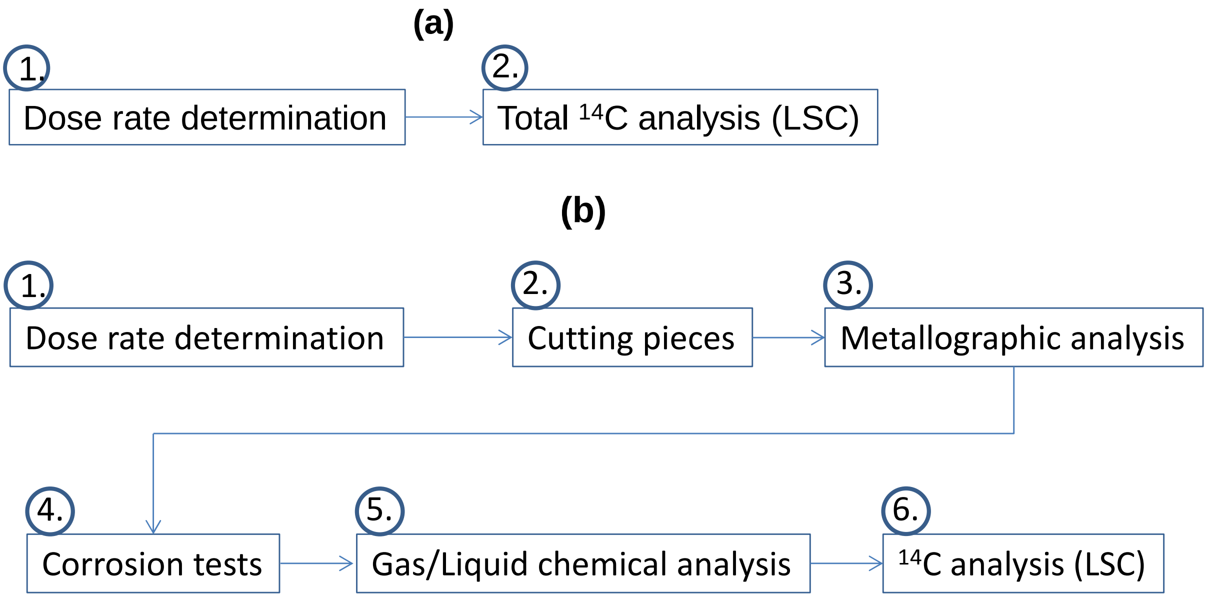


Figure 11.4: Proposed sequence of the total ^{14}C analysis (a) and the corrosion test followed by carbon speciation analysis (b)

12 VTT contribution to CAST WP2 First Annual Report

12.1 *Introduction and objectives*

Radiocarbon (^{14}C) is an important radionuclide when considering the safety of nuclear waste disposal. ^{14}C has a long half-life (5,730 y) and it can form both inorganic and organic species, which may exist as aqueous and volatile gaseous species. Especially organic species can be highly mobile in the geosphere and they can therefore migrate to the biosphere. ^{14}C is a major radiotoxicity contributor in decommissioning waste and it arises from the neutron activation of ^{14}N impurities in steel materials.

The Carbon-14 Source Term (CAST) project aims to improve the understanding of the generation and release on ^{14}C from radioactive waste materials in relevant repository conditions and Work Package 2 (WP2) focuses on unirradiated and irradiated steel materials.

Our study at VTT is part of the WP2 and the main goal is to investigate the release of ^{14}C during corrosion of activated steel in cement-based repository conditions. In order to reach this goal leaching experiments with both unirradiated and irradiated steel materials are conducted in simulated groundwaters and ^{14}C release rate is analyzed. Speciation of ^{14}C is an important feature when evaluating its mobility and migration. Therefore ^{14}C speciation is analyzed in both aqueous and gaseous phase of the leaching experiments, mainly focusing on the distribution of ^{14}C between organic and inorganic species. Prior to the leaching tests solid materials will be well characterized, since the original chemical form of ^{14}C in the steel may have an important effect on ^{14}C speciation in the leaching solution.

12.2 *Steel materials*

Leaching experiments will be conducted with both unirradiated and irradiated steel materials. The unirradiated materials selected for the leaching experiments are crushed and powdered steels and Fe(III) carbide (Fe_3C, cementite), since it has been suggested that ^{14}C arising from nitrogen activation is in the form of carbide in various metals. Two selected steel materials are Loviisa steel, which is identical with the steel in the reactor core components of Loviisa power plant, and Japanese high carbon steel, which is the most pure carbon steel available. Further information of these two steel materials is presented in Table 12.1.

Table 12.1: Properties and element composition of two selected unirradiated steel materials. Loviisa steel was analyzed with optical emission spectrograph (OES) with combustion equipment (LECO) and composition of Japanese high carbon steel is from the manufacturer

Steel Material	Loviisa steel (pipe 91452), Russian	Japanese high carbon steel
Structure	Ti-stabilized austenitic stainless	Carbon steel with highest purity
Composition	[%]	[%]
C	0.08	1.2
Si	0.46	0.1-0.2
Mn	1.25	-
S	0.012	<0.004
P	0.032	<0.025
Cr	17.7	-
Ni	10.6	-
Mo	0.13	-
Cu	0.15	-
Al	0.028	-
W	0.04	-
V	0.03	-
Ti	0.521	-
Co	0.07	-
N_2	0.08	-

The microstructure and chemical composition of Loviisa steel were analyzed with optical microscopy, scanning electron microscope and energy dispersive X-ray spectroscopy (SEM/EDS). The chemical structure was analyzed from a cross section sample of solid Loviisa steel with EDS. Subsequently, the cross section was etched to reveal microstructures of the surface which were then recorded with optical microscopy and SEM. EDS analysis showed that the Loviisa steel composition is within the nominal composition of AISI 321 steel. The SEM analysis showed austenitic steel structure and carbon exists mainly as interstitial atoms in the austenitic steel lattice. Cementite was not observed, instead due to the Ti-stabilization, it was suggested that small amounts of carbon could be in the form of Ti carbide (TiC). The SEM analysis showed also small white precipitates in the etched structures and further EDS analysis showed that precipitates were enriched with Ti and C. Figure 12.1 shows the SEM picture of the surface microstructures of the Loviisa steel.

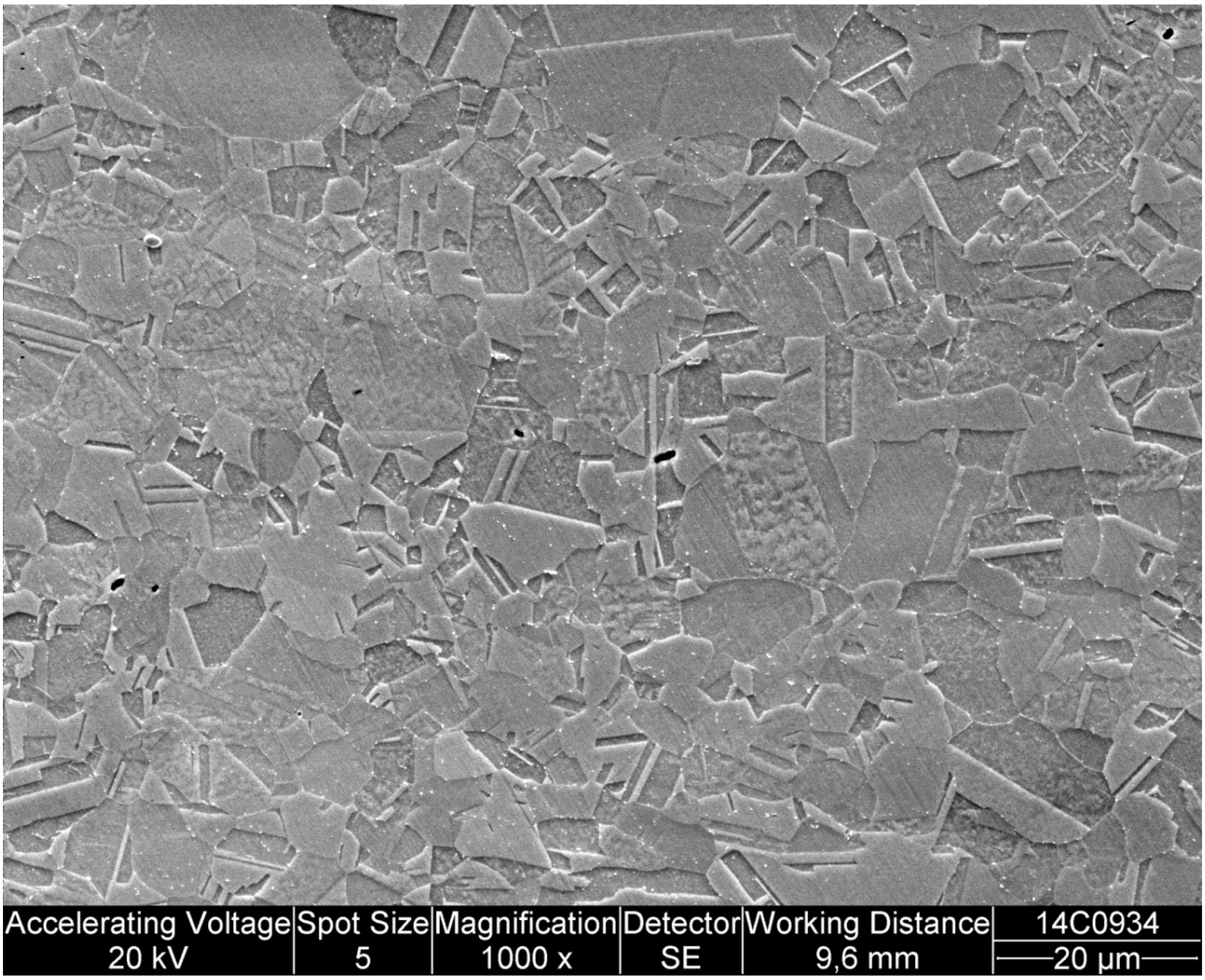


Figure 12.1: SEM picture of the surface microstructures of Loviisa steel

Experiments with irradiated steel material will be conducted with low-active core grid from TVO (Teollisuuden Voima Oyj). Detailed composition and characteristics of this material will be available later 2014.

12.3 Simulated groundwaters

In order to select the most relevant conditions with respect to the final disposal of decommission waste in Finland, simulated groundwaters were chosen as the leaching solution for the experiments. Groundwater samples were collected from a borehole (LPVA5) from the Loviisa site and analyzed. The compositions of prepared simulant groundwaters are based on the composition of this natural groundwater sample from Loviisa site. However, disturbing elements (e.g. redox sensitive elements) and the elements with low concentration were excluded from the simulant waters. The composition of analyzed natural LPVA5 groundwater is presented in Table 12.2.

Table 12.2: The chemical composition of natural groundwater sample (LPVA5) collected from the nuclear power plant site Loviisa. pH of the water was 7.6 in the field and 7.5 afterwards in the laboratory

Element/Species	[mg/L]
Ammonium, NH_4^-	0.89
Bicarbonate, HCO_3^-	104
Barium, Ba	0.037
Boron, B	0.31
Bromine, Br	18
Calcium, Ca	630
Chlorine, Cl	5000
Cobalt, Co	0.002
Fluoride, F	1.1
Iodine, I	0.21
Iron, Fe (total)	1.8
Iron, Fe^{2+}	1.6
Lithium, Li	0.17
Magnesium, Mg	270
Manganese, Mn	3.1
Nickel, Ni	0.019
Potassium, K	25
Silicate, SiO_2	11
Sodium, Na	2200
Strontium, Sr	7.1
Sulphate, SO_4^{2-}	560
Total alkalinity, HCl uptake [mmol/L]	1.7
Total acidity, NaOH uptake [mmol/L]	0.18
Ionic strength [mol/kg]	0.21

The selected compositions of simulant waters were modelled with the geochemical equilibrium code EQ3 to ensure the stability of simulant waters in glove box conditions (argon (Ar) atmosphere, O_2 less than 1 ppm and low CO_2). The final compositions of prepared simulant groundwaters are presented in Table 12.3. The simulant groundwaters were prepared in the glove box from Ar-sparged milliQ water and chemicals with at least PA grade. Two pH values were chosen, pH 12.5 simulates the effect of cement in the repository conditions and pH 8.5 was selected as reference. Prepared simulant waters were held in the glove box several weeks prior to the beginning of the leaching experiments and pH was measured several times to ensure the stability of simulant waters.

Table 12.3: Composition of simulated groundwaters based on natural groundwater composition and geochemical modelling (EQ3). The compositions were modelled for Ar atmosphere with O2 < 1 ppm and low CO2. Simulated groundwaters were prepared with and without HCO3- at pH 8.5 and 12.5

		CA85	CA125	HC85	HC125
pH		8.5	12.5	8.5	12.5
Na^+	[mg/L]	2680	2730	3440	3440
Ca^{2+}	[mg/L]	630	590	-	-
K^+	[mg/L]	25	25	25	25
HCO_3^-	[mg/L]	-	-	104	104
SO_4^{2-}	[mg/L]	560	560	560	560
Cl^-	[mg/L]	4840	4840	4840	4840
Br^-	[mg/L]	18	18	18	18

12.4 *Preliminary leaching experiments*

12.4.1 Pretreatment of the steel materials

For the preliminary leaching tests two previously described materials, Loviisa steel (0.08 % of carbon) and Japanese high carbon steel (1.2 % of carbon), were used. Materials were sawed to small fragments with a band saw and prior to the leaching experiments the fragments were washed with isopropanol and acetone.

12.4.2 Experimental conditions

The batch experiments were conducted in polypropylene vials in a glove box with Ar atmosphere (O_2<1 ppm and low CO_2). In addition to the Ar glove box, test vials were kept in a closed steel container to ensure as homogenous gas phase as possible around the test vials between the samplings. The mass of the solid / leaching solution volume (m/V) ratio was varied including ratios: 50 g/100 mL, 25 g/100 mL and 15 g/200 mL. The simulated groundwaters without carbonate at pH 8.5 and 12.5 were used as leaching solutions. Table 12.4 shows the details of preliminary leaching experiments.

Table 12.4: Experimental conditions of the preliminary leaching experiments

Test code	Solid material	m/V	pH (initial)	pH (70 days)	pH (180 days)	E_h (70 days)
LT-CA125(1)	Loviisa Steel	50 g/100 mL	12.4	12.1	12.2	-223
LT-CA125(2)	Loviisa Steel	25 g/100 mL	12.4	12.2	12.1	-209
LT-CA85(1)	Loviisa Steel	50 g/100 mL	8.5	9.9	9.9	-231
LT-CA85(1)	Loviisa Steel	25 g/100 mL	8.5	9.7	9.8	-228
YHT-CA85(1)	High carbon steel	50 g/100 mL	8.5	9.9	9.7	-413
YHT-CA85(2)	High carbon steel	15 g/200 mL	8.5	9.4	10.6	-483

Table 12.4 shows also the results of E_h measurement (gold electrode, Ag/AgCl/3 M KCl reference) 70 days after initializing the leaching tests. The experiments with high carbon steel at pH 8.5 developed extremely reducing redox conditions with an E_h value lower than -400 mV, which is close to the end of the stability field of water. The results of pH measurements showed that the higher pH 12.5 remained relatively stable during the experiments, but the lower pH 8.5 increased close to the pH value 10.

12.4.3 Sampling and ^{12}C analysis

Five samples were collected after subsequent leaching periods and total amount of dissolved inorganic carbon (TIC) and organic carbon (TOC) were analyzed. The first sampling was done after the leaching time of 75 days. Due to the relatively high measured organic carbon content in the leaching solution, contamination during grinding was suggested and therefore the whole leaching solution was changed to a fresh simulant groundwater solution. Following samplings were done after total leaching times of 160, 256, 368 and 544 days.

After each sampling only the sample volume of fresh leaching solution was added so that the m/V remained the same during the whole experiment.

Samples were filtered before the carbon analysis. The first sample (75 d) was filtered with Whatman™, Puradisc FP30 syringe filters. However, separate tests showed that part of the relatively high amounts of organic carbon measured after the first sampling may result from the polycarbonate filter material. Therefore, the filter type was changed to Sleicher & Schuell, Spartan 30/0.45 RC filters (filter material hydrophilic regenerated cellulose) and the amount of organic carbon decreased significantly.

TIC and TOC analyses were done for filtered samples with TOC analyzer (Analytika Jena N/C UV HS) in Ramboll analytics. The analytical method is based on SFS-EN 1484 standard. Organic carbon in solution is oxidized to carbon dioxide by hard UV radiation supported wet chemical oxidation. Carbon dioxide formed by oxidation is determined directly with non-dispersive infra-red (NDIR) detector. Before the TOC analysis, inorganic carbon is removed from the sample solution by acidification and purging and TIC can be determined separately. Due to the high salinity of the samples, dilution (1:2, 1:3) was necessary. Therefore, the measured contents for inorganic carbon were close to the limit of detection (0.1 mgC/L).

12.4.4 Results

The results of the preliminary leaching tests are presented in Figures 12.2, 12.3 and 12.4a and b. Figure 12.2 shows the results from two leaching tests (m/V 50 g/100 mL and 25 g/100 mL) with Loviisa steel at pH 12.5. Dissolved inorganic and organic carbon contents were measured from filtered samples. The results show that the amount of dissolved organic carbon is higher in both samples. Relatively high organic carbon contents suggest contamination from the filter material (cellulose) or from the grinding process of the solid steel material. The purification after grinding may have not been successful to remove all oil and grease from the grinding process. The bigger mass of solid steel material in the same volume of leaching solution results in higher amount of dissolved carbon, which is expected.

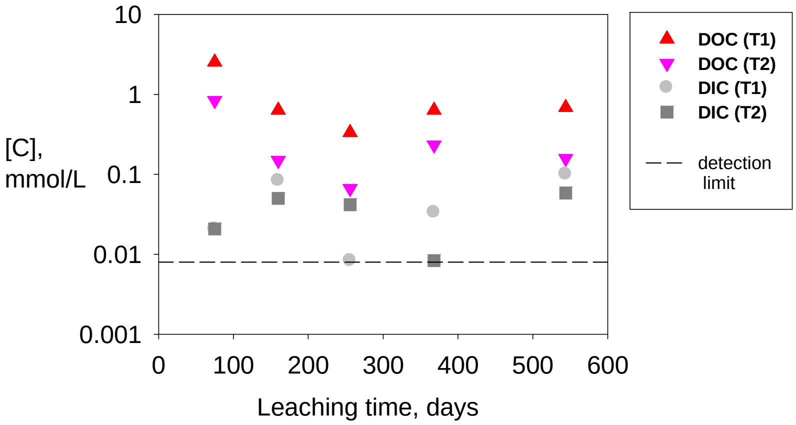


Figure 12.2: Dissolved inorganic (DIC) and organic (DOC) carbon in the preliminary leaching tests of Loviisa steel in simulated groundwater at pH 12.5 as a function of leaching time. T1 represents tests with m/V= 50 g/100 mL and T2 tests with m/V=25 g/100 mL

Figure 12.3 shows the dissolved organic ^{12}C in two leaching tests (m/V 50 g/100 mL and 25 g/100 mL) with Loviisa steel at pH 8.5 and 12.5. The content of organic carbon increases slightly with pH.

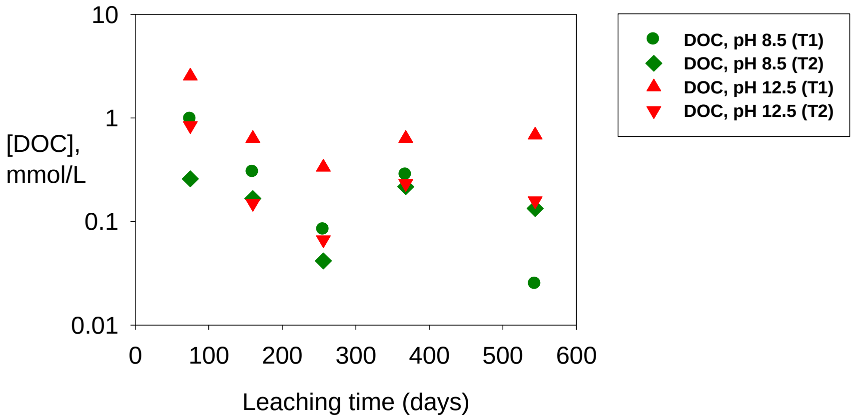


Figure 12.3: Dissolved organic carbon (DOC) in the preliminary leaching tests of Loviisa steel in simulated groundwater at pH 8.5 and 12.5 as a function of leaching time. T1 represents tests with m/V=50 g/100 mL and T2 tests with m/V=25 g/100 mL

Figures 12.4a and b show the measured DOC and DIC in leaching tests with both steel materials (a) Loviisa steel and b) Japanese high carbon steel) at pH 8.5. The DOC is higher than the DIC in both tests. However, the content of inorganic carbon is higher in the tests with High carbon steel than that in the tests with Loviisa steel. The content of organic carbon decreases with increasing leaching time. The content of inorganic carbon increases slightly after 400 days of leaching.

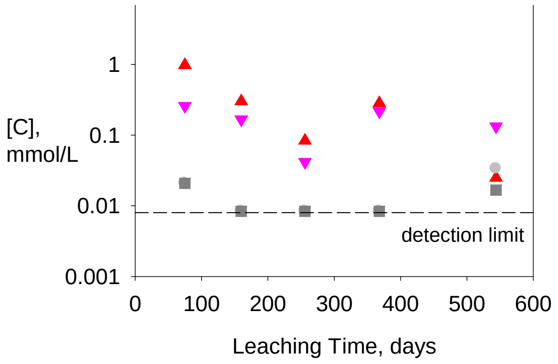


Figure 12.4a: Dissolved organic (red and pink) and dissolved inorganic (grey) carbon in the preliminary leaching tests of Loviisa steel in groundwater at pH 8.5 as a function of leaching time

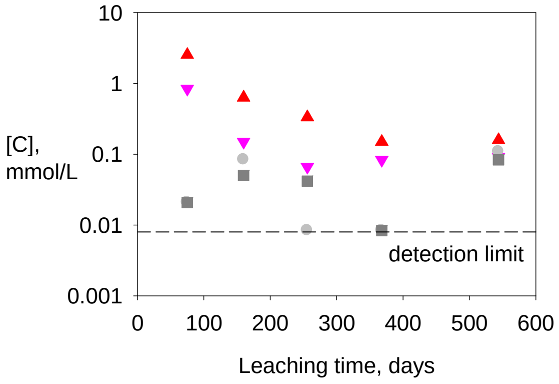


Figure 12.4b: Dissolved organic (red and pink) and dissolved inorganic (grey) carbon in the preliminary leaching tests of High carbon steel in groundwater at pH 8.5 as a function of leaching time

12.5 *Conclusions from the preliminary experiments and future objectives*

Relatively high contents of dissolved organic carbon were measured in the preliminary leaching experiments. Therefore, the possible contamination of the solid materials during the grinding cannot be excluded. To exclude organic species from the possible contamination, new leaching experiments will be conducted with steel powder of similar composition and microstructure as Loviisa steel. This powder will be prepared with gas atomization method and heat treatment to ensure similar microstructure as in the original Loviisa steel. The microstructure of the powders is ensured with optical microscopy, SEM and XRD. This way the grinding procedure is not needed and possible oil or grease contamination can be excluded.

13 Conclusions

In the first project year (October 2013 to September 2014), an extensive literature review on steel corrosion mechanisms and rates as well as the speciation of carbon in iron and steel after release due to corrosion was made within CAST Work Package 2. Further, the development of suited analytical methods to identify and quantify the speciation of ^{14}C in liquid and gaseous samples at extremely low concentrations started early in the project. The design of the corrosion experiments and the sample material to be used have been discussed in two technical meetings.

In the second project year (October 2014 to September 2015), the analytical development will be finalized and lead into a workshop. Further, the majority of the corrosion experiments will be launched in this time span.

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