EUROPEAN
COMMISSION

European
Research Area

CArbon-14 Source Term

CAST

Corrosion of irradiated steel in alkaline conditions: First measurements of the carbon-14 speciation
(D2.19)

E. Wieland, B. Cvetković

Date of issue of this report: 18/5/2018

The project has received funding form the European Union's European Atomic Energy Community's (Euratom) Seventh Framework Programme FP7/2207-2013 under grant agreement no. 604779, the CAST project.

Dissemination Level		
PU	Public	X
RE	Restricted to the partners of the CAST project	
CO	Confidential, only for specific distribution list defined on this document	

EURATOM

CAST – Project Overview

The CAST project (CArbon-14 Source Term) aims to develop understanding of the potential release mechanisms of carbon-14 from radioactive waste materials under conditions relevant to waste packaging and disposal to underground geological disposal facilities. The project focuses on the release of carbon-14 as dissolved and gaseous species from irradiated metals (steels, Zircaloys), irradiated graphite and from ion-exchange materials as dissolved and gaseous species.

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

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

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

CAST		
Work Package: 2	CAST Document no.	Document type:
Task: D2.19	CAST-2018-D2.19	R
Issued by: PSI		Document status:
Internal no.: CAST_Report_D2.19		Final

Document title
Corrosion of irradiated steel in alkaline conditions: First measurements of the carbon-14 speciation

Executive Summary

Carbon-14 is an important radionuclide in the inventory of radioactive waste and is considered to be a significant dose contributing radionuclide in performance assessment. For example, the ^{14}C inventory in the planned cement-based repository for low- and intermediate-level radioactive waste in Switzerland is mainly associated with irradiated steel (~75 %). Therefore, anoxic corrosion of the irradiated steel will determine time-dependent release of ^{14}C-bearing compounds from the cementitious near field into the host rock.

The current situation concerning the carbon species produced in the course of the anoxic corrosion of iron/steel is still unclear. Neither experimental evidence nor thermodynamic modelling allows well-supported conclusions to be drawn regarding the kind of organic compounds formed. The currently unclear situation requires further experimental investigations into the formation of carbon compounds that are produced during the anoxic corrosion of irradiated and non-irradiated iron/steel in conditions relevant to a cement-based repository.

This report summarizes the design of an experiment aimed at identifying the ^{14}C species released during the anoxic corrosion of irradiated steel under the relevant repository conditions and shows the results from the first phase of the project. The project was launched in the framework of the Swiss waste management programme and co-financed by the EU project “CAST”.

List of Contents

1 Introduction

Carbon-14 has been identified as a radionuclide of importance in the inventory of radioactive waste produced in many European countries as well as an important dose contributing radionuclide in radiological assessments [JOHNSON AND SCHWYN, 2008; NAGRA, 2002; NUCLEAR DECOMMISSIONING AUTHORITY, 2012; YIM AND CARRON, 2006]. The half-life of ^{14}C is sufficiently long (5730 y) for its release to be of relevance after repository closure. Carbon-14 is of specific concern due to its potential presence as either dissolved or gaseous species in the disposal facility and the host rock, the high mobility of dissolved carbon compounds in the geosphere caused by weak interaction with mineral surfaces in near neutral conditions, and eventually because it can be incorporated in the human food chain. The chemical form of ^{14}C-bearing species defines the route of release from the engineered system of a geological repository into the host rock. Current safety assessments are based on specific assumptions regarding the rate of ^{14}C release from potential sources, the ^{14}C speciation upon release and the mobility of the different forms of carbon in the cementitious near field and the host rock.

In nuclear power plants ^{14}C is produced in the fuel, in core structural materials, and in reactor coolant due to the interaction of thermal neutrons with the (stable) parent isotopes ^{14}N, ^{17}O and ^{13}C [YIM AND CARON, 2006]. In light water reactors (LWR) the formation of ^{14}C is primarily associated with nitrogen impurities contained in nuclear fuel components and metal components of the core structural materials by ^{14}N activation (^{14}N (n,p) ^{14}C). In Switzerland the main sources of ^{14}C in L/ILW are irradiated metallic nuclear fuel and reactor core components as well as spent filters and ion exchange resins used in the LWRs for the removal of radioactive contaminants in a number of liquid processes and waste streams. Compilations of the activity inventories reveal that in the already existing and future arising of radioactive waste in Switzerland, the ^{14}C inventory is mainly associated with irradiated steel (~75 %) while the ^{14}C portions from nuclear fuel components (e.g. Zircaloy) and waste from the treatment of reactor coolants are much smaller [NAGRA, 2014]. Release of ^{14}C occurs during corrosion of the irradiated steel in the cementitious near field.

Carbon-14 can exist in the inorganic chemical form (CO_2, HCO_3^- and CO_3^{2-}) and organic chemical form in solution or gas phase, respectively, upon release from the irradiated steel parts. In the inorganic form ^{14}C will decay within a disposal facility as $^{14}CO_2$ (and its bases) is strongly retarded in the cementitious near field by precipitation as calcium carbonate or isotopic exchange with stable CO_3^{2-} in calcium carbonate [e.g. ALLARD *et al.*, 1981; BAYLISS *et al.*, 1988; POINTEAU *et al.*, 2003]. Therefore, inorganic ^{14}C has only a negligible effect on dose release. By contrast, dissolved and gaseous species containing ^{14}C are only very weakly retarded by cementitious materials.

Low molecular weight (LMW) oxygenated ^{14}C-bearing organic compounds, e.g. acetate, formate, acetaldehyde, formaldehyde, methanol, and ethanol were found to be formed in the course of steel corrosion (see reviews by [WIELAND AND HUMMEL, 2015] and [SWANTON *et al.*, 2015]). Studies on the uptake of these compounds by mortar indicate weak interaction with cementitious materials [MATSUMOTO *et al.*, 1995; NOSHITA *et al.*, 1996; SASOH, 2008a; WIELAND AND HUMMEL, 2015]. This implies that ^{14}C mainly contributes to dose release due to migration in its organic chemical form in solution, such as the above-mentioned ^{14}C-bearing LMW organics, or as gaseous species.

Information on the chemical form of carbon released during corrosion of metals is limited (see reviews by [WIELAND AND HUMMEL, 2015] and [SWANTON *et al.*, 2015]. Studies with irradiated and non-irradiated stainless steel were conducted in the framework of the Japanese disposal programme for radioactive waste by [YAMAGUCHI *et al.*, 1999], [KANEKO *et al.*, 2003], [SASOH, 2008 b/c], [NOSHITA, 2008], [KANI *et al.*, 2008], [YAMASHITA *et al.*, 2014], and [TAKAHASHI *et al.*, 2014]. Additional information is available from corrosion studies with non-irradiated iron powders carried out in connection with the development of clean-up techniques for chlorinated hydrocarbons using zero-valent iron [HARDY AND GILLHAM, 1996; CAMPBELL *et al.*, 1997; DENG *et al.*,1997; AGRAWAL *et al.*, 2002]. In all these studies both oxidized and reduced hydrocarbons have been observed in iron-water systems in anoxic near neutral to alkaline conditions. The formation of reduced hydrocarbons, such as methane and other volatile compounds, is expected in view of the reducing conditions prevailing at the iron-water interface and as a result of the hydrolysis of carbide species in the iron (see review by [SWANTON *et al*., 2015]). The formation of oxidized hydrocarbons, however, appears to be inconsistent with the negative redox potential at the iron-water interface. All studies observed only organic compounds with a low molecular weight and with a low number of carbon atoms ($C \leq 5$). The current status is that carbon speciation in connection with the anoxic corrosion of iron, steel and Zircaloy is not well understood. In particular, it is unclear why both reduced and oxidized hydrocarbons exist simultaneously in solutions in contact with corroding metals.

Preliminary studies on ^{14}C release from irradiated metals and on the chemical form of ^{14}C were carried out in the past in the framework of the Japanese disposal programme [e.g. YAMAGUCHI *et al*., 1999; KANEKO *et al*., 2003]. Nevertheless, a comprehensive corrosion study with irradiated metals, including also long-term monitoring of the ^{14}C compounds formed, is still missing. Various challenges must be overcome in the design and implementation of a corrosion experiment with irradiated metals in conditions relevant to a cement-based repository (see Section 2). The present study was carried out to implement a well-controlled experiment with irradiated steel in anoxic, alkaline conditions that can be sampled over a longer period of time (i.e. up to few years). This report describes the implementation of the corrosion experiment with irradiated steel and reports results from the first year of sampling.

2 Implementation of the Corrosion Experiment with Irradiated Steel

Figure 1 shows a schematic representation of the set-up of the corrosion experiment with irradiated steel. The corrosion experiment is carried out in a gas-tight autoclave-type reactor assembled behind a lead shielding. Two irradiated steel nut segments (see Section 2.1) are immersed in artificial cement pore water (ACW) which has the chemical composition of $Ca(OH)_2$ saturated alkaline solution (pH = 12.5). The analytical approach involves off-line chromatographic separation of compounds in the fluid and gas phase followed by oxidation of the compounds to prepare samples for ^{14}C measurements with accelerator mass spectrometry (AMS).

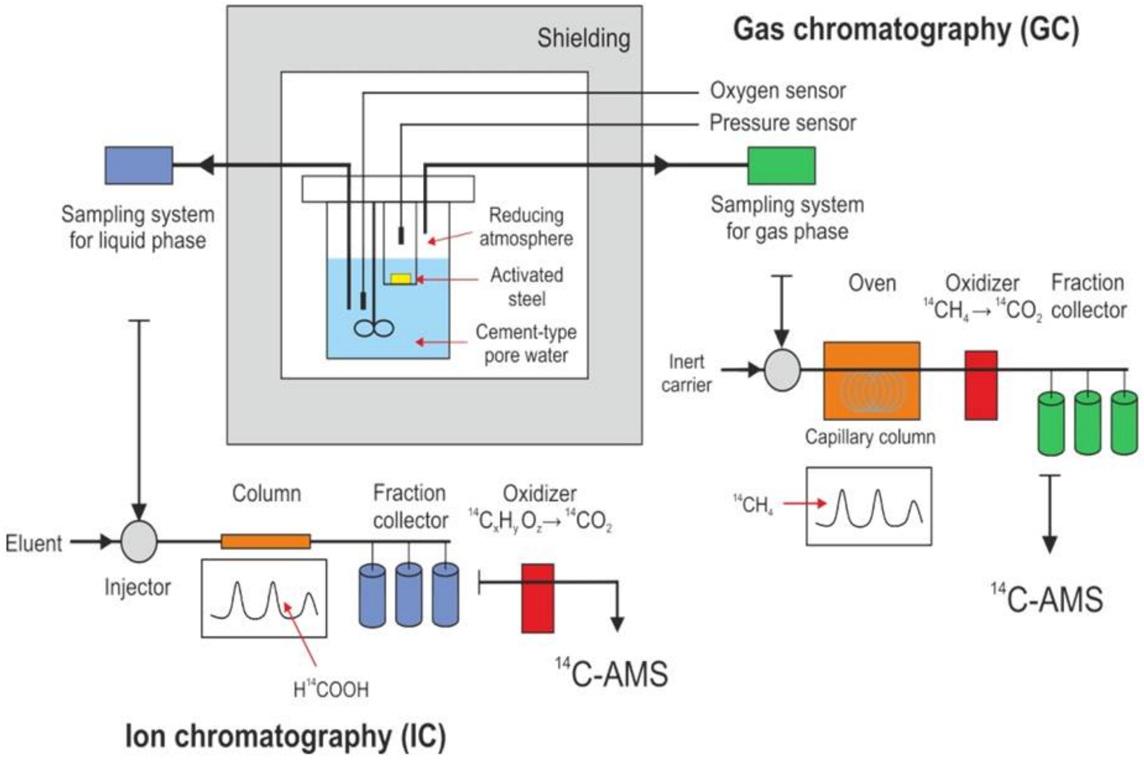

Figure 1: Schematic representation of the set-up and analytical strategy for the planned corrosion experiment with irradiated steel at PSI.

The research plan for the corrosion experiment with irradiated steel was developed in view of the following experimental and analytical constraints:

1) *Limited sample size:* The amount of irradiated steel that was obtained from the nuclear power plant Gösgen in Switzerland (NPP Gösgen) was limited to avoid significant extra costs. Furthermore, it emerged during the evaluation of design options for the corrosion experiment that the existing hot cells in the PSI hot laboratory that would be available for the experiments of irradiated steel were not suitable for emplacement of a corrosion reactor because of the limited space in the hot cell. It was not possible to ensure safe manipulations during operation of the reactor such as fluid and gas sampling. As a consequence, it was decided to assemble the reactor behind a conventional lead shielding, which further limited the amount of irradiated steel used in the experiment. The sample size had to be reduced

in a way that the dose rate in the vicinity of the reactor reached a level in accordance with the regulations and also complied with the rules of the PSI hot laboratory. Dose calculations showed that 5 g irradiated steel at maximum (i.e. one steel nut at most) can be emplaced in a corrosion reactor behind a conventional lead shielding.

2) *Low ^{14}C inventory:* The ^{14}C content of the irradiated stainless steel nuts from the NPP Gösgen was found to be very low (see Section 2.1). Therefore, the ^{14}C inventory of irradiated steel was expected to further limit the concentration of ^{14}C-bearing compounds in the aqueous and gaseous phase inside the reactor.

3) *Slow corrosion:* Iron and steel are in a very passive state in alkaline solutions, such as cement pore water, under fully anoxic conditions and therefore, corrosion rates are expected to be extremely low. Passivation occurs due to the formation of a non-porous oxide film with a thickness of a few nanometres, similar to that in near neutral conditions [SMART *et al.*, 2004; DIOMIDIS, 2014; SWANTON *et al.*, 2015]. Corrosion rates for carbon steel were found to range between 0.1 and 1 µm/a under anoxic alkaline conditions [SMART *et al.*, 2004]. Even lower corrosion rates have been reported for stainless steel and Zircaloy (typically < 0.01 µm/a, range: 0.001 µm/a - 0.02 µm/a; [DIOMIDIS, 2014; SWANTON *et al.*, 2015]).

Scoping calculations showed that the low corrosion rate in combination with the relatively low ^{14}C inventory of the stainless steel nuts and the small amount of material that can be used results in an extremely low concentration of ^{14}C species in the fluid and gas phase during the corrosion experiment [WIELAND AND CVETKOVIĆ, 2015]. This analytical constraint required the development of a very sensitive analytical technique based on the combination of chromatographic separation and ^{14}C detection by ^{14}C AMS.

Carbon-14 AMS measurements were performed on a 200 kV MICADAS (MIni CArbon DAting System) accelerator system (Figure 2) which became operational in May 2013 in the Laboratory for the Analysis of Radiocarbon with AMS (LARA) at the University of Bern [SZIDAT *et al.*, 2014]. In conventional atomic mass spectrometry, samples are atomized and ionized, separated by their mass-to-charge ratio, then measured and/or counted by a detector. However, determination of rare isotopes such as ^{14}C is still not possible using conventional mass spectrometry due to their low natural abundance and high background levels. Substantial technical developments in AMS have allowed the breakthrough of the small device MICADAS for ^{14}C analysis [SYNAL *et al.*, 2007]. The instrument is comparable in terms of precision and detection limit with a large AMS system with the advantage of requiring only small amounts of sample material and allowing short process time. Furthermore, the simplified instrumental set-up reduces running costs and service efforts compared to large AMS systems. The ion source allows targets of solid graphite and gaseous carbon dioxide to be used. The automated gas interface reported by [WACKER *et al.*, 2013a] enables the transfer of carbon dioxide to the gas ion source from different sources, such as sealed glass ampoules, an acidification device for carbonate samples [WACKER *et al.*, 2013b], an elemental analyser [RUFF *et al.*, 2010a] or other combustion instruments [PERRON *et al.*, 2010].

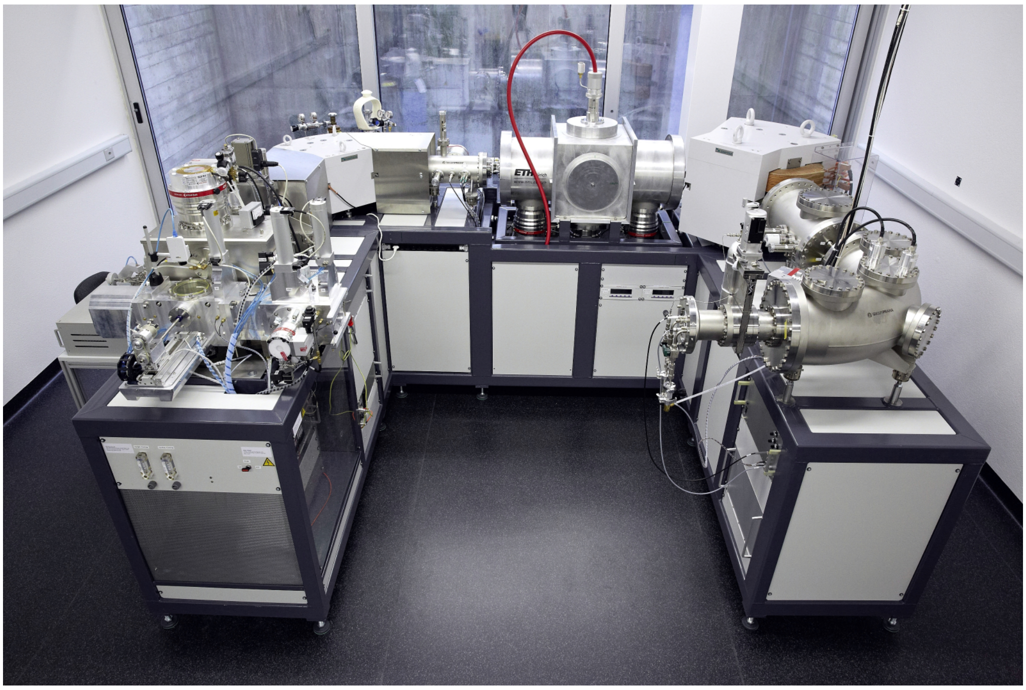

Figure 2: Mini Carbon Dating System (MICADAS) at the Laboratory for the Analysis of Radiocarbon with AMS at the University of Bern (Switzerland).

The main challenges in ^{14}C measurements are isobaric interference (interference from equal mass isotopes of different elements exemplified by ^{14}N in ^{14}C analysis), isotopic interference (interference from equal mass to charge isotopes of different elements), and molecular interference (interference from equal mass to charge molecules, such as $^{12}CH_2^-$, $^{12}CD^-$, or $^{13}CH^-$ in ^{14}C analysis). Most AMS systems employ an electrostatic tandem accelerator that results in a direct improvement in background rejection, resulting in a more than two orders of magnitude increase in the sensitivity of isotope ratio measurements. As the natural abundance of ^{14}C in modern carbon is about 10^{-12} (isotopic ratio of $^{14}C/^{12}C$), a sensitivity of 10^{-15} is a prerequisite for ^{14}C analysis.

Due to the particular requirement, the development of the set-up and analytical techniques for the corrosion experiment and the implementation of the experiment with irradiated steel were divided into different tasks:

1) Determination of the ^{14}C inventory of the irradiated steel nuts (Section 2.1);
2) Development of analytical methods for the identification and quantification of dissolved and gaseous stable carbon and ^{14}C organic compounds (Section 2.2);
3) Development of the experimental set-up (Section 2.3).

2.1 *Characterization of Irradiated Steel*

The corrosion experiment was carried out using irradiated steel that was obtained from the nuclear power plant Gösgen in Switzerland (NPP Gösgen). In the course of the annual maintenance work in NPP Gösgen five guide-tube nuts (~ 5 g each) had been retrieved from the storage pool and transferred to the hot laboratory of PSI in 2012 (Figure 3). The nuts, made of stainless steel, had been mounted at the top and bottom end of fuel rods and subjected to irradiation in the nuclear reactor core of NPP Gösgen for about two years. The activation cycle was terminated in June 2011. Each nut had a contact dose rate of ~ 150 mSv/h. Two nuts were processed in the PSI hot laboratory to prepare small specimens for laboratory experiments [SCHUMANN *et al*., 2014].

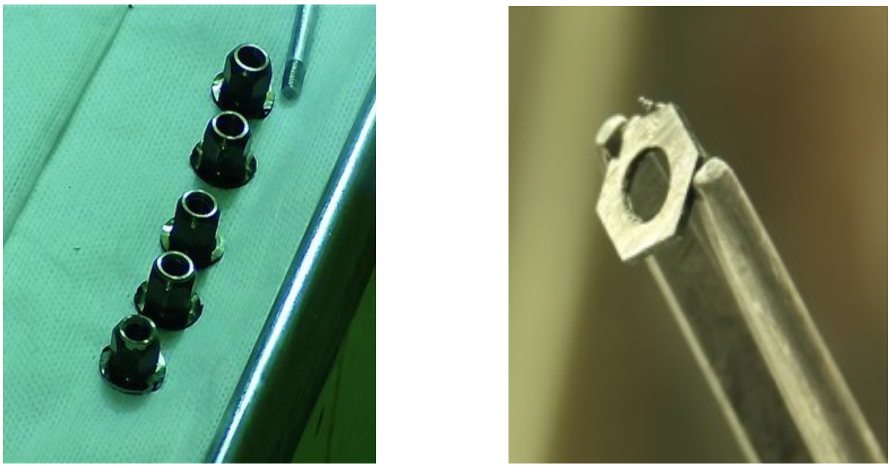

Figure 3: Left: Irradiated steel nuts obtained from NPP Gösgen; Right: Specimens prepared from a steel nut for use in the experiments.

The ^{14}C content of the irradiated stainless steel nuts from the NPP Gösgen was determined experimentally using a wet chemistry digestion technique combined with liquid scintillation counting for ^{14}C activity measurements [SCHUMANN *et al.*, 2014]. Details of the experimental method and a comparison with theoretical predictions of the ^{14}C content made on the basis of a Monte Carlo reactor model for NPP Gösgen are given elsewhere [SCHUMANN *et al.*, 2014]. The ^{14}C activity was determined to be 17.8 ± 2.5 kBq per gram steel nut, which corresponds to a ^{14}C content of ~ 0.107 µg/g. In contrast, the content of stable carbon of stainless steel is much higher. While the type of steel used to fabricate the guide-tube nuts is not exactly known, there is evidence that they were produced from one of the following alloys: X6CrNiTi18-10, X6CrNiNb18-10 or X6CrNiMoTi17-12-2. According to DIN 17440 specifications the carbon content of all the aforementioned steels is ≤ 0.08 weight (wt.)-%.

2.2 *Analytical Techniques*

Test experiments with non-irradiated iron powders showed that only a limited number of organic compounds are formed during steel corrosion. In particular, these are small organic compounds up to C5 either dissolved in the liquid phase, such as carboxylates, alcohols and aldehydes, or volatile compounds enriched in the gas phase, such as alkanes and alkenes [WIELAND AND HUMMEL, 2015; CVETKOVIĆ *et al.*, 2018a]. Dissolved organic compounds can be separated using either high performance liquid chromatography (HPLC) [Takahashi *et al*., 2014] or ion chromatography (IC) [Chi and Huddersman, 2007]. Gas chromatography is the classical technique used to separate and, in combination with mass spectrometry (MS), to identify volatile compounds. In this study high performance ion exchange chromatography coupled to MS (HPIEC-MS) and gas chromatography coupled to MS (GC-MS) were employed to separate and characterize dissolved and gaseous organic compounds.

Scoping calculations revealed that the expected concentrations of the ^{14}C-bearing organic compounds in the planned corrosion experiment with irradiated steel by using the available experimental set-up was very low, i.e. in the sub ppq range (parts-per-quadrillion, 10^{-15}). The required sensitivity of the analytical method for a compound-specific characterization of the fluid and gas phase is thus expected to be several orders of magnitude lower than the detection limits provided by classical detection systems such as MS. Furthermore, it is also lower than the detection limit of ^{14}C activity measurements with liquid scintillation counting (LSC). Therefore, an analytical method based on compound-specific ^{14}C AMS was developed for the identification and quantification of small ^{14}C-bearing organic molecules in the framework of the corrosion experiment with irradiated steel. The main reason is that ^{14}C AMS is an extremely sensitive ^{14}C-counting device (limit of detection (LOD): 10^{-18} g ^{14}C). In combination with chromatographic separation, such as HPIEC or GC, respectively, this should allow ^{14}C-bearing compounds to be determined at extremely low concentrations, i.e. at a concentration level anticipated based on the experimental set-up. As previously mentioned, these low ^{14}C concentrations are caused by the experimental constraints such as the very low corrosion rate of steel in alkaline solution, the small amount of irradiated steel that can be used, the low ^{14}C inventory of irradiated steel, the small volumes of the gaseous and liquid samples that are available from sampling, and further sample dilution during the chromatographic separation process by eluent or carrier gas.

Throughout this study the solutions were prepared by using Fluka or Merck analytical-grade (“pro analysis”) chemicals. Ultrapure water (Milli-Q water; 18.2 MΩ · cm) was generated by a Milli-Q Gradient A10 purification system (Millipore, Bedford, MA, USA) and used for the preparation of solutions and standards.

2.2.1 Ion Chromatography

HPIEC analysis was performed by using an ICS-5000 ion chromatography system (Dionex/Thermo Fisher, Sunnyvale, CA, USA) which consists of an AS 50 auto sampler, a 250 mm × 2 mm i.d. IonPac AS11-HC column in combination with the corresponding guard column, an EG 40 eluent generator, a 2 mm AERS–500 suppressor operated in the external water mode, a CD 25 conductivity detector (CD) and a coupled MSQ™ Plus MS (Thermo Fisher, Sunnyvale, CA, USA). The MS is equipped with an atmospheric pressure ionization (API) interface and is operated in the negative electrospray ionization (ESI) mode. The analytical column was operated at 30 °C (column thermostat TCC-100, Dionex/Thermo Fisher, Sunnyvale, CA, USA). Data acquisition, processing and system control of the IC are accomplished with the Chromeleon 6.80 (SR 11d) software, while the Xcalibur Finnigan Surveyor MSQ 1.1 ELMO is the MS control software.

235 µL of the liquid sample collected from the reactor was spiked with 15 µL of an internal standard solution (see below), injected via full loop injection (14 µL) into the ion chromatograph and eluted at the flow rate of 0.25 mL/min. The optimal mobile phase was a KOH solution produced by the eluent generator with the following gradient scheme: 0-15 min: isocratic with 1.0 mM; 15-35 min: gradient from 1 to 30 mM; 35 - 40 min: isocratic with 30 mM; 40 - 41 min: gradient from 30 to 1 mM; 41 - 50 min: isocratic with 1.0 mM. The MS was operated at the ESI probe temperature of 500 °C. The cone voltages varied from 30 to 50 V, and the ESI needle voltage was -2.5 kV. High purity N_2 (grade 6.5 Messer Schweiz AG, Lenzburg, Switzerland), which was supplied by a separate N_2 tank served as protecting and nebulizing gas, maintaining a N_2 pressure of 5.5 bar. Parameters used for MS detection were as follows: RF-lens: -1.0 V; mass span: 0.5 u; dwell-time: 0.25 s. The analytes were monitored in the selected ion-monitoring (SIM) mode by observing the m/z values of the compounds of interest at different time intervals. Negative ion full scan mass spectra were recorded over the m/z range from 20 to 300 using a scan time of 0.5 s. Peak areas (counts min^{-1}) were used for quantification.

Aqueous calibration standards for the HPIEC measurements were prepared as follows: 50 mL stock solutions of each compound, i.e. sodium formate (puriss. p.a.), sodium acetate (puriss. p.a.) and glycolic acid (99 %) (Sigma Aldrich, Buchs, Switzerland), malonic acid (reagent grade 99.5%, Alfa Aeser, Karlsruhe, Germany), oxalic acid (anhydrous for synthesis, Merck Schuchardt OHG, Hohenbrunn, Germany), and sodium l-lactate (> 98 %, Alfa Aeser, Karlsruhe, Germany) were prepared in ultrapure water to obtain a concentration of 10 mM. A multi-component stock solution (10 mL) containing sodium acetate, sodium formate, malonic acid, oxalic acid, glycolic acid and sodium l-lactate with concentrations 200, 200, 30, 30, 30 and 30 µM, respectively, was prepared by further diluting the individual stock solutions with ultrapure water. 500 µL calibration standards were prepared from this multi-component stock solution in the concentration ranges 0 - 150 µM (acetic and formic acids) and 0 - 30 µM (malonic, oxalic, glycolic, and lactic acids). The standards also contained four isotopic labelled internal standards ([d]formic acid, [2,2,2-d_3]acetic acid-, [1,3-$^{13}C_2$]malonic acid and [$^{13}C_2$]oxalic acid dihydrate; purity grade for all labelled compounds > 99.5 %; all available from Sigma Aldrich, Buchs, Switzerland) at concentrations 30, 30, 15, and 15 µM, respectively. All solutions were stored at 4 °C in the refrigerator.

The dynamic range of the analytical method and reproducibility were checked using standards. The limit of detection (LOD) and the limit of quantification (LOQ) were determined from measurements of five blank replicates.

2.2.2 Gas Chromatography

A GC-MS system consisting of a TRACE™ GC Ultra gas chromatograph (Thermo Fisher Scientific Inc., Waltham, USA) equipped with an ISQ mass spectrometer (Thermo Fisher Scientific Inc., Waltham, USA) in the electron ionization (EI) mode was used. The system is operated with the Thermo Xcalibur 3.0.63 (Thermo Fisher Scientific Inc., Waltham, USA) and the PAL Sample Control (PAL3 System software, CTC Analytics AG, Switzerland) software for data acquisition and processing.

Hydrocarbons were determined with GC-MS by using the headspace method. After 30 min incubation of the sample vial at 50 °C under agitation, 2 mL headspace gas phase was injected into the GC system by using a gas-tight syringe which had been pre-heated to 85 °C. The injection was performed in split mode with a split ratio of 1:18. Helium at a constant flow of 2.0 mL/min was used as carrier gas (Carbagas, AG, Basel, Switzerland, He grade 5.0), and a Restek Rt®-Msieve 5A column (30 m × 0.32 mm with 0.025 mm film) was used for the separation of hydrocarbons. The following oven temperature program was applied: Initial temperature 55 °C isothermal for 4 min, heating up at a rate of 20 °C/min to 290 °C where temperature was kept constant for 10 min, resulting in an overall run time of 26 min.

The MS was operated at standard EI parameters: 70 eV collision energy and 230 °C MS source temperature. The data were acquired in the SIM mode.

Nitrogen (Carbagas, AG, Basel, Switzerland, grade 5.0), helium (Carbagas, AG, Basel, Switzerland, grade 5.0) and argon (Carbagas, AG, Basel, Switzerland, grade 4.6) were used to operate the system or prepare dilutions of standards, respectively. The following reference gases were used for calibration: methane (puriss.; 4.5 (GC) from Sigma Aldrich, Buchs, Switzerland) and a reference gas mixture (Westfalen AG, Münster, Germany) containing 94.8 ppm methane (2.5), 98.0 ppm ethane (2.0), 94.1 ppm propane (2.5), 101.0 ppm n-butane (2.5), 98.5 ppm ethene (2.5), 98.3 ppm acetylene (2.6) and 96.2 ppm propene (2.5) in nitrogen 5.0.

The reference gas mixture was diluted with nitrogen in headspace vials to prepare calibration standards. These samples along with system suitability test (SST) samples were prepared as follows: The gas samples were released into a gas-sampling bag (0.5 L, SKC Limited, Dorset, UK) to achieve ambient pressure. Prior to analysis a headspace vial was twice evacuated and flushed with nitrogen. After the purging procedure 10 mL of the sample were taken from the gas-sampling bag and injected into the purged and evacuated 20 mL headspace vial by using a gas-tight syringe equipped with a valve (Hamilton AG, Bonaduz, Switzerland). A second gas-sampling bag filled with nitrogen was connected to the vial for 5 seconds to achieve pressure compensation in the sample vial. For calibration a gas-sampling bag was filled with the reference gas mixture (see Section 3.2.1). Between 0.3

and 10 mL volume of the calibration gas was withdrawn (valve equipped gas-tight syringe, Hamilton AG, Bonaduz, Switzerland) and injected into a purged and evacuated 20 mL headspace vial. Prior to the headspace analysis pressure compensation in the vial was allowed by using a second gas-sampling bag filled with nitrogen, which was connected to the vial for 5 seconds. For the SST samples a reference gas volume of 10 mL was transferred. Blank samples were prepared in the same way, but without injection of reference gas into the vials.

The dynamic range of the method and reproducibility were determined using standards. LOD and LOQ were determined from measurements of five blank replicates.

2.2.3 Compound-specific Carbon-14 AMS of Dissolved Species

Chromatographic separation of the dissolved organic compounds was carried out by using the ICS-5000 ion chromatography system described above and operated in the same conditions as outlined in Section 2.2.1. An aliquot of 800 µL fluid sampled from the reactor was transferred into a pre-cleaned IC-vial and spiked with 2 µL of a 6 mM ^{14}C-free acetate solution (stable carbon carrier). The solution was injected into the IC system via the injection loop (14 µL), separated and eluted at a flow rate of 0.25 mL/min. Sampling of the individual fractions of carboxylic acids was carried out by connecting the outlet of the TCD to a fraction collector (Foxy Jr.® Fraction collector, Teledyne Isco, Lincoln, NE, USA). Fractions were collected based on the retention times of the single compounds, which were determined prior to chromatographic separation by using suitable non-labelled standards (Section 2.2.1). The individual fractions (acetate, formate, malonate, oxalate, lactate) were directly collected into pre-washed and weighed polypropylene(PP)-IC-vials. The fractions were then spiked with 1.25 M ^{14}C-free acetate solution to yield a stable carbon concentration of 2 µg/µL required for AMS analysis. Fractionation was performed in triplicates.

The following procedure was applied to purge the IC after each sample separation by injecting ultrapure water and using an adapted elution programme (0 - 1 min: isocratic with 1.0 mM; 1 - 2.5 min: gradient from 1 → 30 mM; 2.5 - 4.5 min: isocratic with 30 mM; 4.5 - 5.0 min: gradient from 30 → 1 mM; 5 - 11.5 min: isocratic 1 mM).

Carbon-14 AMS measurements were performed on the MICADAS at the LARA at the University of Bern. The samples were injected into an elemental analyser (EA) coupled online with the MICADAS via a gas interface, which is described elsewhere [RUFF *et al.*, 2010a; RUFF *et al.*, 2010b; SALAZAR *et al.*, 2015]. Briefly, liquid samples (10 µL) or standards, respectively, were tightly packed in tin foil for flash combustion and loaded into the oxidation oven of the EA (ELEMENTAR, Hanau, Germany) at 850 °C by an autosampler and combusted with a pulse of oxygen. The EA directs the gases through a water trap containing Sicapent (Merck, Darmstadt, Germany) and through a zeolite trap (zeolite X13, Sigma Aldrich, Schnelldorf, Germany), which is heated up stepwise to release N_2, CO_2 and residual gases consecutively. The outlet of the EA is connected to a gas interface system (GIS) through a 1/1600 O.D. tubing (10 m long) and the flow is directed to a second zeolite trap located at the GIS at 80 mL/min. The GIS trap is gradually heated to 450 °C and releases the CO_2 into a syringe of known volume. A manometer is used to determine the amount of carbon. Helium is added to make a mixture of 10 % CO_2 at ~ 0.16 MPa, and eventually, the mix is transferred into the gas ion source of the MICADAS at a flow rate of ~ 40 µL/min. Simultaneously with the measurement, a flushing step is applied to the EA-GIS for 4 min which consists of running the EA at 100 mL/min without adding a sample, and heating up the CO_2 trap of the EA. This high flow is directed to the GIS trap which, at the same time, is heated up for flushing. The entire procedure is automatically controlled by a LabView program, which is based on an earlier version reported by [WACKER *et al.*, 2013a]. The results can be corrected for cross-contamination as the carrier over effect is relatively constant for our working range of $^{14}C/^{12}C$ ratios.

The standards were solid crystals of sodium acetate (fossil; p.a., Merck, Darmstadt, Germany), C5, C6 and C7 from IAEA and oxalic acid II from NIST (SRM 4990C) with $^{14}C/^{12}C$ ratios of 23.05 ± 0.02 pMC, 150.61 ± 0.11, 49.35 ± 0.12 pMC and 134.07 ± 0.05 pMC, respectively.

The results reported in this study are presented in terms of fraction modern ($F^{14}C$) for the radiocarbon measurements as well as in molarity (mol ^{14}C/L) and activity (Bq/L), whereof the latter units are dependent on conditions of the experiment, such as sample weight, volume of leaching solution and addition of carrier. For the experimental parameters applied in this study the following conversion of units can be used:

$$1\ F^{14}C \equiv 2.74 \cdot 10^{-12}\ g\ ^{14}C/L = 195.7\ fmol\ ^{14}C/L = 0.452\ Bq/L \qquad (1)$$

Blank samples were prepared from the ^{14}C-free sodium acetate solution (2 µg stable carbon/µL). The blanks were run to identify possible contaminations and were subjected to the same treatments as the samples. Furthermore, blank samples were run during the HPIEC analysis and prepared for each set of injections. The blank samples were either prepared in ultrapure water or artificial cement porewater that had been passed through an OnGuard cartridge (Section 2.3.3). The blanks were treated and injected in the same conditions as the subsequent samples prepared for the AMS analysis and fractions were collected at the retention time of the targeted fractions and analysed by AMS along with these fractions.

Detection limits and performance of the MICADAS were reported by [SZIDAT *et al.*, 2014]. Determination of recovery and reproducibility of the compound-specific ^{14}C AMS analytical approach for dissolved organic compounds was reported by [CVETKOVIĆ *et al.*, 2018b].

2.2.4 Total Radiocarbon by ^{14}C AMS

For the determination of the total ^{14}C concentration an aliquot of 1 mL solution was transferred into a 4.5 mL glass vial (Labco Limited, Lampeter, UK) in the glove box with N_2 atmosphere. The vial was tightly closed and directly used for AMS analysis. ^{14}C AMS analysis was performed as describe in the previous section.

2.2.5 Total Organic Radiocarbon (TO^{14}C) by ^{14}C AMS

0.8 mL of the liquid sample after cartridge treatment was transferred into an IC vial and spiked with the appropriate volume of 1.25 M ^{14}C-free acetate solution to give a stable carbon concentration of 2 µg/µL. The vial was tightly closed and directly used for AMS analysis. ^{14}C AMS analysis was performed as describe in Section 2.2.3.

2.2.6 Radioanalysis (γ and β counting)

The activity of ^{60}Co was determined by using a Packard Cobra 5003 auto gamma counter and the energy window between 1050 and 1400 keV. Samples were prepared by transferring a 1.5 mL aliquot into a gamma vial. The samples were diluted to a total volume of 5 mL with ultrapure water. Four calibration standards in the appropriate concentration range were prepared from a ^{60}Co source solution (Eckert & Ziegler Isotope Products Valencia, USA). A count rate of ~ 21 cpm was determined in 5 mL ultrapure water.

Liquid scintillation counting (LSC) is the standard method used to determine the ^{14}C activity. LSC analysis was carried out as follows: The 5 mL aliquot previously used for gamma counting was mixed with 15 mL scintillator (Ultima Gold XR, Packard Bioscience S.A.). Beta counting was carried out using a Canberra Packard Tricarb 2250 CA LSC and the energy window between 4 and 65 keV. Standards for radioassay were prepared in the same manner by adding appropriate volumes of ^{14}C acetate tracer solution to 5 mL acidified ACW and 15 mL scintillator. The count statistics were typically $2\sigma \leq 2\%$ or better. A count rate of ~ 25 cpm was determined for 5 mL ACW blanks.

A series of calibration measurements were performed on samples containing both ^{60}Co and ^{14}C with the aim of determining the contribution of ^{60}Co to the beta spectrum of ^{14}C. To this end, ^{60}Co standards were analysed by both gamma and beta counting and a conversion factor accounting for the activity contribution of ^{60}Co to the ^{14}C spectrum in the energy window between 4 and 65 keV was determined.

2.2.7 Non-purgeable Organic Carbon (NPOC)

The concentration of non-purgeable organic carbon (NPOC) was determined on 2.5 ml cartridge-treated sample solutions using a Shimadzu TOC-WP® analyser. The samples were acidified with 20 % H_3PO_4 prior to analysis. Determination of NPOC is based on UV-promoted persulfate wet oxidation and detection of CO_2 by infrared (IR) detection (for further details see [GLAUS AND VAN LOON, 2003]). The samples were diluted with ultrapure water to perform the measurements in the dynamic range of the method. The samples were analysed along with 6 standard solutions with carbon concentrations ranging between 1 mg/L and 30 mg/L. The detection limit was ~ 0.5 mg/L carbon.

2.3 Experimental Set-up

Two irradiated steel nut specimens were used to carry out the corrosion experiment (Figure 3, right) (Section 2.1). Each ~1 g specimen had a contact dose rate of ~30 mSv/h which required an experimental set-up based on a shielded reactor system.

2.3.1 Reactor System

The experimental set-up consists of a custom-made gas-tight overpressure reactor (stirred autoclave type “Versoclave Type 3”, Büchi AG, Uster, Switzerland) placed inside an in-house made cage with a 10 cm thick lead shielding (Figure 4). The reactor has a PEEK inlet and is equipped with a digital pressure transmitter, a temperature sensor and a sensor to detect dissolved oxygen (Visiferm DO Arc, Hamilton, USA). Leak tests confirmed gas-tightness of the reactor (Figure 5). The overpressure reactor is designed in such a way that all manipulations necessary for regular sampling can be carried out outside the lead shielding to minimize exposure to radiation (Figure 4).

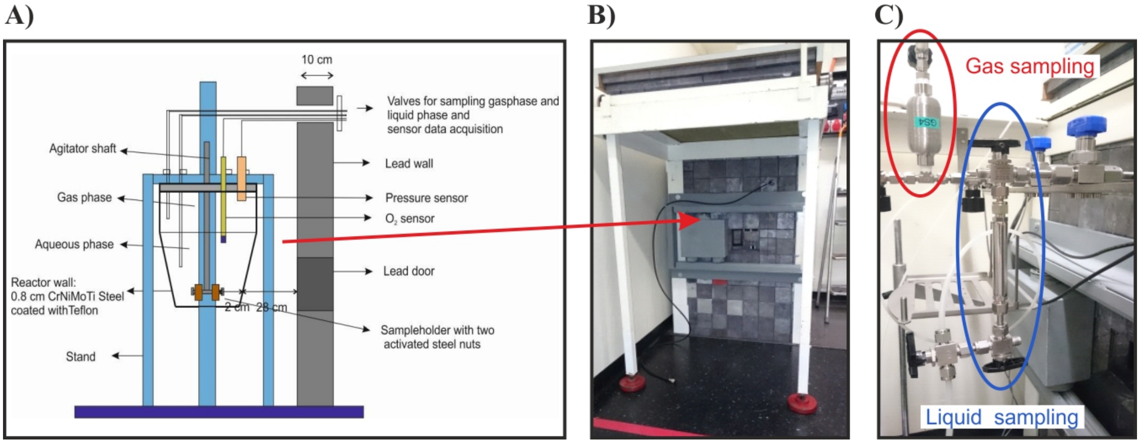

Figure 4: A) Sketch of the reactor, B) picture of the lead shielding with door, and C) the sampling system for liquid and gaseous samples placed outside the shielding.

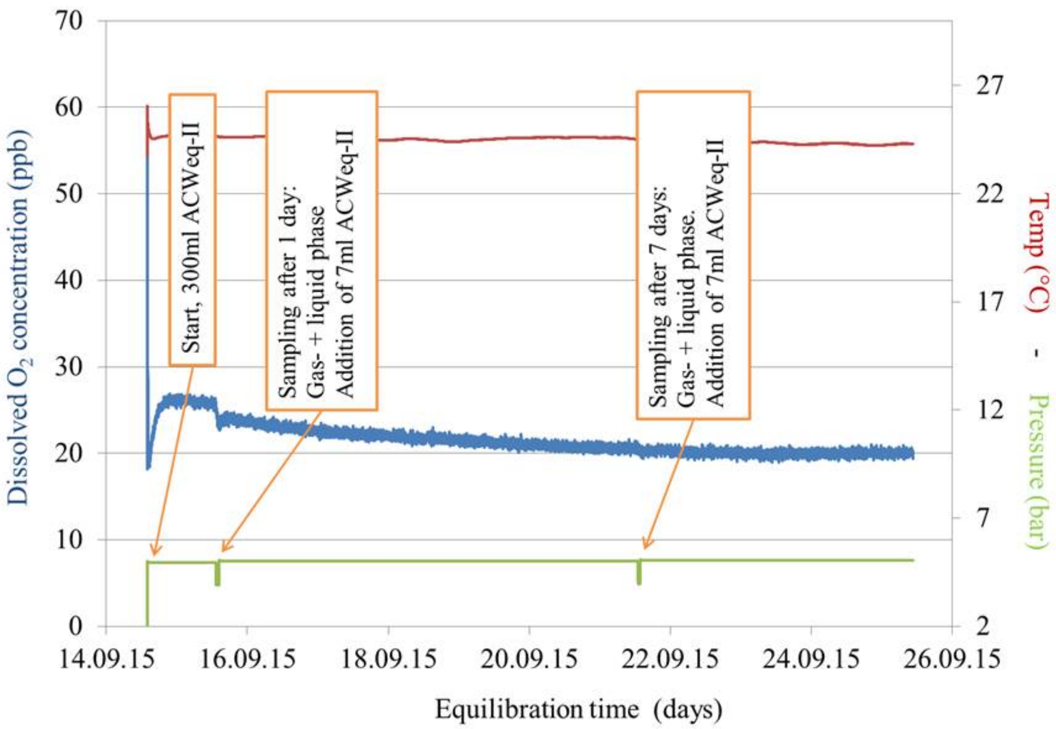

Figure 5: Monitoring pressure (in green), temperature (in red) and O_2 concentration (in blue) during a first sampling test experiment.

2.3.2 Start of Experiment

Artificial cement pore water (ACW) with pH = 12.5 (saturated w.r.t. portlandite) was prepared as follows: CaO was prepared by heating $CaCO_3$ (Merck "pro analysis") at 1000°C until the weight remained constant. 2 g CaO was added to 1000 mL degassed ultrapure water, which was prepared by boiling Milli-Q water under a N_2 purge for 1 h. The suspension was equilibrated for 2 days in a glove box with N_2 atmosphere, left standing for 14 h, filtered under N_2 atmosphere through 100 nm polyethersulfone membrane filters (Criticap-M™, Gelman Science, USA) and stored under the inert atmosphere conditions until further use.

The reactor vessel was pre-washed with ultrapure water and ACW. After closing the reactor and purging it with N_2, 300 mL ACW was introduced. To this end, a gas-tight metallic sample container (500 mL) was evacuated, purged with N_2 and again evacuated to draw in 300 mL ACW under the inert atmosphere conditions. The container was connected to the in-outlet of the sampling system for liquids and the solution transferred into the reactor by applying a slight N_2 gas overpressure. After closing the inlet valve an overpressure of 4 bar was applied to the reactor. The solution was regularly sampled over a time period of 14 days and analysed for total ^{14}C by AMS, carboxylic acids by HPIEC and NPOC with the aim of determining background activities and concentrations. Sampling was carried out as described in Section 2.3.3.

The corrosion experiment was started after completely removing the ACW solution used for the background tests. Two irradiated steel nut specimens (Figure 3) were mounted to the sample holder of the stirring unit (Figure 4). 300 mL ACW was transferred into the reactor. A pressure of 5 bar N_2 was applied to the gas volume (200 mL). The system was equilibrated for 2 days. Then, the entire volume of 300 mL ACW was sampled and discarded (not analysed). 300 mL fresh ACW solution was transferred into the reactor, and pressure was adjusted to 5 bar N_2. The solution was regularly sampled after the time intervals given in Table 2 and analysed for the parameters listed in Tables 2 – 4.

2.3.3 Sampling

7 mL sampling tubes made of stainless steel were used to store the aqueous samples withdrawn from the corrosion reactor. Each tube is equipped with two valves at the in- and outlet and was connected to the liquid outlet valve of the corrosion reactor, evacuated and purged with N_2 for at least three times to remove oxygen. Fluid was withdrawn from the reactor by opening the valves in-between the reactor and the evacuated sampling tube. The tube was closed, disconnected from the reactor and transferred into a glove box with N_2 atmosphere for further handling. The sampling tube was weighed before and after sampling to determine the exact sample volume.

The valves of the sampling tube were opened and the alkaline solution released into a pre-cleaned 20 mL vial in the glove box with N_2 atmosphere. The sample was split into two portions: One portion was directly used for further analysis (2.5 mL; no pre-treatment) and the second portion (4.5 mL) was subjected to a cartridge pre-treatment (OnGuard Ag/Ba/H-cartridge, Dionex, Sunnyvale, CA, USA) to remove interfering anions (e.g. Cl^-) and to adjust pH ~ 6 (Figure 6).

The non-pretreated and cartridge-treated aliquots were analysed using the analytical methods shown in Figure 6 and described in detail in Section 2.2.

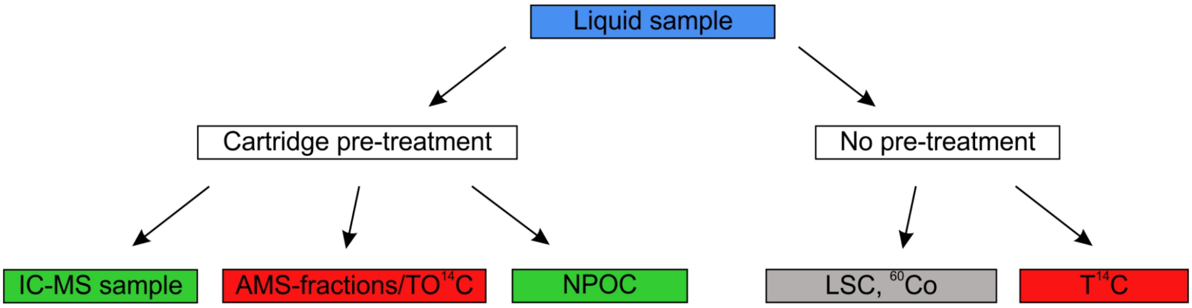

Figure 6: Flow chart of sample treatment and analysis (see text).

Gas samples were collected using a 50 mL gas-collecting tube, which was connected to the gas outlet of the corrosion reactor. The gas-collecting tube was evacuated and purged with nitrogen for at least three times prior to the sampling. The gas samples were collected instantaneously by opening the valves in-between reactor and the gas-collecting tube due to the applied 5 bar pressure in the reactor.

The gas samples were released from the gas-collecting tube into a plastic gas-sampling bag (0.5 L gas bag, SKC Limited, Dorset, UK) to allow pressure balance. For the analysis a head-space vial was evacuated and a 10 mL sample withdrawn from the gas-sampling bag was injected through the septum by using a gas-tight syringe equipped with a valve (Hamilton AG, Bonaduz, Switzerland). A second gas-sampling bag filled with nitrogen was connected to the GC vial for 5 seconds to allow pressure compensation in the sample vial. The sample was injected into the GC-MS system by using the headspace method (Section 2.2.2).

After sampling aqueous and gaseous phase 7 mL fresh ACW solution was transferred into the reactor via the sampling tube by applying N_2 overpressure. The gas pressure in the reactor was then adjusted to its initial value (5 bar N_2 pressure).

Pressure, temperature and O_2 concentration were continuously monitored during the sampling process.

2.3.4 Sample Preparation by Freeze-drying

The concentrations of the ^{14}C-containing organic compounds in the individual IC-fractions were below the detection limit of ^{14}C AMS for the first series of samplings. As a consequence, a pre-concentration step was developed on the basis of a freeze-drying procedure as follows: 3 or 4 replicates of each compound were collected in pre-cleaned and weighed IC vials after IC separation (500 µL fraction volume) and 1 µL 0.1 M NaOH was added to adjust pH ~ 11. At this pH loss of carboxylates by evaporation was negligible. All samples were immediately frozen in liquid nitrogen, transferred into the freeze dryer (Alpha 1-2 LDplus, Christ, Osterode, Germany), dried for 3 hours and weighed to determine the pre-concentration factor. Then, the replicates were combined to one single sample and subjected to an additional freeze-drying step for about 3 hours. After the second freeze-drying step the samples were weighed to determine the overall pre-concentration factor. The samples were unfrozen and the pH was re-adjusted to ~ 5 - 6 by adding 1 µL 0.1 M HCl.

In addition to the IC fractions blank samples prepared from ultrapure water were treated in the same manner to account for possible contaminations during the pre-concentration step.

Eventually, all samples analysed by AMS were spiked with the fossil stable carbon carrier (acetate) to give a final carbon concentration of 2 µg/µL.

3 Results

The background parameters of the reactor system (e.g. ^{14}C activities, concentration of organic compounds etc.) were determined before the corrosion experiment with irradiated steel was started. To this end 300 mL ACW solution was introduced via the sampling system into the previously pre-washed and closed reactor and 4 bar N_2 overpressure was applied. The solution was regularly sampled over a period of 15 days (Table 1). After evaluating the background conditions the corrosion experiment with the irradiated steel nut specimens was started as described above. Tables 2-4 summarize the results obtained during about one year of reaction time. The results were corrected for the dilutions of liquid and gas phase caused by the injection of 7 mL fresh ACW at each sampling and pressure adjustment after each sampling.

3.1 *Determination of Background Parameters*

The NPOC of the ACW solution sample from the reactor was ~ 650 µM and therefore increased by ~ 300 µM within one hour upon contact with the PEEK liner (Table 1). Note that the blank NPOC of ACW was determined to be a factor of ~2 lower (342 µM). Note further that both parameters, i.e. NPOC and the concentrations of the carboxylates were constant after 1 hour contact between the PEEK liner and ACW. Hence, it seems that the PEEK liner is a significant carbon source in the reactor. The concentration of carboxylates, which are considered to be important corrosion products [WIELAND AND HUMMEL, 2015], however, was very low, i.e. slightly above the LOQ in the case of formate and acetate and below the LOQ in the case of oxalate, malonate, glycolate and lactate. It should be noted that most of these compounds had previously been identified as corrosion products in the experiment with non-irradiated iron powders (Table 7) [CVETKOVIĆ *et al.*, 2018a]. The above findings suggest that the high NPOC background is caused by the presence of polymeric, still unidentified organic material rather than the presence of carboxylates.

The blank concentration of ^{14}C was determined to be 0.095 F^{14}C in ACW before injection into the reactor system (Table 1). This blank could be caused by the presence of trace concentrations of $^{14}CO_2$ in ACW. This value is a factor of ~ 2 higher than the ^{14}C blank obtained during chromatographic separation of ^{14}C-containing organic compounds by HPIEC [CVETKOVIĆ *et al.*, 2018b]. The ^{14}C blank (TO^{14}C) further increased to 0.36 F^{14}C after contacting ACW with the PEEK liner in the closed reactor system. Chromatographic separation of an aliquot showed, however, that the ^{14}C blank of the individual carboxylate fractions ranged between 0.011 F^{14}C in the case of formate to 0.071 F^{14}C in the case of oxalate (Table 1). These values are close to the background value determined earlier (0.05 ± 0.01 F^{14}C) [CVETKOVIĆ *et al.*, 2018b].

Table 1: Background measurements: Concentrations of stable carbon carboxylic acids, NPOC, and total organic ^{14}C (TO^{14}C) determined by AMS.

Time [d]	**NPOC [µM]**	**TO^{14}C [F^{14}C]**	**HPIEC analysis of stable carbon carboxylic acids * [µM]**					
			FA	AA	OA	MA	GA	LA
Blank	*342*	*0.095*	*8*	*5*	*<0.1*	*<0.15*	*<0.5*	*<0.5*
0.04	642	-	11	7	<0.1	<0.15	<0.5	<0.5
1	634	-	9	5	<0.1	<0.15	<0.5	<0.5
3	646	-	10	6	<0.1	<0.15	<0.5	<0.5
15	626	0.360 #	5	<5	<0.1	<0.15	<0.5	<0.5

* Analysis of carboxylic acids: FA: formic acid (LOD = 3 µM, LOQ = 5 µM); AA: acetic acid (LOD = 3 µM, LOQ = 5 µM); OA: oxalic acid (LOD = 0.05 µM, LOQ = 0.1 µM; MA: malonic acid (LOD = 0.05 µM, LOQ = 0.15 µM); GA: glycolic acid (LOD = 0.2 µM, LOQ = 0.5 µM); LA: lactic acid (LOD = 0.2 µM, LOQ = 0.5 µM. Presence of additional carboxylates was checked, e.g. butyric acid (LOD = 0.2 µM, LOQ = 0.5 µM), propionic acid (LOD = 0.2 µM, LOQ = 0.5 µM), and valeric acid (LOD = 1 µM, LOQ = 3 µM) which were found to be below the detection limit.

An aliquot of the sampled solution was subjected to chromatographic separation and the concentration of ^{14}C-containing formate, acetate, oxalate and malonate was determined in the respective HPIEC fractions by AMS. The following concentrations were determined: formate: 0.011 F^{14}C; acetate: 0.020 F^{14}C; oxalate; 0.071 F^{14}C; malonate: 0.043 F^{14}C.

The results from the background tests support the idea that polymeric, ^{14}C-containing organic material released from the PEEK liner or other sources in the reactor are dissolved in ACW. Therefore, other carbon sources in addition to the irradiated steel seem to be present in the reactor. Nevertheless, this material is not contained in any of the fractions of the individual carboxylates that have been collected after chromatographic separation and therefore, the carbon contaminants do not contribute to the ^{14}C concentration of the individual ^{14}C-containing organic compounds that are expected to be produced during corrosion of irradiated steel and sampled after chromatographic separation.

It should be noted that the blank concentration of ^{14}C was not determined by LSC in these experiments because no ^{14}C activity was detected by LSC in ACW solutions used to pre-clean and pre-condition the PEEK liner (^{14}C activity below LOD).

3.2 Monitoring of Temperature, Pressure and O_2

Pressure, temperature and the concentration of O_2 monitored between samplings are listed in Table 2.

Table 2: Oxygen, pressure, and temperature measurements. Temperature and oxygen were determined before the sampling. Pressure was recorded before and after sampling.

Date	Time [d]	Oxygen [ppb]	Pressure [bar]		Temperature [°C]
			Start	End	
17/5/2016	0	58.84	5.03	4.96	24.4
18/5/2016	1	43.22	5.15	5.14	23.1
1/6/2016	15	38.86	5.02	5.01	23.2
15/6/2016	29	37.52	5.04	5.00	23.4
18/8/2016	93	43.20	5.06	4.99	23.5
27/2/2017	286	59.73	5.19	5.21	22.7
3/7/2017	412	69.5	5.02	5.01	23.4

The temperature was found to vary between 22.7 and 24.4 °C. After each sampling the pressure was adjusted to 5 bar pressure with N_2 (pressure at start). The pressure was mostly constant during the time interval between the samplings (pressure at end). In some cases the pressure changed slightly which might be caused by temperature changes between each sampling. The O_2 concentration ranged from ~ 39 to ~ 59 ppb. Both values are considered to be close to the detection limit of the sensor. Variations in O_2 measurements could be caused by changes in the sensitivity of the sensor with time (e.g. due to temperature changes). Note further that the O_2 concentration in solution could also vary with temperature and therefore slightly change with time.

3.3 *Analysis of Liquid Phase*

Table 3 summarizes ^{60}Co activity, NPOC and the concentrations of the stable carbon carboxylic (formic, acetic, oxalic, malonic, glycolic, and lactic acids) in solution.

Table 3: ^{60}Co activity, NPOC and concentrations of formic acid (FA), acetic acid (AA), oxalic acid (OA), malonic acid (MA), glycolic acid (GA), lactic acid (LA).

Time [d]	**^{60}Co [Bq/mL]**	**NPOC [µmol C/L]**	**HPIEC analysis of stable carbon carboxylic acids * [µM]**					
			FA	AA	OA	MA	GA	LA
Blank	*n.d.*	*n.d.*	*<5*	*<5*	*<0.1*	*<0.15*	*<0.5*	*<0.5*
1	n.d.	n.d.	7	<5	0.3	<0.15	<0.5	<0.5
15	n.d.	204	8	<5	0.5	<0.15	1.3	1.6
29	5.2	216	7	<5	0.5	<0.15	1.4	1.2
93	5.2	390	13	<5	0.7	<0.15	1.7	2.8
286	4.4	515	49	21	0.3	<0.15	1.6	2.5
412	3.3	546	20	10	1.0	<0.2	1.3	4.1

* For LOD and LOQ see Table 1. n.d.: not determined.

The ^{60}Co activity was taken as a measure of the corrosion process in an earlier study [CVETKOVIĆ *et al.*, 2018b]. There, the corrosion of an irradiated steel nut specimens was studied under poorly controlled oxic conditions. In the previous experiment the ^{60}Co activity was found to increase with time, thus indicating progress of the corrosion process. In this study the ^{60}Co activity was already constant after 29 days and thereafter tended to decrease with increasing time (day 93 - 412). This indicates that ^{60}Co was not present as aqueous species upon release from irradiated steel.

The NPOC increased with progressive reaction from initially ~ 200 µM to ~ 550 µM after 412 days. Note that the NPOC almost doubled between the early phase of the experiment (t < 30 days ~ 200 µM) and after 93 days (390 µM). This increase cannot be attributed to the release of small organic molecules during corrosion of the irradiated steel as their concentrations are low compared to the NPOC (Table 2). It is conceivable that this increase in NPOC is caused by the release of organic material from the PEEK liner or an additional carbon source in the reactor. Note that the increase in NPOC between 93 and 412 days reaction could partially be attributed to the production of formate and acetate, which are considered to be important organic corrosion products. Nevertheless, there is a substantial proportion of NPOC that cannot be attributed to the corrosion of irradiated steel.

The concentration of formate increased with time, i.e. from ~ 2 µM after 29 days to ~ 15 µM after 412 days reaction. In the same time interval, the acetate concentration increased from < 5 µM to ~ 5 µM. The lactate concentration increased over the same time interval while its concentration was almost an order of magnitude lower than those of formate and acetate. In contrast, the concentrations of the other carboxylates, i.e. oxalate, malonate and glycolate, were found to be almost constant within the uncertainty of the analytical method while their values were still close to the LOD. Corrosion of the irradiated steel is considered to be the main process generating the carboxylates with carbon bound as alloying element in steel as the main source of stable carbon.

The ^{14}C concentrations of the samples are listed in Table 4. The ^{14}C activity determined by LSC corresponds to the total ^{14}C activity in an aliquot of the sample collected from the reactor, i.e. prior to cartridge pre-treatment (Figure 6). Thus, the ^{14}C activity results from the presence of all ^{14}C-containing compounds irrespective of their speciation that is inorganic ^{14}C, ^{14}C-containing organic compounds and background ^{14}C-containing polymeric materials. Furthermore, the ^{14}C activity determined by LSC is subjected to a large uncertainty (estimated at > 50 %) due to presence of ^{60}Co, which significantly contributes to the count rate of LSC in the energy window between 4 and 65 keV (> 80% of counts). Therefore, the ^{14}C activity determined by LSC is considered to be a non-specific measure of the ^{14}C activity poorly constrained by carbon speciation. In the present study the ^{14}C activity determined by LSC was only used as guidance in conjunction with the preparation of the ^{14}C AMS samples.

The ^{14}C AMS data listed in Table 4 correspond to the ^{14}C activity resulting from the ^{14}C-containing organic compounds produced during corrosion, i.e. the total organic ^{14}C content (TO^{14}C).

Table 4: Total ^{14}C concentration determined by LSC and AMS. The concentrations of individual ^{14}C-containing carboxylic acids were below the LOD of ^{14}C AMS for a direct measurement without pre-concentration.

Time	**LSC ^{14}C ***	**AMS ^{14}C (TO^{14}C) #**		
[d]	**[Bq/L]**	**[F^{14}C]**	**[Bq/L]**	**[M]**
1	<140	0.10	0.05	$1.96 \cdot 10^{-14}$
15	<140	0.99	0.45	$1.94 \cdot 10^{-13}$
29	n.d.	1.56	0.70	$3.06 \cdot 10^{-13}$
93	470	3.53	1.60	$6.92 \cdot 10^{-13}$
286	420	2.94	1.33	$5.76 \cdot 10^{-13}$
412	260	1.46	0.66	$2.86 \cdot 10^{-13}$

* LOD of LSC: 25 cpm in 5 mL ≈ 100 Bq/L. LOQ of LSC: 35 cpm in 5 mL ≈ 140 Bq/L. n.d.: not determined.

The data are corrected for the background value (0.59 F^{14}C). The conversion factors given in Eq.(1) were used for the conversion between the different units.

The results from the AMS measurements of the first samplings showed an increase in the TO^{14}C up to 93 days, thus indicating progressive corrosion of irradiated steel (Table 4). The TO^{14}C content of the solution sampled at 412 days, however, was significantly lower. The reason for this decrease in the TO^{14}C is presently unknown. It could imply that the decomposition of the ^{14}C-containing organic compounds occurred with time, thus giving rise to a loss of aqueous ^{14}C due to volatilization, while a microbiologically induced effect seems less probable with a view to the high pH of the solution. Nevertheless, the latter result must be further substantiated in future samplings before a final appraisal can be made.

Identification and quantification of the individual ^{14}C-containing organic compounds by compound-specific ^{14}C AMS was not possible for the samplings up to 286 days because the concentration of these compounds was below the detection limit of the AMS method. To improve the analytical method, a pre-concentration step based on freeze-drying (Section 2.3.4) was developed to increase the ^{14}C concentration of the fractions. The freeze-drying process was applied on the sample collected after 412 days. Pre-concentration by a factor ~ 15 was achieved which allowed the ^{14}C-containing compounds to be detected above the LOD of AMS (Table 5). The activities of the acetate and formate fractions were determined to be 0.007 Bq/L (0.015 F^{14}C), which demonstrates the need of a pre-concentration step for monitoring the very low concentrations of ^{14}C-containing organic compounds. Traces of lactate were also detected slightly above the LOD (0.007 F^{14}C).

The TO^{14}C content was estimated to be 0.75 Bq/L (=1.64 F^{14}C) by adding up the activities of the three analysed fractions (Table 5). Note that this estimate of TO^{14}C was based on the assumption that all carboxylates carry only one ^{14}C (single labelled). The estimated TO^{14}C agrees well with the result from the direct measurement of TO^{14}C (Table 4). This finding shows that the entire TO^{14}C content can be attributed to ^{14}C-containing formate, acetate and lactate, which account for 112 ± 25 % of the directly measured TO^{14}C listed in Table 4. The finding further shows that the cartridge treatment efficiently removed possible ^{14}C background contributions from solution, in particular ^{14}C inorganic carbon and ^{14}C-containing polymeric materials.

Table 5: ^{14}C-bearing formate, acetate and lactate analysed by AMS after pre-concentration. Note that malonate and oxalate fractions were not analysed.

Fraction	Measured concentration[*]		Dilution corrected data[#]			
	[F^{14}C]	Error	[Bq/L]	Error	[M]	Error
Formate (FA)	0.015	0.006	0.31	0.12	$1.33 \cdot 10^{-13}$	$5.28 \cdot 10^{-14}$
Acetate (AA)	0.015	0.006	0.24	0.09	$1.02 \cdot 10^{-13}$	$3.94 \cdot 10^{-14}$
Lactate (LA)	0.009	0.004	0.20	0.09	$8.61 \cdot 10^{-14}$	$3.98 \cdot 10^{-14}$
FA + AA + LA = TO^{14}C	-	-	0.75	0.30	$3.21 \cdot 10^{-13}$	$1.32 \cdot 10^{-13}$

[*] LOD of the AMS method with pre-concentration: 0.007 F^{14}C

[#] Measured concentrations were corrected using the dilution factor resulting from chromatographic separation by HPIEC.

3.4 *Analysis of Gas Phase*

Methane and ethene were the only hydrocarbons detected in the gas phase (Table 6). Note that the concentration of ethene is close to the LOD while methane is the only gaseous carbon species showing a pronounced increase in concentration with time. Other hydrocarbons that had previously been observed during the corrosion of non-irradiated iron/steel [Wieland and Hummel, 2015] were below the detection limit of the analytical method. At the time being, however, we are not able to identify and quantify the ^{14}C-containing hydrocarbons in the gas phase. The required analytical procedure based on compound-specific ^{14}C AMS is under development (see Section 5.2).

Table 6: GC-MS measurements of gaseous stable carbon compounds in samples at ambient pressure.

Time **[d]**	**GC analysis of hydrocarbons*** **[µM]**	
	Methane	Ethene
Blank	*<0.06*	*<0.03*
1	<0.06	<0.03
15	<0.06	<0.03
29	0.07	<0.03
93	0.42	<0.03
286	0.55	0.08
412	0.99	0.06

* LOD and LOQ of hydrocarbons were as follows: methane (LOD = 0.02 µM, LOQ = 0.06 µM) and ethene (LOD = 0.01 µM, LOQ = 0.03 µM). Presence of additional hydrocarbons was checked, e.g. ethane (LOD = 0.07 µM, LOQ = 0.2 µM), acetylene (LOD = 0.005 µM, LOQ = 0.016 µM), propane (LOD = 0.05 µM, LOQ = 0.15 µM), propene (LOD = 0.01 µM, LOQ = 0.02 µM) and butane (LOD = 0.03 µM, LOQ = 0.09 µM) which all were found to be below the LOD.

4 Discussion

4.1 *Release of Corrosion Products*

The release of ^{60}Co, ^{14}C- and stable carbon bearing carbon species during corrosion of the irradiated steel nut specimens indicates progressing corrosion. The inventory of ^{60}Co in the irradiated steel used for the corrosion experiment is well known (79450 ± 2780 kBq/g; [SCHUMANN *et al*., 2014]). The content of stable carbon of irradiated steel is estimated to be 0.08 wt.% (= 800 ppm) while the ^{14}C content is more than 3 orders of a magnitude lower (17.8 ± 2.5 kBq g^{-1} = 0.107 ± 0.015 µg g^{-1} = 0.107 ± 0.015 ppm = $(1.07 \pm 0.15)\cdot 10^{-5}$ wt.%).

The release of ^{60}Co and the production of ^{14}C-containing and stable carbon species during the course of the anoxic corrosion of irradiated steel is expected to be very slow due to the very low corrosion rate in alkaline solution (range of a few nanometers per year) [SMART *et al*., 2004; DIOMIDIS, 2014; SWANTON *et al*., 2015]. Based on the low corrosion rate it was anticipated that the concentration of the ^{14}C- and stable carbon species would be very low, in particular well below the detection limit of classical methods for liquid and gas phase analysis (IC-MS, GC-MS). Gamma counting allows the ^{60}Co activity in solution to be determined due to the high ^{60}Co activity of irradiated steel while the expected ^{14}C activity released from irradiated steel was expected to be well below the LOD of LSC.

Time evolution of the ^{60}Co activity in the liquid phase and the concentration of total ^{14}C and stable carbon in the liquid and gas phase was estimated for the given experimental set-up (liquid phase: 300 mL; gas phase: 200 mL at 5 bar total pressure corresponding to 1000 mL at 1 bar total pressure, irradiated steel: 1.718 g and total surface area = 11.15 cm^2 in contact with ACW (pH = 12.5)) as a function of corrosion rates (Figures 7 and 8).

For the preliminary modelling it was assumed that ^{60}Co is present as aqueous species upon release from irradiated steel, suggesting that sorption onto the steel surface and the reactor wall can be ignored. This assumption seems to be justified in view of the Co speciation in hyper-alkaline media, i.e. the formation of predominately $Co(OH)_3^-$ species, while the assumption is not supported by the currently available experimental data. Note that preferential uptake of ^{60}Co by the surface layer of steel could be one of the processes affecting the apparent corrosion rate.

For the modelling it was further assumed that the stable carbon and ^{14}C inventories associated with the irradiated steel were either released entirely as aqueous or gaseous carbon species. Hence, partition of the released ^{14}C and stable carbon between aqueous and gaseous phase was not taken into account.

The ^{60}Co activity was not determined experimentally in the first samplings before 29 days (Table 3). The ^{60}Co activity even slightly decreased between 29 and 412 days from 5.2 to 3.3 Bq/mL. This low activity is in line with the expected slow corrosion of steel in these conditions (Figure 7) while the slight decrease might be an experimental artefact caused by adsorption of ^{60}Co to a contacting surface (steel surface, PEEK liner, sampling tube). Based on ^{60}Co activity measurements an initial corrosion rate of ~ 20 nm/a was estimated over the time period of 1 month while the corrosion rate is expected to be much lower (~ 2 nm/a) after the initially fast corrosion. Although these rates are comparable to those determined in previous studies conducted in similar conditions [e.g. SMART *et al.*, 2004; DIOMIDIS, 2014; SWANTON *et al.*, 2015] it is presently uncertain whether or not ^{60}Co is an adequate measure of the corrosion rate [DE VISSER-TÝNOVÁ *et al.*, 2017].

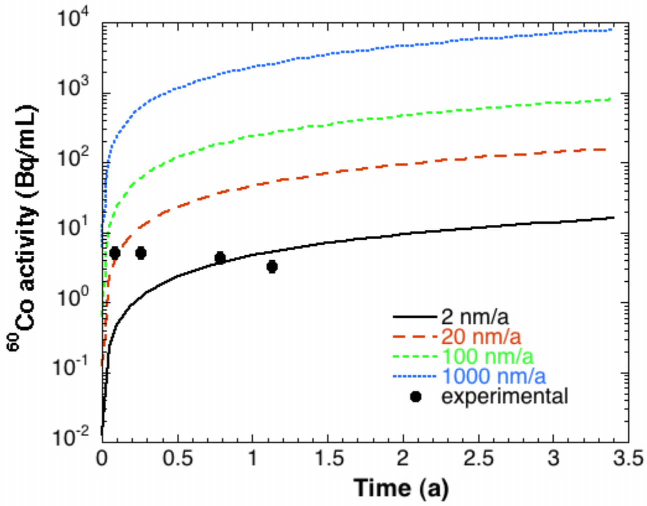

Figure 7: Estimate of the ^{60}Co activity in solution for the experimental set-up (see text) as a function of corrosion rate.

The total organic ^{14}C concentration (TO^{14}C) was found to range in value between 0.10 F^{14}C after one day and 3.53 F^{14}C after 92 days. This corresponds to a ^{14}C concentration ranging between $9.58 \cdot 10^{-14}$ and $3.38 \cdot 10^{-12}$ M (Table 4). This increase in the aqueous ^{14}C concentration with time indicates that the production of ^{14}C-bearing organic compounds is related to the corrosion process in line with a corrosion rate ~ 20 nm/a over the first 92 days (Figure 8a). After the first 92 days, however, the TO^{14}C seems to decrease with time. At present it is not clear whether or not this decrease is statistically significant, i.e. outside the uncertainty range of the experiments. Further sampling will enable us to assess whether or not the low TO^{14}C values after 92 days are within the uncertainty of the experimental approach.

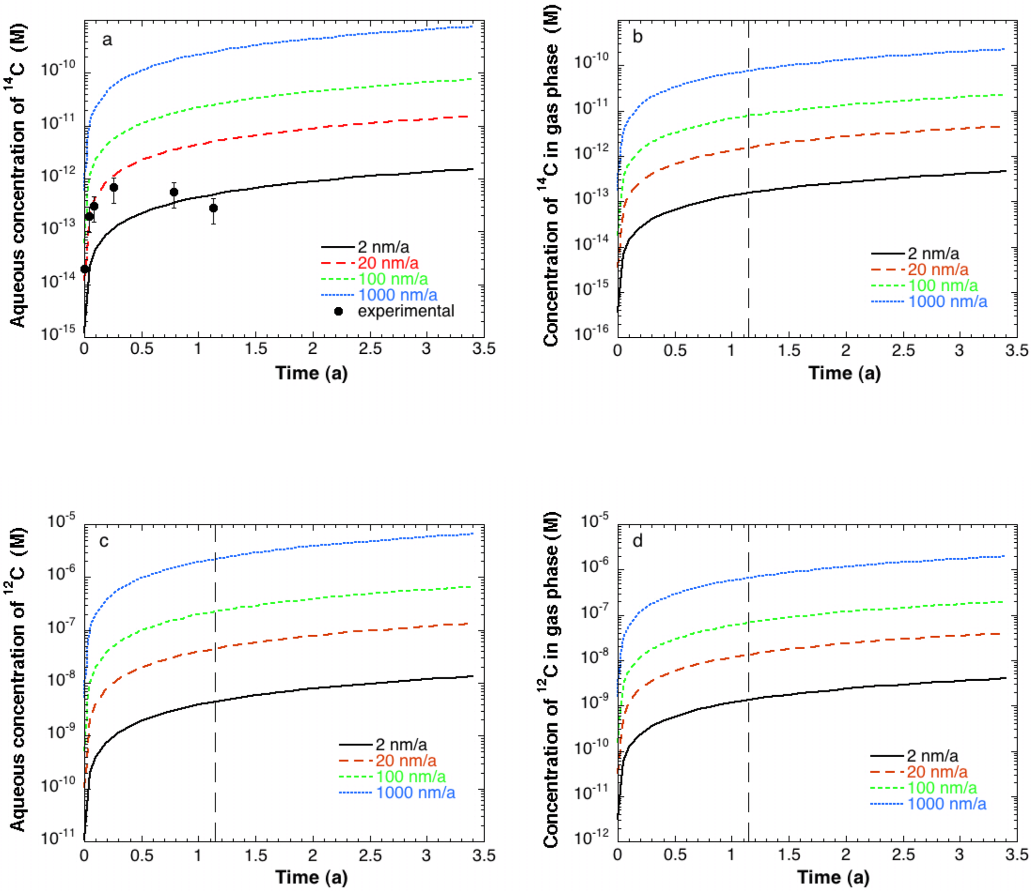

Figure 8: Estimates of the total ^{14}C (a/b) and stable carbon (c/d) concentrations in liquid and gas phase for the experimental set-up (see text) as a function of corrosion rate. The vertical broken line indicates 412 days reaction.

At the present time we can only speculate about the processes that could cause a decrease in the TO^{14}C. It is conceivable that sorption of LMW organics to magnetite and subsequent decomposition of these compounds in presence of magnetite occurred [e.g. PALMER AND DRUMMOND, 1986; GROOTENDORST *et al.*, 1994]. Loss of aqueous ^{14}C solely due to sorption of ^{14}C-bearing LMW organics to magnetite is probably negligible as sorption of anionic compounds to oxidic surfaces is expected to be very low in strongly alkaline conditions. Sorption/decomposition of ^{14}C-bearing LMW organics would cause a loss of aqueous ^{14}C according to the chemical behaviour of the degradation products, e.g. ^{14}C-bearing carbonate sorbing to magnetite or volatilization of ^{14}C-bearing gaseous species into the gas phase of the reactor. Eventually, microbiologically induced loss of aqueous ^{14}C seems less likely with a view to the high pH of the solutions (12.5), which strongly limits microbial activity.

The total ^{14}C concentration in solution (TO^{14}C) determined by ^{14}C AMS may not account for all ^{14}C species present in the reactor because gaseous ^{14}C species and ^{14}C-bearing inorganic species may have been formed during corrosion of irradiated steel. Therefore, a corrosion rate of ~ 20 nm/a in the first 92 days corresponds to the lower bound as it is based on the assumption that the total amount of ^{14}C released from irradiated steel is present in the dissolved organic chemical form (TO^{14}C). Thus, the effective corrosion rate may be higher. Note that the concentration of ^{14}C-bearing gaseous compounds cannot be determined by using the standard GC-MS technique because their concentration is below the LOD (Figure 8b). Analytical methods are currently being developed in-house based on compound-specific ^{14}C AMS which will allow the identification and quantification of ^{14}C-bearing inorganic species (i.e. $1^{14}CO_3^{2-}$) and gaseous ^{14}C-bearing compounds.

Time evolution of the concentration of the stable carbon bearing compounds is difficult to interpret solely on the basis of steel corrosion. The concentration of the main aqueous stable carbon compounds formate and acetate ranged from less than 5 µM after one day reaction (see LOQ given in Table 1) to 44 µM in the case of formate (background corrected) and to 16 µM in the case of acetate (background corrected) after 286 days (Table 3). After 412 days, the concentrations of formate and acetate are lower. Note that both compounds were identified by compound-specific ^{14}C AMS as the main ^{14}C-bearing carboxylates formed during the corrosion of irradiated steel (Section 3.3). This finding suggests that also the stable carbon bearing carboxylates could be corrosion products. The increase in the formate, acetate, and lactate concentrations within the first 286 days supports the idea that the production of the stable carbon bearing carboxylates results from corrosion. Furthermore, the concentrations of formate and acetate decreased after 412 days in agreement with a decrease in the TO^{14}C content (Figure 8a). Therefore, both the ^{14}C-bearing and stable carbon bearing carboxylates show the same time-dependent trend. Note that the concentrations of the other carboxylates considered in this study, i.e. oxalate, malonate and glycolate, were about an order of magnitude lower.

The concentration of dissolved organic carbon in the aqueous phase (NPOC) was estimated to be ~ 40 - 100 µM based on the measured concentrations of the individual carboxylates (Table 3) and by taking into account the carbon content of each compound. Based on the modelling, however, the estimated concentration of all stable carbon bearing compounds in solution is expected to range in value between ~ 0.01 and 0.2 µM after 412 days based on the above given range (20 - 1000 nm/a) of corrosion rates (Figure 8c). Thus, by comparison with the experimentally determined total concentrations of the dissolved stable carbon bearing species it emerges that the latter concentrations are at least 3 orders of magnitude higher than the stable carbon concentration estimated based on the stable carbon content of irradiated steel specimens and assuming corrosion rates ranging between 20 and 1000 nm/a (Figure 8c). This finding suggests that a significant portion of the carboxylates was either released already at the start of the corrosion process (instant release) or that irradiated steel is not the main source of the stable carbon bearing carboxylates. The latter conclusion is supported by the NPOC measurements. The former conclusion is supported by our previous study on the corrosion of non-irradiated iron in alkaline media [CVETKOVIĆ *et al*., 2018a].

The experimentally determined stable carbon concentration in the gas phase amounts to ~ 0.7 µM after 412 days (Table 6). The concentration of stable carbon in the gas phase is predicted to range in value between ~ 0.01 and 0.64 µM after 412 days on the basis of the relevant range (20 – 1000 nm/a) of corrosion rates (Figure 8d). Thus, the predicted stable carbon concentration in the gas phase after 412 days agrees with the experimental data on the assumption that corrosion occurred at a rate of ~ 1000 nm/a in the early phase of the process (Figure 8d). Additional data are needed to corroborate this finding.

The limited set of experimental data that are available from the first samplings suggest that the release rate of the ^{14}C-bearing organic compounds (TO^{14}C) and of gaseous stable carbon bearing species (i.e. methane) could be consistent if the temporal evolution of the TO^{14}C represents solely the lower bound of the corrosion rate of irradiated steel. Hence, both types of species could be produced during the corrosion of irradiated steel. The reason for the discrepancy between predicted and experimental data in case of the aqueous stable carbon bearing species, however, is presently not understood and can be attributed to either i) a much higher production rate of stable carbon compared to estimates based on the TO^{14}C production during steel corrosion (e.g. by instantaneous release at the start of the corrosion process) or ii) a not yet identified additional source of stable carbon in the reactor and subsequent production of the aqueous stable carbon bearing organic compounds. The temporal evolution of the concentration of the stable carbon bearing gaseous species (mainly due to methane formation) would imply an initial corrosion rate ~ 1000 nm/a while the concentration of the stable carbon bearing dissolved compounds (carboxylates) would imply an even higher corrosion rate. It is expected that the generation of the stable carbon and ^{14}C-bearing species is comparable and in line with an initial corrosion rate ranging from 20 to 1000 nm/a. Note that the initial corrosion rate based on ^{14}C release, as given by the temporal evolution of the TO^{14}C content, is expected to range between 20 and 100 nm/a.

The presence of another source of stable carbon in the reactor system in addition to the irradiated steel nut specimens is also considered. This additional source could contribute to the concentrations of the stable carbon bearing species determined in the aqueous phase and to a lesser extent to those in the gas phase. The unidentified, presumably polymeric carbon compounds may be degraded with time, which gives rise to the observed increase in the concentrations of stable carbon bearing compounds, such as formate and acetate. At present, we cannot exclude that the organic compounds contributing to the NPOC could be converted into stable carbon bearing compounds identified by HPIEC-MS under the given experimental conditions (gamma radiation, hyper-alkaline solution, presence of H_2). Note further that the NPOC background does not contribute to ^{14}C fractions (formate, acetetate etc.) because their background concentrations were found to be close to the background value (~0.05 F^{14}C) of the compound-specific ^{14}C AMS method [CVETKOVIĆ *et al*., 2018b].

4.2 *Carbon Speciation*

An experimental corrosion study with non-irradiated iron particles provided important information on the type of organic compounds formed during corrosion of iron/steel (Table 7) [CVETKOVIĆ *et al*., 2018a]. The main findings can be summarized as follows: 1) only a limited number of organic compounds are produced during corrosion, 2) only small molecules up to C5 are produced, 3) both oxidized (carboxylic acids, alcohols, aldehydes) and reduced (methane etc.) carbons species are formed. It was postulated that the same compounds could be formed during corrosion of irradiated steel.

Table 7: Carbon species expected to be formed as a result of steel corrosion [CVETKOVIĆ *et al*., 2018a]. All table entries were identified in corrosion experiments with non-irradiated iron/steel. In italic: ^{14}C-bearing compounds identified in the corrosion experiment with irradiated steel.

Alkane/alkene	Alcohols/aldehydes	Carboxylate ions	Carbonate
Methane (CH_4)	Methanol (CH_3OH)	*Formate* ($HCOO^-$)	CO_2
Ethane (C_2H_6)	Ethanol (C_2H_5OH)	*Acetate* (CH_3COO^-)	CO_3^{2-}
Ethene (C_2H_4)	Formaldehyde (CH_2O)	Propanoate ($C_2H_5COO^-$)	(CO)
Propane (C_3H_8)	Acetaldehyde (C_2H_4O)	Butanoate ($C_3H_7COO^-$)	
Propene (C_3H_6)	Propionaldehyde (C_3H_6O)	Malonate ($CH_2(COO^-)_2$)	
Butane (C_4H_{10})		Oxalate ($C_2O_4^{2-}$)	
Butylene (C_4H_8)		*Lactate* ($CH_3CHOHCOO^-$)	
Pentene (C_5H_{10})			

The individual ^{14}C-bearing compounds produced during the anoxic corrosion of irradiated steel were successfully identified and quantified in the sample collected after 412 days reaction (Table 5). ^{14}C-containing formate, acetate and lactate were found to be the dominant carboxyates detected by compound-specific ^{14}C AMS above the LOD. Detection of these compounds was enabled by using freeze-drying as a pre-concentration step of the individual fractions. Furthermore, the total ^{14}C content of these compounds agrees well with the TO^{14}C determined directly in solution, indicating that formate, acetate and lactate are the main ^{14}C-bearing species present in solution and contributing to the TO^{14}C. This finding supports the idea that the same types of carboxylates are produced during the corrosion of non-irradiated iron powder and irradiated steel.

5 Summary and Outlook

5.1 *Summary*

Information on the type of ^{14}C-bearing carbon species produced during the anoxic corrosion of irradiated metals is required to support safety assessment of nuclear waste repositories containing irradiated metallic waste materials (e.g. irradiated steel, Zircaloy). A unique corrosion experiment with irradiated steel from NPP Gösgen, Switzerland, is currently being carried out with the aim of identifying and quantifying the ^{14}C-bearing carbon species produced in the course of the corrosion of irradiated steel under hyper-alkaline, anoxic conditions. As the concentration of the ^{14}C-bearing species is expected to be very low, we developed a specific analytical technique by combining chromatographic separation of the individual compounds with ^{14}C detection by AMS (compound-specific ^{14}C AMS). The method has a low detection limit for ^{14}C-bearing organic compounds and a large dynamic range (~3 orders of a magnitude), and it was developed to quantify selected, potentially ^{14}C-bearing carboxylates that are expected to be formed during corrosion of irradiated steel as well as for the determination of the total organic ^{14}C content (TO^{14}C). In addition, conventional techniques (HPIEC-MS, GC-MS) were employed to determine the concentration of stable carbon bearing compounds in the liquid and gas phase with the aim of exploring the speciation of stable carbon.

The specific set-up developed for the corrosion experiment allows continuous monitoring of important physico-chemical parameters (pressure, temperature, dissolved oxygen) and further allows aliquots of fluid and gas to be sampled from the reactor outside the lead shielding. Analysis of the liquid and gas phase from the first samplings shows that the concentrations of the organic compounds (stable carbon and ^{14}C-bearing) are still very low and close or even below the detection limit of the analytical methods employed for this study. The first results show, however, that ^{14}C AMS can be employed to determine TO^{14}C. The TO^{14}C content was found to increase with time up to 92 days thus indicating the production of aqueous ^{14}C-bearing organic compounds during progressing corrosion of irradiated steel. Comparison of modelled and experimental data suggests that the corrosion rate ranges in value between ~ 20 and 100 nm/a in the early phase of the corrosion process. This value is in accordance with rates determined for the corrosion of steel in hyper-alkaline media. After 92 days, however, the TO^{14}C content was observed to decrease with time. At present, it is not yet understood whether the trend is caused by the degradation of the ^{14}C-containing organic compounds or it is within the uncertainty of the experimental approach.

Analysis of the ^{14}C-bearing individual compounds was successful in the solution collected after 412 days upon the development of a pre-concentration step prior to ^{14}C detection by ^{14}C AMS. The results clearly demonstrate that compound-specific ^{14}C AMS allows identification and quantification of the ^{14}C-bearing individual compounds at the ultratrace concentrations. Formate, acetate and lactate were identified as the main ^{14}C-containing compounds. The total ^{14}C content of associated with the three single compounds agrees well with the TO^{14}C content determined in solution.

The concentration of stable carbon bearing compounds in the aqueous phase was found to be significantly higher than the concentration modelled on the basis of the corrosion rate estimated from the temporal evolution of the TO^{14}C content. This finding suggests that another source of stable carbon in addition to irradiated steel could be present in the reactor and contribute to the aqueous concentration of the stable carbon bearing compounds. It is conceivable that still unknown carbon species that contribute to the NPOC content of the aqueous phase could be additional sources of stable carbon and that these compounds may be degraded with time to produce carboxylates and possibly gaseous carbon species, such as methane.

5.2 Outlook: GC Separation and ^{14}C Detection by AMS for Gaseous Compounds

As previously mentioned in Section 4.1, the concentration of the ^{14}C-bearing gaseous compounds cannot be determined in the present study by using standard GC-MS as the concentrations of these compounds are below the LOD of the latter method. This prompted us to launch the development of a compound-specific ^{14}C AMS methodology for their quantification. The development involves two steps: 1) Separation, oxidation and trapping of individual compounds, 2) on-line measurement of ^{14}C by ^{14}C AMS.

Separation, oxidation and trapping: The first step involves the chromatographic separation of the individual compounds, followed by their oxidation to $^{14}CO_2$ and subsequent trapping of $^{14}CO_2$ in trapping valves. Individual hydrocarbons, alcohols and aldehydes can be separated by GC. An aliquot of the gas sample containing the compounds of interest is loaded into a first sampling loop while at the same time a second sampling loop is loaded with a ^{14}C-free stable carbon carrier standard gas containing the same compounds. Both loops are released and the analytes are separated, oxidized and collected for AMS measurements. The concentration of the stable carbon carrier (20 µg per analyte) is adjusted in a way to yield the required amount of stable carbon for the AMS analysis and in addition to enable the detection of the compound of interest by thermal conductivity detection (TCD). TCD allows to control chromatographic separation. The chromatographically separated, individual compounds are then oxidized in a combustion reactor to CO_2 which is trapped in the trapping valves of the fraction collector.

On-line measurement: The trapping valves can be connected to the gas inlet system of the AMS with integrated external trap for enrichment [RUFF *et al*., 2010b]. $^{14}CO_2$ can directly be injected into the ^{14}C AMS via the gas inlet system.

The ^{14}C AMS-based methodology is currently being developed.

6 References

Agrawal, A., Ferguson, W. J., Gardner, B. O., Christ, J. A., Bandstra, J. Z., Tratnyek, P. G. 2002. Effects of carbonate species on the kinetics of dechlorination of 1,1,1-trichloroethane by zero-valent iron. *Environmental Science & Technology,* 36(20), 4326-4333.

Allard, B., Torstenfelt, B., Andersson, K. 1981. Sorption studies of $H^{14}CO_3^-$ on some geological media and concrete. *Material Research Society Symposium Proceedings,* 3, 465-473.

Bayliss, S., Ewart, F. T., Howse, R. M., Smith-Briggs, J. L., Thomason, H. P., Willmott, A. 1988. The solubility and sorption of lead-210 and carbon-14 in a near-field environment. *Material Research Society Symposium Proceedings,* 112, 33-42.

Campbell, T. J., Burris, D. R., Roberts, A. L., Wells, J. R. 1997. Trichloroethylene and tetrachloroethylene reduction in a metallic iron-water-vapor batch system. *Environmental Toxicology and Chemistry,* 16(4), 625-630.

Chi, G. T., Huddersman, K. D. 2007. Novel ion chromatography technique for the rapid identification and quantification of saturated and unsaturated low molecular weight organic acids formed during the Fenton oxidation of organic pollutants. *Journal of Chromatography A,* 1139(1), 95-103.

Cvetković, B., Rothardt, J., Büttler, A., Kunz, D., Schlotterbeck, G., Wieland, E. 2018a. Formation of low molecular weight organic compounds during anoxic corrosion of zero-valent iron. *Environmental Engineering Science (in press)*.

Cvetković, B., Salazar, G., A., Kunz, D., Szidat, S., Wieland, E. 2018b. Analysis of carbon-14 containing organic compounds released from activated steel using accelerator mass spectrometry. *Analyst (submitted)*.

De Visser-Týnová, E., Stijkel, M., Swanton, S., Otlet, B., Walker, J. 2017. C-14 Release and speciation from irradiated stainless steel under alkaline reducing conditions. *European Commission, Brussels,* CAST WP2 Deliverable 2.8.

Deng, B. L., Campbell, T. J., Burris, D. R. 1997. Hydrocarbon formation in metallic iron/water systems. *Environmental Science & Technology,* 31(4), 1185-1190.

Diomidis, N. 2014. Scientific basis for the production of gas due to corrosion in a deep geological repository. *Nagra, Wettingen, Switzerland*, Nagra Work Report NAB 14-21.

Glaus, M., Van Loon, L. R. 2003. A generic procedure for the assessment of the effect of concrete admixtures on the retention behaviour of cement for radionuclides: Concept and Case studies, *Paul Scherrer Institut, Villigen PSI, Switzerland,* PSI Bericht 04-02, and *Nagra, Wettingen, Switzerland,* Nagra Technical Report NTB 03-09.

GROOTENDORST, E. J., PESTMAN, R., KOSTER, R. M., PONEC, V. 1994. Selective reduction of acetic acid to acetaldehyde on iron oxides. *Journal of Catalysis* 148, 261-269.

HARDY, L. O., GILLHAM, R. W. 1996. Formation of hydrocarbons from the reduction of aqueous CO_2 by zero-valent iron. *Environmental Science & Technology,* 30(1), 57-65.

JOHNSON, L., SCHWYN, B. 2008. Proceedings of a Nagra/RWMC workshop on the release and transport of C-14 in repository environments, *Nagra, Wettingen, Switzerland,* Nagra Work Report NAB 08-22.

KANEKO, S., TANABE, H., SASOH, M., TAKAHASHI, R., SHIBANO, T., TATEYAMA, S. 2003. A study on the chemical forms and migration behavior of carbon-14 leached from the simulated hull waste in the underground condition. *Materials Research Society Symposium Proceedings*. 757, 621-626.

KANI, Y., NOSHITA, K., KAWASAKI, T., NASU, Y., NISHIMURA, T., SAKURAGI, T., ASANO, H. 2008. Decomposition of C-14 containing organic molecules released from radioactive waste by gamma-radiolysis under repository conditions. *Radiation Physics and Chemistry,* 77(4), 434-438.

MATSUMOTO, J., BANBA, T., MURAOKA, S. 1995. Adsorption of carbon-14 on mortar. *Materials Research Society Symposium Proceedings,* 353, 1029-1035.

NAGRA 2002. Project Opalinus Clay: Safety report. Demonstration of disposal feasibility for spent fuel, vitrified high-level waste and long-lived intermediate-level waste (Entsorgungsnachweis). *Nagra, Wettingen, Switzerland*, Nagra Technical Report NTB 02-05.

NAGRA 2014. Modellhaftes Inventar für radioaktive Materialien MIRAM 14. *Nagra, Wettingen, Switzerland,* Nagra Technical Report NTB 14-04.

NOSHITA, K. 2008. Fundamental study of C-14 chemical form under irradiated condition in *Proceedings of a Nagra/RWMC workshop on the release and transport of C-14 in repository environments*, JOHNSON, L and SCHWYN, B. (editors), *Nagra, Wettingen, Switzerland*, Nagra Work Report NAB 08-22, p. 65 - 70.

NOSHITA, K., NISHI, T., MATSUDA, M., IZUMIDA, T. 1996. Sorption mechanism of carbon-14 by hardened cement paste. *Materials Research Society Symposium Proceedings,* 412, 435-442.

NUCLEAR DECOMMISSIONING AUTHORITY 2012. Geological disposal. Carbon-14 Project - Phase 1 Report, NDA/RWMD/092.

PALMER, D. A., DRUMMOND, S. E. 1986. Thermal decarboxylation of acetate. Part I. The kinetics and mechanism of reaction in aqueous solution. *Geochimica et Cosmochimica Acta* 50, 813-823.

PERRON, N., SZIDAT, S., FAHRNI, S., RUFF, M., WACKER, L., PREVOT, A. S. H., BALTENSPERGER, U. 2010. Towards on-line C-14 analysis of carbonaceous aerosol fractions. *Radiocarbon,* 52(2), 761-768.

POINTEAU, I., COREAU, N., REILLER, P. 2003. Etude experimentale et modélisation de la rétention de $^{14}CO_3^{2-}$ par les matériaux constituant le béton dans le cadre des études de faisabilité d'un stockage de déchets graphites. *Andra, Paris, France,* FRP 18 CEA 03-001.

RUFF, M., FAHRNI, S., GÄGGELER, H. W., HAJDAS, I., SUTER, M., SYNAL, H. A., SZIDAT, S., WACKER, L. 2010a. On-line radiocarbon measurements of small samples using elemental analyzer and MICADAS gas ion source. *Radiocarbon,* 52(4), 1645-1656.

RUFF, M., SZIDAT, S., GÄGGELER, H. W., SUTER, M., SYNAL, H. A., WACKER, L. 2010b. Gaseous radiocarbon measurements of small samples. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms,* 268, 790–794.

SALAZAR, G., SZIDAT, S. 2014. *Flow dynamics technique for sampling and separation of neutrals from analytes based on their axial momentum density differences.* Annual Meeting of the American Society for Mass Spectrometry, Baltimore, U.S.A.

SALAZAR, G., ZHANG, Y. L., AGRIOS, K., SZIDAT, S. 2015. Development of a method for fast and automatic measurement of aerosol sample by on-line coupling of an elemental analyzer with a MICADAS. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms,* 361, 163–167.

SASOH, M. 2008a. Investigations of distribution coefficients for C-14 from activated metal in *Proceedings of a Nagra/RWMC workshop on the release and transport of C-14 in repository environments*, JOHNSON, L and SCHWYN, B. (editors), *Nagra, Wettingen, Switzerland*, Nagra Work Report NAB 08-22, p. 83-86.

SASOH, M. 2008b. Study on chemical behaviour of organic C-14 under alkaline conditions in *Proceedings of a Nagra/RWMC workshop on the release and transport of C-14 in repository environments*, JOHNSON, L and SCHWYN, B. (editors), *Nagra, Wettingen, Switzerland*, Nagra Work Report NAB 08-22, p. 79 - 82.

SASOH, M. 2008c. The study for the chemical forms of C-14 released from activated steel in *Proceedings of a Nagra/RWMC workshop on the release and transport of C-14 in repository environments*, JOHNSON, L and SCHWYN, B. (editors), *Nagra, Wettingen, Switzerland*, Nagra Work Report NAB 08-22, p. 21-23.

SCHUMANN, D., STOWASSER, T., VOLMERT, B., GUENTHER-LEOPOLD, I., LINDER, H., WIELAND, E. 2014. Determination of the C-14 content in activated steel components from a neutron spallation source and a nuclear power plant. *Analytical Chemistry,* 86(11), 5448-5454.

SMART, N. R., BLACKWOOD, D. J., MARSH, G. P., NAISH, C. C., O'BRIEN, T. M., RANCE, A. P., THOMAS, M. I. 2004. The anaerobic corrosion of carbon and stainless steel in simulated cementitious repository environments: A summary review of Nirex Research. *AEA Technology, Harwell, United Kingdom*, AEAT/ERRA-0313.

SWANTON, S. W., BASTON, G. M. N., SMART, N. S. 2015. Rates of steel corrosion and carbon-14 release from irradiated steels - state of the art review, *European Commission, Brussels,* CAST WP2 Deliverable 2.1.

SYNAL, H.-A., STOCKER, M., SUTER, M. 2007. MICADAS: A new compact radiocarbon AMS system. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms,* 259(1), 7-13.

SZIDAT, S., SALAZAR, G. A., VOGEL, E., BATTAGLIA, M., WACKER, L., SYNAL, H.-A., TÜRLER, A. 2014. C-14 analysis and sample preparation at the new Bern Laboratory for the analysis of radiocarbon with AMS (LARA). *Radiocarbon,* 56(2), 561-566.

TAKAHASHI, R., SASOH, M., YAMASHITA, Y., TANABE, H., SAKURAGI, T. 2014. Improvement of inventory and leaching rate measurements of C-14 in hull waste, and separation of organic compounds for chemical species identification. *Materials Research Society Symposium Proceedings,* 1665, 139-148.

WACKER, L., FAHRNI, S. M., HAJDAS, I., MOLNAR, M., SYNAL, H. A., SZIDAT, S., ZHANG, Y. L. 2013a. A versatile gas interface for routine radiocarbon analysis with a gas ion source. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms,* 294, 315-319.

WACKER, L., FUELOEP, R. H., HAJDAS, I., MOLNAR, M., RETHEMEYER, J. 2013b. A novel approach to process carbonate samples for radiocarbon measurements with helium carrier gas. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms,* 294, 214-217.

WIELAND, E., HUMMEL, W. 2015. Formation and stability of carbon-14 containing organic compounds in alkaline iron-water systems: Preliminary assessment based on a literature survey and thermodynamic modelling. *Mineralogical Magazine,* 79, 1275-1286.

WIELAND, E., CVETKOVIĆ, B. 2015. Development of a compound-specific C-14 AMS technique for the detection of C-14 labelled organic compounds at very low concentrations. *European Commission, Brussels,* CAST WP2 Deliverable 2.3.

YAMAGUCHI, T., TANUMA, S., YATSUTOMI, I., NAKAYAMA, T., TANABE, H., KATSURAI, K., KAWAMURA, W., MAEDA, K., KITAO, H. and SAIGUSA, M. 1999. A study on chemical forms and migration behaviour of radionuclides in hull wastes. *Radioactive Waste Management and Environmental Remediation*, *ICEM 99*, Sept 26-30, Nagoya, Japan, ASME.

YAMASHITA, Y., TANABE, H., SAKURAGI, T., TAKAHASHI, R., SASOH, M. 2014. C-14 release behavior and chemical species from irradiated hull waste under geological disposal conditions. *Materials Research Society Symposium Proceedings,* 1665, 187-194.

YIM, M.-S., CARON, F. 2006. Life cycle and management of carbon-14 from nuclear power generation. *Progress in Nuclear Energy,* 48(1), 2-36.