

Carbon-14 Source Term

CAST



Final synthesis report on results from WP2 (D2.18)

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CAST – Project Overview

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

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

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

For more information, please visit the CAST website at:

<http://www.projectcast.eu>

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Executive Summary

Carbon-14 is an important radionuclide in the inventory of radioactive waste in many disposal programmes due to its significant dose contributions in safety assessments for geological repositories. Knowledge on ^{14}C release from the waste and its chemical form (speciation) is limited which gives rise to uncertainty in the treatment in safety assessment. ^{14}C is formed by the neutron activation of ^{14}N and other nuclides. The majority is contained in activated metals, mainly Zircaloy or steels.

In Work Package (WP) 2 of the CAST project twelve partners from different countries came together to study the release of ^{14}C from activated steels, e.g. from reactor internals or the reactor pressure vessel. The objectives of WP2 were to develop suitable analytical techniques for measurement of ^{14}C speciation, to validate existing activation models, to measure the ^{14}C release and speciation in leaching experiments and finally to advance our understanding of ^{14}C behaviour released upon steel corrosion.

In task 1 of WP2 a literature research was made, and a State-of-the-Art report was published (D2.1). The outcome was that the corrosion process of steels is well understood. The corrosion rates under a variety of conditions are known and their uncertainties are low. A good understanding exists on the prevalence of carbon in steels forming different kinds of carbides. In only a limited number of experiments the release of stable carbon from steels was studied and even less studies exist on the release of ^{14}C from activated steels. Dissolved and gaseous compounds were found in both cases.

In task 2 analytical methods were developed to measure the speciation of ^{14}C in gaseous and liquid samples at low concentrations due to the expected slow release. Methods comprise ion chromatography for dissolved species and gas chromatography coupled with mass spectrometry for gaseous species. For the low-level detection, accelerated mass spectrometry was applied. Other techniques involved selective oxidation with subsequent capture. A method for separation of other radionuclides from ^{14}C was developed.

Task 3 involved a series of leaching experiments using samples of activated stainless steels, mild steel and some other, non-activated materials. Most experiments applied alkaline, anaerobic conditions but some tests involved neutral and acidic pH values as well as aerobic conditions. The ^{14}C speciation could not be measured in all experiments. In many cases, a fast initial release of both ^{12}C and ^{14}C to the gas and liquid phase could be observed after immersion of the samples into the leaching solution. Later, within some days to a few weeks, the release rate decreased significantly. As a first approximation, this release rate seems to correspond to the corrosion rate of steel, which is, however, subject to rapid changes in the early stage of the experiment. The conclusion of a ^{14}C release congruent with the steel corrosion is therefore subject to high uncertainty. The measured speciation of ^{14}C comprises both organic and inorganic compounds in the liquid phase. Methane and minor contributions of CO were found in the gas phase. No systematic differences in the behaviour of ^{12}C and ^{14}C could be observed. Since no rigorous comparison of the behaviour of both isotopes could be made, it cannot be excluded that differences exist. The ^{14}C concentration in selected samples has been estimated using different activation models and compared to measured activity concentrations. An uncertainty factor of 3 to 4 has been found whereby the measured concentrations were higher than estimated.

In task 4 a critical discussion of the results and a synthesis was made. When bounding the possible long-term behaviour, the system evolution for two different situations is considered: an early and a late resaturation, corresponding to a crystalline host rock with higher water influx and a clay host rock with extremely low water supply, respectively. Corrosion rates remain low for both situations. In the early stage, the release of ^{14}C as carbonate or carboxylic acids can be expected according to the experiments. As the resaturation process, also in the case of high water supply, will take much longer in reality

than simulated in the experiments, the observed fast initial release will stretch over a longer period of time.

The long-term release rate and speciation of ^{14}C was experimentally not accessible within the time frame of the CAST project. There are, however indications, what the long-term evolution might be. It could be observed that samples featuring a higher dose rate (Wood/NRG) tend to produce more carbonate in the liquid phase and CO in the gas phase. In an experiment using a piece with a lower dose rate (PSI), the solution was dominated by carboxylic acids and the gas phase by methane. The conclusion is drawn that the higher dose rate and the presence of oxidants due to radiolysis might influence the speciation of carbon after release from activated steel. A later reduction of the dose rate in a time frame of several 100 to 1,000 years due to the decay of some short-lived radionuclides, e.g. ^{60}Co , would mean that the effect of radiolytically produced radicals would cease and the speciation would be shifted to compounds featuring no oxygen-containing functional groups. In such a case, hydrocarbons would be mainly expected. That would mean that a higher percentage of produced ^{14}C compounds would be expected in the gas phase. This suggestion needs further experimental studies to be supported.

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1 Introduction

In many radioactive waste disposal programmes, ^{14}C is an important radionuclide with a potential for significant dose contributions in safety assessments for a geologic repository. In nuclear reactors ^{14}C is mainly formed by neutron capture from ^{14}N , ^{17}O or ^{13}C . Little is known, however, on the chemical form of ^{14}C after release from the waste and the migration of the potential carrier compounds. This gives rise to a considerable uncertainty regarding the fate of ^{14}C and a conservative treatment in safety assessment. The EU project CARbon-14 Source Term (CAST) aims to improve our understanding of the ^{14}C release from different radioactive waste materials, including irradiated metals from reactor internals (steels and Zircaloy), spent ion exchange resins and irradiated graphite, under conditions relevant to geological disposal. The results are evaluated in the context of national safety assessment of the countries involved and disseminated to stakeholders.

In many countries, the majority of ^{14}C in a repository for low and intermediate level waste is contained in activated steel. The radionuclide is assumed to be congruently released during corrosion, but with unknown speciation. Work package 2 of the CAST project studies the release and speciation of ^{14}C from activated steel in a cementitious environment. The objectives of this work are the development of suitable analytical techniques and their application to measure the ^{14}C release from representative activated steel samples to the gas and aqueous phase and the ^{14}C speciation.

Twelve organisations participated in CAST WP2. The progress of work in WP2 was periodically reported in annual reports [Mibus et al., 2015a], [Mibus et al., 2015b] and [Mibus et al., 2017]. A literature research on steel corrosion and release of stable carbon and ^{14}C was made and the results were published in [Swanton et al, 2015]. An important task was the development of suited analytical methods to measure the ^{14}C speciation at very low concentrations. The results were published in [Wieland and Cvetkovic, 2016] and [Bahri et al., 2017]. A number of leaching and corrosion experiments was conducted under a variety of conditions and are published in a several reports: [Rodriguez Alcala et al., 2017], [Leganes Nieto et al., 2018], [Bottomley et al., 2018], [Herm et al., 2017a], [De Visser

Tynova et al., 2018], [Wieland and Cvetkovic, 2018], [Sakuragi, 2017], [Druyts et al., 2017] and [Heikola and Ollila, 2018]. Three separate reports evaluate the influence of parameter variation, namely the influence of the steel sort [Druyts and Caes, 2018], the influence of pH [Herm et al., 2017b] and the influence of oxygen [Rodriguez Alcala et al., 2018]. A final synthesis of the results with special view on the expected long-term behaviour under the conditions of a cement based geological repository was made, which is subject of this report.

2 State of the Art

2.1 Scope

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

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

The results of the review have been presented in Deliverable D2.1 of the CAST project [Swanton *et al.* 2015].

In the following sub-sections, the key findings of the review concerning steel corrosion rates and the release of carbon (stable carbon-12 and carbon-13) and carbon-14 from steels based on information available up to mid-2014, are outlined.

2.2 Corrosion Rates of Steel

The review of corrosion data extended a previous compilation of data for carbon and stainless steels, undertaken in 2006/07 [Smart and Hoch 2010], to include new information in the published literature as well as new information from national programmes supplied by partners in WP2. The review considered the various environments that could be experienced by waste packages containing cement-encapsulated irradiated metal wastes during their long-term management (i.e. during surface storage and transportation), and then in a geological disposal facility (GDF), both before and after resaturation with a groundwater (that could have a high chloride concentration). For each environment, relevant corrosion

rate data for carbon steel and stainless steels were compiled and reviewed critically. The literature review focussed on metal loss and gas generation resulting from general corrosion rather than localised corrosion. The effects of a number of variables (including oxygen concentration, temperature and chloride concentration) on corrosion rates were considered.

Although a number of additional datasets were identified and summarised in the review, in general, they have not changed the view of the likely corrosion rates for carbon steel and stainless steel in the conditions expected during waste disposal, developed previously [i.e. in Smart and Hoch 2010]. However, a paper by Yoshida *et al.* [2013 and later Sakuragi *et al.* 2016b] provided data for the very low corrosion rates experienced by stainless steels under anoxic alkaline conditions, that previously had proved very difficult to measure. These results are important in relation to the issue of carbon-14 release from stainless steels in the longer term in the post-closure phase of a GDF. The data are all below $0.01 \mu\text{m yr}^{-1}$ which was the value recommended as an upper limit in the previous review (and a value of $0.02 \mu\text{m yr}^{-1}$ used in a Japanese assessment [Fepec and Jaea, 2007]). The new data indicated a mean anaerobic corrosion rate of $0.0008 \mu\text{m yr}^{-1}$ for 18/8 stainless steel at 30°C after two years exposure. The data also showed a decrease of the anaerobic corrosion rate under alkaline conditions with time (the significance of which is not yet clear), and a temperature dependence, neither of which could be discriminated previously.

Further experiments performed as part of the CAST project [Sakuragi 2017], over a duration of $6\frac{1}{2}$ years, have confirmed very low corrosion rates for 18/8 stainless steel under anaerobic alkaline conditions (see Figure 2.1), and measured an even lower steady corrosion rate of $0.0004 \mu\text{m yr}^{-1}$ at 30°C between 1 and $6\frac{1}{2}$ years using a gas flow hydrogen monitoring technique.

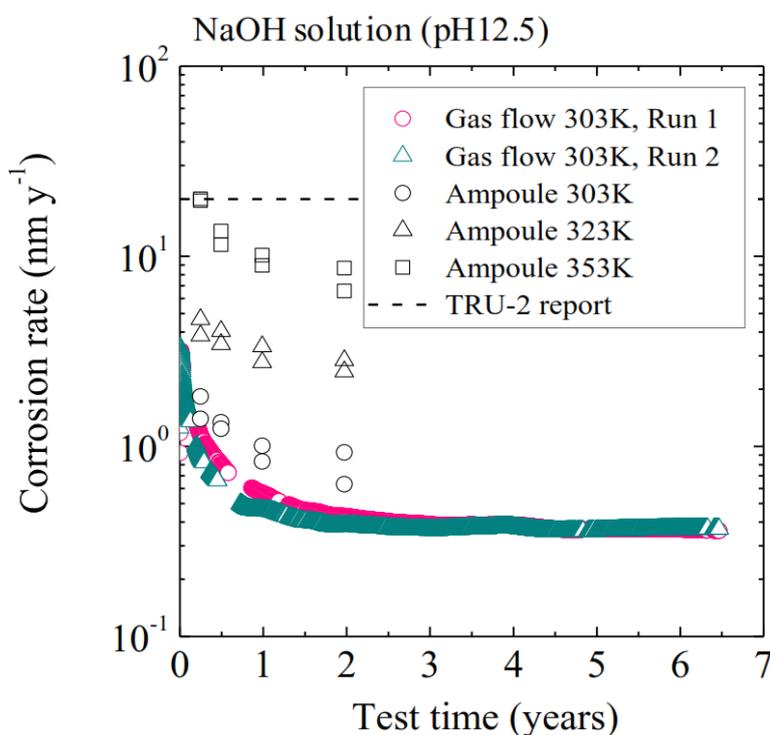


Figure 2.1: Anaerobic corrosion rates of 18/8 stainless steel as a function of time and temperature in a dilute NaOH solution of pH 12.5 measured by the gas flow method [SAKURAGI *et al.*, 2016a] and by the glass ampoule method [YOSHIDA *et al.* 2013, SAKURAGI *et al.* 2016b]. The dashed line is the corrosion rate ($0.02 \mu\text{myr}^{-1}$) assumed in a Japanese safety case (TRU-2 report) [FEPEC and JAEA, 2007].

2.3 Effects of Irradiation on Steel Corrosion

All of the corrosion data compiled in the review was obtained for unirradiated materials, whereas waste reactor steels will have undergone neutron irradiation. It is known that neutron irradiation can change the microstructure of steels. This process, known as radiation damage, has the potential to impact on the corrosion behaviour of waste steels. In addition, the wastes themselves will be a source of α -, β - and γ -radiation resulting from the radioactive decay of neutron-activation products contained therein. This will contribute to an irradiated near-field environment. In particular, irradiation can result in radiolysis of near-field water with the potential to generate reactive, oxidising species, such as hydroxide radicals and peroxide, which may also affect steel corrosion rates.

The review did not consider the potential impact of either irradiation damage or radiolysis on the corrosion behaviour of steels in detail. However, as several of the experiments performed in CAST WP2 have been made on irradiated steel samples, both prior radiation damage and radiolysis may have a bearing on the corrosion rates in the experiments. Some of the potential effects noted in the review can be summarised as follows.

Neutron irradiation of steels causes atomic displacements which result in the formation of vacancies and interstitial atoms in the atomic lattice. The subsequent diffusion of vacancies and counter-diffusion of atoms to reduce the excess energy can result in segregation of alloy components in the matrix due to differences in their rates of diffusion [Was 2007, 2012]. This process can alter the corrosion susceptibility of particular locations in the microstructure of the material. In the context of stainless steel AGR¹ cladding material, for example, neutron irradiation can lead to the development of radiation-induced depletion of chromium at grain boundaries, which renders the material more susceptible to intergranular corrosion and stress-corrosion cracking [Knowles, 2002]. However, the overall impact of neutron irradiation damage on the long-term corrosion rates of waste steels is unknown [Was, 2012].

Most studies of the effects of radiation on steel corrosion have been undertaken on carbon steels under near-neutral conditions by γ -irradiation; both increases and sometimes decreases in the corrosion rate have been reported. In one study of 304L stainless steel, Juhas *et al.* [1984] found that a γ -irradiation field of 1,000 Gy hr⁻¹ over one year actually reduced the measured corrosion rates of the steel in a low-ionic strength groundwater under partially aerated conditions (5ppm O₂).

Of more relevance to geological disposal, recent work for the Belgium national programme [Smart *et al.* 2009, Winsley *et al.* 2011] examined the anaerobic corrosion behaviour of carbon steel at pH 13.4 in concrete and aqueous environments as a function a number of parameters including γ -irradiation (at 25 Gy hr⁻¹). This programme has shown little effect of

¹ Advanced Gas-cooled Reactor

radiation at this dose rate on the anaerobic corrosion rate of carbon steel and the long-term corrosion rates have been found to be $<0.1 \mu\text{m yr}^{-1}$.

2.4 Carbon and Carbon-14 Releases from Irons and Steels

At the outset of CAST, only very limited experimental information was available on carbon-14 releases from irradiated steels. Therefore, the review also considered the releases of stable carbon (carbon-12 and carbon-13) from inactive irons and steels to understand the likely speciation of carbon-14 releases from irradiated steels. The review found that information on the chemical forms of carbon released from steels by corrosion is also limited and the processes involved are not well understood.

The speciation of carbon releases from steels on corrosion is likely to be determined both by the chemical form of the carbon in the steel and the corrosion conditions, in particular the availability of oxygen.

In the low carbon-content steel wastes of interest in CAST WP2 (generally $<0.3\text{wt}\%$ carbon), carbon may be present in steels in the form of interstitial carbides, dissolved in the principal iron phase of the steel (ferrite in carbon steel or austenite in 300-series stainless steel), as a distinct carbide phase with other alloying components (e.g. niobium, manganese) and/or as carbonitride phases. The distribution of carbon between different species will depend on the steel composition and its production process.

The reactivity of the different carbon species that may be present in a steel on contact with water varies considerably [Toth, 1971]. Some alloying components (e.g. niobium, titanium) form very stable interstitial carbide phases that react only slowly with acids releasing methane and hydrogen. In contrast, the electropositive metals (e.g. aluminium) form reactive carbides that are essentially ionic in character, rapidly releasing hydrocarbons related to the nature of the carbide ion present (acetylene in the case of calcium carbide, CaC_2) on contact with water. The smaller-sized transition metal elements (e.g. iron, manganese) form so-called intermediate carbides in which carbon atoms may form chains through a distorted metal lattice; multiple carbide stoichiometries are possible and these carbides may be hydrolysed by water and dilute acids releasing a range of hydrocarbon

species and hydrogen [Cataldo, 2003]. In general, carbonitride phases tend to be more resistant to hydrolysis than the equivalent carbide phase.

There is considerable uncertainty whether carbon-14 produced by activation of nitrogen-14 will be present in the same chemical forms in irradiated steels as the carbon present in the steels at the time of their production; radiation-induced segregation of alloying components of steel may also contribute to a redistribution of the carbon species.

On the basis of the known information on the reactions of metal carbides and carbonitrides with water, the following carbon 14 release behaviour might be expected on leaching an irradiated steel.

- As the steel slowly corrodes, the carbon 14 in its different chemical forms will be exposed to the waste disposal environment; different forms of carbon 14 may be expected to be released in different ways.
- Dispersed ionic and intermediate carbide phases and interstitial carbon present in the iron phase may be hydrolysed over relatively short time periods to form methane, and other hydrocarbons.
- Intermediate carbonitrides may be hydrolysed at a much slower rate than the equivalent carbides to yield a range of products that may include hydrocarbons and compounds containing C-N bonds such as amines and cyanides.
- Stable carbides and carbonitride phases may react only very slowly (if at all) and may be released in particulate form.

Experiments on inactive iron-water systems have shown clear evidence for the release of carbon as hydrocarbon species as a result of the hydrolysis of carbide species in the iron [Hardy and Gillham 1996, Campbell *et al.* 1997, Deng *et al.* 1997]. A variety of species ranging from C1 to C5 hydrocarbons have been identified in the gas phase in separate studies, and quantitative conversion of carbide carbon to hydrocarbons has been reported by Deng *et al.* [1997]. Deng *et al.* [1997] have proposed that hydrocarbon formation occurs through processes similar to those occurring in the Fischer-Tropsch (FT) synthesis of

hydrocarbons from CO/H₂ mixtures over a transition metal catalyst. It is suggested that the carbide species exposed at the iron surface may be similar to the intermediates formed on the surfaces of metal catalysts in the FT synthesis. These intermediates have been shown to form by the chemisorption and decomposition of CO and hydrogen on the metal surface; and include methylidyne (carbide), methylene and methyl species [Kaminsky *et al.* 1986]. It is noted that in the case of iron corrosion in water, hydrogen is generated at the metal surface under anaerobic conditions as a result of the corrosion reactions. Thus, hydrogenation of the carbide, hydrocarbon chain growth and subsequent hydrocarbon desorption may occur by the same processes that occur in FT synthesis.

In contrast to the above experiments with iron-water systems, in experiments on inactive carbon steel and iron carbide, which focused on releases to solution, carbon releases were reported to arise primarily as soluble organic species, with some of the dissolved carbon being inorganic [Kaneko *et al.* 2003, Sasoh 2008a]. A range of low-molecular weight organic species were tentatively identified on the basis of high performance liquid chromatography. Carbon releases from iron carbide were identified as both inorganic and organic.

Prior to CAST, three experimental studies had been performed on carbon-14 releases from irradiated steel, all in Japan [Sasoh 2008a, 2008b, Kogawa 2008, Miyauchi *ET AL* 2011]. Unfortunately, a lack of reports available in English, providing sufficient details of the materials and the experimental methodologies used, hinders a proper evaluation of these studies. The findings of these studies are outlined below:

- In an experiment in which a sample of irradiated stainless steel from the upper grid of a BWR was leached in a pH 10 cement-equilibrated water, carbon-14 was reported to be released to the solution phase as a mixture of inorganic (25-34%) and organic (66-75%) species [Sasoh 2008a, 2008b]. No measurements were made of gas phase releases, and no information is available concerning the amount of carbon-14 released.
- In experiments with irradiated metals where the sample was first acid-cleaned to remove the passivating oxide film, carbon-14 is reported to be released from

irradiated stainless steel, nickel alloy and zirconium alloy into solution at rates that are consistent with metal corrosion rates [Kogawa 2008].

- Miyauchi *et al* [2011] report the release of a small amount of carbon-14 to the gas phase on leaching irradiated stainless steel in alkaline solution for 42 months; the distribution of the 4.76 Bq released was reported to be 25% to the gas phase with a ratio of organic to inorganic carbon 14 of nearly one in the solution phase. Organic species in solution were reported to be predominantly in anionic forms (i.e. carboxylates) rather than neutral species (e.g. alcohols).

These findings required corroboration under CAST WP2.

The review highlighted the lack of well-documented inactive studies of the release of stable carbon from low-carbon and stainless steels that included measurements of carbon releases to both the gas phase and to the solution phase under anaerobic alkaline conditions. Such studies were undertaken as part of CAST WP2 [Cvetković, *et al.* 2017], and the results are summarised in Section 5. These results provide a clearer understanding of the speciation of carbon releases from steels undergoing corrosion, and informed the development of advanced methods for determining the speciation of much smaller quantities of carbon 14 released from irradiated steels in the corrosion experiments performed under CAST WP2.

3 Overview and Experimental Conditions

3.1 *Leaching Experiments*

Work Package 2 is dedicated to the release of ^{14}C from activated steels. The experiments involved samples of different stainless steels, mild steel and also iron or iron carbide. Activated samples of stainless steels and mild steel were employed in the leaching experiments.

In a cement based deep geological repository, alkaline and anaerobic conditions will be prevalent. Therefore, an alkaline solution mimicking a portlandite pore water of pH 12.5 under exclusion of oxygen was chosen as a reference. Nonetheless, a variety of conditions has been studied to account for uncertainties in the evolution of the near field and effects of interim storage. To this end, a range of pH values was studied in several experiments. In addition to the anaerobic reference conditions, ambient air was chosen in selected tests.

The details are reported in the single experimental reports (see list after Table 3.1). An overview on the samples used, the experimental conditions and the analytical techniques applied are given in Table 3.1.

Table 3.1: Overview of leaching experiments and measurements

Partner	Sample	Conditions	Analytics	Ref.
Ciemat	SS304, activated, Jose Cabrera NPP	Solutions: 0.01M NaOH pH 12 1M H ₃ PO ₄ pH 1 Ambient Temp. Synthetic Air	Liquid phase: Combust., LSC IC, LSC Gas phase; GC-MS, LSC	[1]
Enresa	SS304/SS316, Activated, Jose Cabrera NPP	Solution: Purified water, pH 7 Ambient Temp. Synthetic Air	Liquid phase: Gamma spectrometry, AMS	[2]
JRC	SS 15:15Ti, activated, PHENIX	Experiments not started	Experiments not started	[3]
KIT	X7CrNiAl17.7 Plenum spring activated, PWR Gösgen	24% H ₂ SO ₄ + 3% HF, pH 1 Ar atmosphere, ambient T	Liquid phase: Oxidation Gas phase: CO ₂ captured in 2M NaOH LSC	[4]
NRG/ Wood	CT specimen, SS316L(N), activated, HFR Petten	Solution: 0.1M NaOH, pH 13 Gas phase: N ₂ , ambient Temp.	Inorganic ¹⁴ C by acid sep. Select. oxid. Capture as CO ₂ , CO, hydrocarb. (LSC)	[5]
PSI	SS X6CrNiTi 18-10 or similar; Activated PWR Gösgen	Solution: Ca(OH) ₂ sol. pH 12.5 Gas phase: N ₂ ambient temp.	HPIEC-MS, GC-MS, ¹⁴ C AMS, NPOC	[6]
RWMC	SS 18Cr-8Ni Non-irradiated	Solution: NaOH pH 12.5 deionised water Gas phase: N ₂ or Ar	H ₂ measurement GC API-MS	[7]
SCK·CEN	CS JRQ (BR2 PV)	Solution: Ca(OH) ₂ sol. pH 12.5 Gas phase: N ₂ ambient temp.	Liquid phase: TC, TIC, NPOC LSC Gas phase: IC, LSC	[8]
VTT	SS (not spec.)	Solution: AGW pH 8.5 0.01 M NaOH pH 12.4	Liquid phase: LSC, gamma spectrometry	[9]

[1]	Rodriguez Alcala et al. [2017]	AMS	Accelerator Mass Spectrometry
[2]	Leganes Nieto et al. [2018]	GC-MS	Gas Chromatography - Mass Spectrometry
[3]	Bottomley et al. [2018]	HPIEC-MS	High Performance Ion Exclusion - Mass Spectrometry
[4]	Herm et al. [2017a]	IC	Ion Chromatography
[5]	De Visser Tynova et al. [2018]	LSC	Liquid Scintillation Counting
[6]	Wieland and Cvetkovic [2018]	NPOC	Non Purgable Organic Carbon
[7]	Sakuragi [2017]	TC	Total Carbon
[8]	Druyts et al. [2017]	TIC	Total Inorganic Carbon
[9]	Heikola and Ollila [2018]		

3.2 Activation of Steel

The majority of the samples originate from reactor internals or, in the case of SCK·CEN, from the reactor vessel of nuclear power plants. Some samples have been irradiated in research reactors (e.g. the NRG sample from the HRF Petten). The irradiation parameters and history are sufficiently known in most of the cases to estimate the ^{14}C content in the samples. The N_2 content of the samples, in contrast, an important parameter governing the ^{14}C formation, is mostly only known from industrial material specifications.

In two cases, activation calculations in combination with ^{14}C analyses of the metal samples have been performed. The ^{14}C inventory of a stainless-steel sample used in the corrosion experiment at PSI (D2.19) has been studied in an earlier study before the CAST project. The results are reported in [Schumann et al., 2014].

In the other case, the ^{14}C inventory of the stainless-steel plenum spring was experimentally measured after acidic digestion using liquid scintillation counting (for details see [Herm 2014] and [Herm et al. 2017a]). The activation calculation of the sample employed two independent approaches: (i) Simulating the neutron flux using the Monte Carlo N-particle code (MCNP) and subsequently calculating the activation with the CINDER code. (ii) The SCALE/TRITON package was used to develop cladding macro-cross-section libraries,

which were used in the ORIGEN-S code. The full description including further references are given in [Herm et al., 2017a]. The details of the calculations compared to experimental values are compiled in Table 3.3.

Table 3.3: Overview of the activation calculations and comparison of the results with measured ¹⁴C specific activities for irradiated steel samples.

	Study KIT [Herm et al., 2017a] stainless-steel plenum spring		Study PSI [Schumann et al., 2014] guide tube nut
Irradiation Model	MCNP model of fuel assembly	SCALE/TRITON model of fuel assembly	MCNP reactor model of Gösgen PWR
Activation	CINDER	ORIGEN-S	GRS-AKTIV2
N impurity [wt.%]	0.008	0.008	0.0112 ± 0.0031
Experimental ¹⁴ C inventory [Bq/g]	2.7(±0.3)×10 ⁵		17.8(±2)×10 ³
Calculated ¹⁴ C inventory [Bq/g] ¹	8.5×10 ⁴	9.5×10 ⁴	4.5×10 ³
Ratio Exp./Calc. (rounded)	3.2	2.8	4

¹ No uncertainties reported

The model calculations using 2 different samples and 3 different approaches were able to estimate the inventory within an uncertainty factor of 3 to 4. It has to be noted that all calculations underestimated the inventory. The authors assume that the most sensitive parameters are the nitrogen content and the modelled local neutron flux. A systematic study involving a larger number of samples and sample types is still missing. Hence the uncertainty factors derived in this study are only indicative.

4 Carbon Release

4.1 Release of Stable Carbon

4.1.1 Oxidic Conditions

Leaching tests were performed to quantify the release of ^{12}C and ^{14}C from irradiated SS304/SS316 stainless steel in a near neutral solution [Leganés Nieto et al., 2018]. The test coupon was cut from the upper internals of Jose Cabrera NPP. To produce the test coupon several cutting steps were necessary and thus the piece would have a mixed surface consisting of pre-existing oxides and freshly cut areas. The dose rate of the piece at the beginning of the test was measured at 10.8 mSv/h and the ^{14}C activity was calculated to be 77.2 KBq. The leaching test lasted 455 days in total and consisted of 7 leaching steps. After each step the leaching solution was replaced. During the test the pH varied between 6.1 and 7.2 and the temperature varied between 16 and 25 °C.

Post-leaching analyses indicated that the amount of ^{14}C was below the detection limit of the Accelerated Mass Spectrometer used. However, the total amount of carbon, which would be predominantly ^{12}C , was measured by AMS (Fig. 4.1).

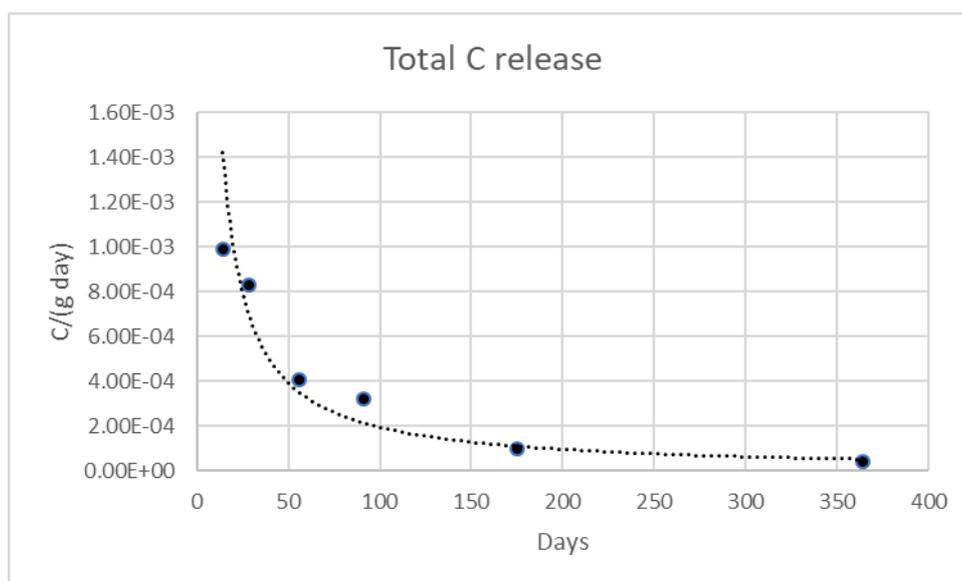


Fig. 4.1: Total carbon release rate.

The results indicate a fast initial release which decreases by an order of magnitude within the first year of exposure. The release rate of carbon was found to correlate linearly to the release rate of ^{60}Co . The corrosion rate of steel was not measured during the leaching tests.

4.1.2 Anoxic Conditions

The release of ^{12}C was investigated by leaching tests lasting several months with carbon and stainless steel [Heikola and Ollila, 2018; Druyts et al., 2017] in alkaline solutions.

Leaching tests with inactive stainless steel and high carbon steel samples were performed in pH 8.5 and 12.4 solutions by [Heikola and Ollila, 2018]. The pH of the solution that was initially 12.4 did not significantly change over the 180 days of testing. In contrast, the solutions that were initially at pH 8.5, increased in pH over 180 days of leaching to 9.7-10.6. The leached carbon was measured in solution with a TOC analyser. The evolution of the release rate with time was similar to that reported for oxic conditions, i.e. it decreased by about 1 order of magnitude during the first year for both materials. During the second year of testing, the release rate was very low. Furthermore, slightly higher amounts of carbon were found in the solutions with the higher pH. Additional tests performed on Fe_3C and AISI316Ti indicated different release rates for the two materials but confirmed the dependence of the release rate on the solution pH (Table 4.1.). Although AISI316Ti steel powder has much lower carbon content, relatively more carbon was released from AISI316Ti stainless steel powder compared to Fe_3C powder.

Table 4.1.: C release rates for Fe_3C and modified AISI316Ti stainless steel powders (fraction/a) [Heikola and Ollila, 2018].

Material	pH 8.5 solution	pH 12.5 solution
<i>Fe₃C</i>	4.8×10^{-4}	8.4×10^{-4}
<i>modif. AISI316Ti</i>	2.9×10^{-3}	3.7×10^{-3}

Leaching tests were performed on irradiated and unirradiated low carbon steel [Druyts et al., 2017] in saturated portlandite solution (pH 12.5). Accelerated (by polarisation in the transpassive region) corrosion tests were done on the same materials in 0.5 M CaCl_2 solution. The irradiated material contained a ^{14}C activity of 175 Bq/g calculated from an

activation simulation in which the measured N content was used. It is interesting to note that the authors performed additional corrosion tests in order to determine the accuracy of the corrosion rate calculation by the release of ^{60}Co . Despite the difficulties due to precipitation of Co as a hydroxide in alkaline environment, the simplifying assumptions of uniform ^{60}Co distribution in the sample and of similar diffusion rates for Co and Fe through the passive film, the outcome of their analyses (7 nm total corrosion depth after 1 year of leaching) is not very different from some of the rates reported in literature [Senior et al., 2017]. The current response of the accelerated tests was used to calculate the corrosion rate, which varied between 150 $\mu\text{m/a}$ for the non-irradiated samples to 63 $\mu\text{m/a}$ for the irradiated sample. However, these rates assume all current is due to corrosion, even though water hydrolysis is expected to take place at such potentials, leading to an overestimation of the corrosion rate. The leached C was analysed only at the end of the tests (after 231 days), so no release rate information is available.

4.2 Release of Carbon-14

4.2.1 Oxidic Conditions

Similar test pieces to those described in Section 4.1.1 and from the same source were used for leaching tests under alkaline (NaOH pH 12) and acidic (1M H_3PO_4) [Rodríguez Alcalá et al., 2017]. The leaching test in alkaline solution consisted of several steps over 281 days. However, only the 1st sampling after 15 days of exposure led to a ^{14}C concentration above the detection limit of the Liquid Scintillation Counter (LSC) used (3.6% of the total ^{14}C was leached). The authors calculated the corrosion rate based ^{60}Co release on the assumption of a homogeneous ^{60}Co distribution throughout the steel. The corrosion rate decreased from $\sim 3.6 \mu\text{m/a}$ after 15 days to 270 nm/a after 281 days. Similarly, only the 1st sampling led to measurable ^{14}C in the acidic solution (5.7% of the total after 14 days). Based on the measured ^{60}Co release, the corrosion rate was estimated to decrease from $\sim 200 \mu\text{m/a}$ after 14 days to 20 $\mu\text{m/a}$ after 263 days.

4.2.2 Anoxic Conditions

A corrosion experiment with irradiated austenitic stainless steel was performed in anoxic conditions in NaOH (pH = 13) solution [De Visser-Týnová et al., 2018]. The inorganic ^{14}C content of the solution was analysed after 1, 3, 6, 13, 22 and 59 weeks. The results indicate a ^{14}C release rate which is the highest during the first 1-2 weeks and the decreases significantly leading to an almost constant cumulative ^{14}C amount after week 3. Similar trends were found for the gas phase. It is interesting to note that the authors calculated an equivalent corrosion rate based on the amount of ^{14}C released during the 1st week and the total amount of ^{14}C in the sample. Assuming that ^{14}C is uniformly distributed in the material, the corrosion rate during the 1st week of testing was 520 nm/a. This value is significantly higher than what is expected for stainless steel under anoxic alkaline conditions, suggesting that ^{14}C is enriched close to the sample surface. Other potential reasons for the observed rate is the presence of residual oxygen during the early stages of the test, significantly larger effective surface area due to roughness, the effects of prior corrosion or radiation damage, or increased reactivity of the surface compared to the bulk. A similar calculation for the later stages of the test led to an average corrosion rate of 3 nm/a for the period between 1 week and 5 months. This value is broadly consistent with corrosion rates reported under similar conditions [Sakuragi, 2017].

A corrosion experiment with irradiated stainless steel was conducted in carbonate-free $\text{Ca}(\text{OH})_2$ solution (saturation w.r.t. portlandite) for a total of 412 days [Wieland and Cvetkovic, 2018]. Corrosion rates were estimated based on ^{60}Co . The early stage corrosion rate was ~20 nm/a while 2 nm/a were calculated for the end of the test. The concentration of dissolved ^{14}C evolves in a similar way to the corrosion rate during the early stages. For periods longer than 92 days the total ^{14}C carbon in solution was found to decrease with time. For the moment it is uncertain whether this is due to decomposition of the ^{14}C -bearing compounds or within the uncertainty of the experimental method.

5 Carbon Speciation in Aqueous and Gaseous Phase

The speciation of ^{14}C determines possible routes of its migration from the engineered barrier of a deep geological repository into the surrounding geological formations. Therefore, knowledge about the chemical form of ^{14}C is required in support of safety assessment. Further progress in our understanding of the speciation of ^{14}C has been made in the framework of the CAST project as summarised below.

^{14}C released during the corrosion of irradiated steel is either bound as aqueous species in the inorganic chemical form ($\text{H}_2^{14}\text{CO}_3$ and its bases) or in the organic chemical form, or ^{14}C may be carried by gaseous and volatile species. Experimental studies are required that allow the proportions of the three different chemical forms of ^{14}C to be assessed. This information results from the identification and quantification of the individual ^{14}C containing compounds produced during the corrosion of irradiated steel. It is anticipated that the chemical conditions applied in the experimental studies might have an effect on the types of ^{14}C species formed during corrosion, in particular the pH of the solution (acid, neutral, alkaline) and whether or not oxygen is present in the experiments (i.e. oxic versus anoxic conditions).

Irradiated steel also contains stable carbon in addition to ^{14}C . Stable carbon is added as alloying element and its content is typically up to 1.5 weight (wt)% in carbon steel and is typically below 0.15 wt% in the case of stainless steel. The question has been raised whether or not the speciation of ^{14}C and stable carbon is identical upon release from irradiated steel during corrosion as their original chemical form in steel might be different [Swanton et al., 2015]. Comparison of the speciation of stable carbon and ^{14}C determined in the same experiment could help in further clarifying this open issue.

The following discussion is structured along the above criteria, i.e. whether carbon-12 or ^{14}C speciation was studied in the experiment and with a view to the specific chemical conditions applied in the experiments, e.g. pH of solution and oxic/anoxic atmosphere.

5.1 Speciation of Stable Carbon

Several participants addressed the chemical speciation of stable carbon during corrosion of iron, stainless steel, carbon steel, and iron carbide. The experiments were carried out in near neutral and alkaline media in oxic or anoxic conditions, respectively.

5.1.1 Oxic Conditions

Leaching tests were performed to quantify the release of stable carbon from irradiated steel in deionised water (pH 7±1) [Leganés Nieto et al., 2018]. Information on the chemical species formed upon release is not available.

A leaching test was conducted to determine the speciation of ^{14}C released from irradiated stainless steel in oxic leachates (NaOH pH 12 and 1 M H_3PO_4) between 15 and 281 days [Rodríguez Alcalá et al., 2017]. In the alkaline leachate CO was identified as carbon species in the gas phase while the concentrations of the aqueous species, in particular carboxylates, was below the Limit Of Detection (LOD). CO was also the only carbon species present in the gas phase during acid leaching while oxalate was the only water-soluble carbon species detected above the LOD. Neither alcohols nor aldehydes were detected. Both the gaseous species, CO, as well as the aqueous species, oxalate, identified in this study are considered to be stable carbon compounds.

5.1.2 Anoxic Conditions

The speciation of stable carbon was investigated in long-term leaching tests with carbon steel and stainless steel and conducted by two participants [Heikola and Ollila, 2018; Druyts et al., 2017]. These tests were summarised in Druyts and Caes [2018]. Furthermore, the speciation of stable carbon was studied in batch-type short-term corrosion studies with iron powders [Cvetković et al., 2017].

After finishing the leaching test with carbon steel the gas phase was analysed in one of the experiments [Druyts et al., 2017]. The gaseous carbon species were identified and quantified once at the end of the experiment after 231 days leaching. The following hydrocarbons were

identified: methane (10.4 $\mu\text{L/L}$), ethane (1.7 $\mu\text{L/L}$) and ethene (0.6 $\mu\text{L/L}$). In addition, carbon dioxide (CO_2) was detected. Nevertheless, the authors concluded that CO_2 was presumably a contaminant rather than produced during leaching.

The aqueous phase was analysed in two leaching tests with stainless steel (pH 8.5 and 12.5) [Heikola and Ollila, 2018]. Carbon was found to be predominately present in the organic chemical form (76/100 %) with minor proportions present in the inorganic chemical form (24/0 %). Note that possible contributions to the organic carbon content due to contamination by surfactants cannot be excluded and the issue was raised by the authors. The results suggest that the larger proportion of carbon was present in the organic chemical form rather than in the inorganic chemical form. Methanol, ethanol and 1-propanol were the volatile alcohols detected at concentrations close to the LOD. No organic compounds were detected in the gas phase.

A leaching experiment with iron carbide (Fe_3C), conducted in anoxic near neutral and alkaline conditions (simulated groundwater with pH 8.5 and 12.4), confirmed the presence of the aforementioned alcohols. In addition ethane, propane, propylene, butane, 2-butene, 2-methylbutane, pentane, pentene and hexane were identified as gaseous carbons species [Heikola and Ollila, 2018].

Cvetković et al. [2017] studied the carbon speciation produced in short-term experiments (maximum 35 days) using micron-size iron powders immersed in alkaline solutions (pH = 11, 12.5 and 13.3). Aqueous and gaseous phase were analysed to determine the main compounds. Methane was the main gaseous species formed in all systems regardless of the pH of the solution. The concentrations of the C2 – C4 species were significantly lower. The order of concentrations was reported to be: methane \gg ethane \sim ethene \sim propylene $>$ propane $>$ butane. Acetate was the main carbon compound present in the aqueous phase. Formate and oxalate were present at lower concentrations while malonate was identified at close to the LOD. The order of concentrations was given as follows: acetate \gg formate $>$ oxalate \gg malonate. In addition, alcohols (methanol, ethanol) and aldehydes (formaldehyde, acetaldehyde, propionaldehyde) were identified, but at concentrations close to the LOD. The results from experiments performed on the basis of a sequential

replacement of the solutions in contact with iron powders indicated that gaseous species were formed as a result of the corrosion process in anoxic conditions while the presence of carboxylates was attributed to the exposure of the iron powders to oxic conditions prior to corrosion. The latter compounds were instantaneously released into solution at the very beginning of the corrosion process.

The findings from the batch-type leaching corrosion tests carried out in alkaline anoxic conditions are consistent. Note that carbon steel was used in the former test while the latter tests were carried out with iron powders. Methane was the main carbon species while C2 – C4 hydrocarbons, such as ethane, ethene etc., were only minor species with respect to their concentrations. Acetate was the main water-soluble carbon species while formate and oxalate were less important with respect to their concentrations.

5.2 Carbon-14 Speciation

Irradiated stainless steel samples were the ^{14}C source used in the following studies. Leaching tests were carried out in acidic and alkaline media.

5.2.1 Acidic Anoxic Conditions

The speciation of ^{14}C was determined in acidic conditions by using a mixture of dilute $\text{H}_2\text{SO}_4/\text{HF}$ [Herm et al., 2017a; Herm et al., 2017b]. The strongly acid media led to complete digestion of the stainless steel specimen within a day. About 70% of the total ^{14}C inventory was released as dissolved organic compounds into the aqueous phase and about 30% as organic compounds into the gas phase during the course of complete digestion of the irradiated stainless steel specimen. The portion of ^{14}C in the inorganic chemical form, both in the aqueous and gaseous phase, was less than 1%. The individual ^{14}C bearing species were not identified in this study.

5.2.2 Alkaline Anoxic Conditions

A corrosion experiment with irradiated austenitic stainless steel was performed in anoxic conditions in 600 cm^3 NaOH (pH = 13) solution [De Visser-Týnová et al., 2018]. The

irradiated specimens had been stored for a period of almost 20 years in a waste disposal facility. The specimens were not subjected to particular pre-treatment prior to use in the experiments. The experiment was carried out in duplicate (experiments C2 and C3) in borosilicate glass containers with zirconia liners, with gas and liquid sampling systems emplaced in a shielded cell with an inert, N₂ atmosphere. The experiments were sampled periodically up to 59 weeks leaching. ¹⁴C analysis was based on gas sampling rigs which allowed separation and quantification of ¹⁴C released as CO₂, CO (including volatile oxygen-containing organic species) and gaseous hydrocarbons, in particular CH₄. A procedure was applied that allowed leached ¹⁴C present as carbonate to be quantified in the liquid phase. No specific analytical method for the identification and quantification of the water-soluble organic ¹⁴C fraction, in particular small carboxylic acids, was available. A method for total ¹⁴C analysis is under development; preliminary results are available for samples collected after 59 weeks.

In this experiment, ¹⁴C was released primarily to solution as ¹⁴C bearing carbonate (¹⁴CO₂) (~ 99 % in C2 and ~ 90 % in C3). Only about ~ 1% (C2) and ~ 10 % (C3) of the total ¹⁴C was released to the gas phase, mainly in the chemical form of ¹⁴C-hydrocarbons (~ 90 %) and some ¹⁴CO (~ 10 %). No ¹⁴CO₂ was detected in the gas phase. Release of the water-soluble ¹⁴C containing compounds was fast, initially. The steady state of release was reached after ~ 3 weeks. The activity of the volatile species, i.e. ¹⁴C-hydrocarbons and ¹⁴CO, increased continuously with time in one experiment (C2), while in C3, the rate of gas-phase release decreased over time after the initial 3-week phase of faster release. Measurements of total ¹⁴C release after 59 weeks were slightly higher than the inorganic ¹⁴C measurements indicating that some ¹⁴C was also released as soluble organic species, about 20% in C2 and 40% in C3. Thus, the total ¹⁴C releases in the experiments at earlier durations are likely to have been underestimated.

A corrosion experiment with irradiated stainless steel was conducted by another participant of CAST using a 500 mL gas-tight autoclave-type reactor with a PEEK liner emplaced behind a lead shielding [Wieland et al., 2017]. Two 1g stainless steel specimens were immersed in 300 cm³ carbonate-free Ca(OH)₂ solution (saturation w.r.t. portlandite) covered with 200 cm³ N₂ atmosphere at 5 bar pressure. The analytical method was based on

compound-specific ^{14}C AMS which allowed the concentration of the individual water-soluble carboxylic acids and the total organic ^{14}C fraction (TO^{14}C) to be quantified. No quantification of the ^{14}C carbonate fraction or the volatile hydrocarbons was undertaken. Both methods are under development.

^{14}C containing acetate, formate and lactate were identified and quantified. The proportions were as follows: acetate ~ 32 %, formate ~ 40 %, and lactate ~ 25 %. The total concentration of these compounds corresponds to the total TO^{14}C , which was determined by direct analysis of an aliquot of the alkaline solution using ^{14}C AMS. This finding indicates that three carboxylates are the main water-soluble organic ^{14}C containing compounds. The TO^{14}C content strongly increased within the first 93 days of reaction in accordance with a fast initial release of the carboxylates. After this first phase, however, the rate of release dropped significantly.

In the latter experiment, also the individual stable carbon compounds (volatile and aqueous species) were separated and quantified using standard analytical techniques, i.e. high performance ion exchange chromatography and gas chromatography both with mass spectrometry detection. Methane (CH_4) and ethene (C_2H_4) were the main carbon species detected in the gas phase while acetate, formate and lactate were the main water-soluble carbon species identified. Nevertheless, the concentration of the carboxylates was found to be very high, in particular much higher than predicted on the basis of ^{12}C release from the irradiated steel specimens. The reason for this finding is unclear but it was speculated that another stable carbon source was present in the reactor in addition to irradiated steel, for example the PEEK liner.

5.3 Summary of Stable Carbon and Carbon-14 Speciation

Table 5.1 summarises the stable carbon and ^{14}C species that had been identified in corrosion experiments carried out in the framework of the CAST project along with those previously reported in the literature. Note that all ^{14}C species identified in the corrosion experiment with irradiated steel in alkaline conditions were also observed in the corrosion experiments with non-activated iron or steel (Table 5.1). Methane (CH_4) and carbon monoxide (CO)

were identified as the main gaseous species while formate (CH_2O_2) and acetate ($\text{C}_2\text{H}_4\text{O}_2$) were found to be the main water-soluble organic carbon species. Lactate ($\text{C}_3\text{H}_6\text{O}_3$) was present at lower concentration. In addition, inorganic carbon (CO_3^{2-}) might be formed during the course of the corrosion process. All other carbon species could be present, however, at significantly lower concentration.

Table 5.1: Stable carbon and carbon-14 species reported by CAST and in earlier studies

Stable Carbon	Reference	Carbon-14	Reference
Alkane/alkene		Alkane/alkene	
*methane (CH ₄)	[1], [3]	Hydrocarbons	[4]
ethane (C ₂ H ₆)	[1], [2], [3]		
ethene (C ₂ H ₄)	[1], [3]		
propane (C ₃ H ₈)	[1], [2], [3]		
propylene (C ₃ H ₆)	[1], [2], [3]		
butane (C ₄ H ₁₀)	[1], [2], [3]		
2-butene(C ₄ H ₈)	[1], [2]		
2-methylbutane (C ₅ H ₁₂)	[2]		
pentane (C ₅ H ₁₂)	[2]		
pentene (C ₅ H ₁₀)	[1], [2]		
hexane (C ₆ H ₁₄)	[2]		
Carbon dioxide (CO₂)	[1]	Carbon monoxide (CO)	
* Carbon monoxide (CO)	[1], [6]		[4]
Alcohols/aldehydes			
methanol (CH ₄ O)	[1], [2], [3]		
ethanol (C ₂ H ₆ O)	[1], [2], [3]		
propanol (C ₃ H ₈ O)	[1], [2]		
formaldehyde (CH ₂ O)	[1], [3]		
acetaldehyde (C ₂ H ₄ O)	[1], [3]		
propionaldehyde (C ₃ H ₆ O)	[1], [3]		
Carboxylic acids		formic acid (CH ₂ O ₂)	
*formic acid (CH ₂ O ₂)	[1], [3]	acetic acid (C ₂ H ₄ O ₂)	[5]
*acetic acid (C ₂ H ₄ O ₂)	[1], [3]		[5]
propionic acid (C ₃ H ₆ O ₂)	[1]		
butyric acid (C ₄ H ₈ O ₂)	[1],		
malonic acid (C ₃ H ₄ O ₄)	[1], [3]		
oxalic acid (C ₂ H ₂ O ₄)	[1], [3]	lactic acid (C ₃ H ₆ O ₃)	
lactic acid (C ₃ H ₆ O ₃)	[3]		[5]
* Carbonate (CO₃²⁻)	[1]	Carbonate (CO₃²⁻)	
			[4]

* denotes main species

[1] Wieland and Hummel [2015]

[2] Heikola and Ollila [2018]

[3] Cvetković et al. [2017]

[4] De Visser-Týnová et al. [2018]

[5] Wieland et al. [2017]

[6] Rodriguez Alcalá et al. [2017]

5.4 Time Dependence of Carbon Species during Corrosion

The experimental data obtained in the corrosion studies with irradiated steel suggest that, both in acidic and alkaline conditions, the largest portion of ^{14}C is present as dissolved species, either in the organic or inorganic chemical form [De Visser-Týnová et al., 2017; Herm et al., 2017a; Herm et al., 2017b]. The proportion of gaseous species is much less, i.e. ~30 % in acidic conditions [Herm et al., 2017a] and 1 % or 10 %, respectively, in alkaline conditions [De Visser-Týnová et al., 2018]. Hydrocarbons were identified as the main species in the latter study. The corrosion experiments with irradiated steel in alkaline conditions suggest a continuous release of ^{14}C -hydrocarbons with time in experiment C2 up to 59 weeks. However, in the duplicate experiment (C3), the rate of ^{14}C -hydrocarbon release decreased with time between 3 and 59 weeks. This may be related to the significantly higher initial release rate (factor 10) in C3 compared to C2, so that the gas phase release in C3 may not have reached a steady-state. The significantly higher initial release rate in C3 could be caused by differences in the initial stage of the irradiated material (e.g. difference in reactive surface area, non-uniform distribution of ^{14}C , etc.). The concentration of the water-soluble species remained constant over longer times in experiment C3 while a small increase with time was observed in the experiment C2 [De Visser-Týnová et al., 2018].

Hence, ^{14}C hydrocarbons (in particular $^{14}\text{CH}_4$) may be continuously produced during the course of the corrosion process. In contrast, the water-soluble fraction was most likely released at the start of the experiment. In addition, however, there is some evidence for slow but continuous increase in the concentration of the water-soluble ^{14}C species with time [De Visser-Týnová et al., 2018]. Additional samplings are needed to resolve the open issue regarding the long-term fate of the water-soluble ^{14}C species. Currently it is inferred from the results that the concentration of gaseous species may increase with time and eventually exceed the concentration of the water-soluble ^{14}C species on the assumption that instantaneous release of the water-soluble ^{14}C species occurred in the very beginning of the corrosion experiments. This implies a shift of ^{14}C release to the gaseous chemical forms in the long term. Note further that a continuous production of CH_4 during corrosion was supported by earlier studies using non-irradiated iron powders [Cvetković et al., 2017].

The proportion of the water-soluble organic and inorganic chemical forms of ^{14}C produced during corrosion or irradiated steel is uncertain. In strongly acidic conditions, the main fraction was associated with the organic chemical form while the portion of inorganic carbon was negligible [Herm et al., 2017a]. In contrast, it was proposed that the inorganic chemical form predominantly forms in alkaline conditions [De Visser-Týnová et al., 2018]. Hence, quantification of the ratio of water-soluble organic to inorganic carbon is still an open issue.

The concentrations of the water-soluble chemical forms were found to be high already in the very early phase of the leaching process which could indicate instantaneous release of these compounds from the surface of the steel. It was postulated that the water-soluble oxygenated hydrocarbons were generated during exposure of the steel/iron surface to oxidising conditions and subsequently detached from the surface or the oxide layer of steel/iron [Cvetković et al., 2017]. This interpretation implies that oxidised species are only produced in the initial phase of the leaching process rather than in the longer term as a result of corrosion of the irradiated steel.

The portion of carbon released in the initial phase of the leaching process was quantified in terms of instantaneous release of ^{14}C compounds. It was estimated that instant release accounts for $\sim 5 \cdot 10^{-4} \%$ and $\sim 3 \cdot 10^{-5} \%$ of the total ^{14}C inventory of irradiated steel using the ^{14}C inventories and concentrations of dissolved ^{14}C species reported by De Visser-Týnová et al. [2018] and Wieland et al. [2017]. It is to be noted that the amount of instantaneously released ^{14}C is much less than the amount estimated on the basis of the corrosion experiments with non-irradiated iron powders, which accounts for $\sim 0.2 \%$ of the total stable carbon inventory [Cvetković et al., 2017]. It is further to be noted that instantaneous release is caused by oxidised carbon species being attached to the surface of steel or accommodated by the oxide layer of steel. The inventory of the latter species depends on the kind of, and exposure time to oxidative treatment of steel prior to the start of the leaching experiments, e.g. exposure and storage in air, etc.

5.5 Effect of pH and Radiation

The compilation of compounds given in Table 5.1 shows that the same types of main carbon species were observed in corrosion studies with irradiated and non-irradiated steel/iron carried out in alkaline media. Note that the results from studies in strongly acidic conditions are not taken into account as these conditions are not directly related to a repository environment. Furthermore, information on the carbon speciation in near neutral conditions gained in the framework of the CAST project is limited as an adverse effect on carbon speciation due to the presence of surfactants was suspected in the related experiments.

The rate of release of gaseous and water-soluble species with time in the corrosion studies with non-irradiated materials (iron, Fe₃C) in alkaline conditions seems to be consistent with that determined in the corrosion experiments with irradiated steel. In particular, the water-soluble species are released to solution in the very early stage of the leaching process while the concentration of the gaseous species, mainly methane, seems to slowly increase with time. Hence, the same global picture of species production was observed with non-irradiated and irradiated materials. This suggests that both pH and radiation presumably have only a minor effect on carbon speciation and release rate in the experiments with irradiated steel. On the other hand, in two experiments leaching stainless steel samples under alkaline, anaerobic conditions (NRG/Wood [De Visser Tynova et al, 2018] and PSI [Wieland and Cvetkovic, 2018]) quite a different speciation was measured. In the NRG/Wood experiments carbonate (liquid phase) and CO (gas phase) were the dominating species, while PSI reported carboxylic acids (liquid phase) and methane (gas phase). It is interesting to note that the NRG/Wood samples featured an estimated dose of 10 – 20 Gy/h while in the case of PSI a dose 2 orders of magnitude lower was estimated. Here, an influence of the irradiation cannot be excluded.

5.6 Chemical Stability of Carbon Species

At the present time, the chemical stability of ¹⁴C containing compounds in the conditions relevant to a cement-based repository (alkaline pH, presence of H₂, low to moderate radiation exposure) has to be assessed on the basis of thermodynamic modelling and a

review of the literature published in other areas of research. Note further that the stability and degradation of organics was not specifically addressed by the CAST project. The following considerations are aimed to assess whether low molecular weight organic compounds (e.g. carboxylates) are chemically stable in the hyper-alkaline conditions of a cement-based repository or can be decomposed into hydrocarbons and carbonate by non-microbiological processes.

A preliminary assessment on the basis of thermodynamic modelling showed that the ^{14}C containing low molecular weight organic molecules may not be chemically stable under the hyper-alkaline, reducing conditions of a cement-based repository in case of complete thermodynamic equilibrium [Wieland and Hummel, 2015]. On the assumption of complete thermodynamic equilibrium, methane and carbonate are the most stable carbon species in reducing, alkaline conditions while other alkanes, such as ethane, and small carboxylic acids are only minor species. This finding is in line with an earlier study reported by Thorstenson [1970]. Nevertheless, it is conceivable that complete thermodynamic equilibrium is not achieved in the C-H-O system at moderate temperatures. Kinetic hinderance of the formation of methane, alkanes and alkenes and, accordingly, of the decomposition of oxygenated hydrocarbons, such as carboxylic acids, to CO_2 and CH_4 implies that the oxygenated hydrocarbons could be metastable and persist over a very long period of time in a repository. Assuming kinetic hindrance is justified based on evidence provided from studies on the type and concentration of organic compounds in sedimentary basins [Shock, 1988]. Field observations and results from laboratory experiments have successfully been interpreted in terms of metastable thermodynamic equilibria, for example the high concentrations of acetic acid observed in sedimentary basins. Other field observations and experimental results, however, could not be explained in terms of metastable equilibria, for example the relative abundances of acetic and propanoic acids observed in sedimentary basins. If the explanation via metastable equilibria fails then reaction mechanisms and kinetic arguments are used rather than thermodynamic considerations. Hence, although the concept of metastable states in water-rock-organic systems is very useful to rationalise field observations and experimental findings, it has not yet any predictive capabilities, and in particular no predictive capability in connection with the assessment of the non-microbiological degradation of organics in the cement-based near field of a repository for

radioactive waste. It is to be noted that microbiological degradation of organics is expected to prevail in near neutral to moderately alkaline conditions, such as at the interface between the engineered barrier and the host rock, where microbial activity is not inhibited by the hyper-alkaline conditions of a cement-based near field.

Information about the chemical stability of carboxylic acids is available from other areas of research, such as catalytic conversion of organic compounds. For example, the decomposition of carboxylic acids was found to be controlled by decarboxylation reactions in anoxic conditions. Such reactions involve breaking of C-C bonds, such bonds are controlled by high activation energies [e.g., Bell et al., 1994; Onwudili and Williams, 2010; Palmer and Drummond, 1986]. This explains the high resistance of most aliphatic carboxylic acids to decomposition at temperatures below 300°C. Only formic acid was observed to decompose at lower temperatures due to the absence of a C-C bond. Literature further suggests that the chemical stability of small aliphatic carboxylic acids increases significantly with increasing pH. By contrast, the presence of catalyst surfaces such as stainless steel, montmorillonite, hematite, etc. appears to significantly accelerate the decomposition of carboxylic acids. It was observed that, in reducing conditions and at elevated temperature (175°C) and high pressure (350 bar), the presence of CO₂ and H₂ in solution, resulting from the decomposition of aliphatic carboxylic acids, may lead to the formation of new organic compounds such as long-chain linear alkanes, alkanols and alkanolic acids via Fischer-Tropsch synthesis [McCollom and Seewald, 2003].

The literature survey suggests that decarboxylation of the carboxylic acids in repository relevant conditions cannot be excluded while the reaction may be very slow at ambient temperature. Nevertheless, it should be noted that the experimental studies on the decomposition of organic compounds published in the literature have been performed in acidic or neutral pH conditions at high temperature (>250°C) and high pressure (>200 bar). To the best of our knowledge experimental studies on the chemical stability of organic compounds in conditions relevant to a cement-based repository, i.e. alkaline conditions, enhanced partial pressure of H₂, presence of steel as potential catalyst, are still lacking. In particular, knowledge of potential catalysts and reactants necessary to promote the degradation process in a repository environment is important. Therefore, experimental

studies in combination with thermodynamic modelling are needed to assess the long-term chemical stability of the most important water-soluble ^{14}C containing carboxylates that are produced during the corrosion of irradiated steel, in particular formate and acetate.

6 Expected Long-term Evolution and Uncertainties

In the evaluation of the release and speciation of ^{14}C under geological disposal conditions, uncertainties are introduced at an early stage, i.e. the ^{14}C inventory. The inventory is calculated based on the N content of the steel and other metallic materials and the neutron flux during reactor operation that depends on the specific position of the piece. Significant uncertainties exist in both the actual amount of N, which can differ significantly from the nominal amount reported by the manufacturer, and on the exact position of the metal in question in the reactor. Uncertainties in the range of 300-400% have been identified between modelled and measured inventories of irradiated steel samples studied under CAST (see section 3.2).

An additional uncertainty is related to the surface state of the metallic pieces. Surface oxides that were present during operation will tend to be thicker and will have been irradiated, thus ^{17}O activation may be important and produce ^{14}C additional to that from ^{14}N activation. Different surface oxides would be present on metallic surfaces that have been formed by cutting during decommissioning and conditioning of the waste in cement. Oxides would form under oxic unsaturated conditions during interim storage. For carbon steel, corrosion rates in the range of 100 nm/yr are expected under such conditions. We currently have no information on the fate and speciation of ^{14}C released under interim storage conditions.

During the early stages of disposal, exposure conditions will remain relatively unchanged (oxic, unsaturated). The only major difference would be an increase of the relative humidity to 100% relatively soon after sealing of the emplacement cavern. An appreciable effect would be expected in the case of early water ingress, leading to oxic and saturated conditions. Such conditions would be expected in repositories constructed in fractured crystalline rocks. Corrosion rates of a few μm per year have been measured for stainless steel in simulated cement porewater, followed by a relatively quick release of ^{14}C species [Leganes Nieto et al., 2018]. Under oxic conditions, only CO was detected, in accordance to the prevailing oxidising conditions.

In absence of early water ingress, as would be expected in clay-based repositories, oxic unsaturated conditions are expected to gradually evolve to anoxic unsaturated conditions as oxygen trapped in the cement pore space is consumed by corrosion and other processes. While we have no experimental information on the release and speciation of ^{14}C under such conditions, corrosion rates for carbon steel embedded in unsaturated, anoxic cement are extremely low, in the range of 2-4 nm/yr [Senior, 2017].

The released dissolved ^{14}C species can only slowly diffuse away in the thin water film of the unsaturated cement backfill and accumulate near the metal / cement interface; as soon as phases become supersaturated, they may precipitate. Carbonate forms calcite, oxalate might form calcium oxalate (whewellite) in the calcium rich cement pore water. Gaseous compounds in contrast, may diffuse through the gas filled pore space or even be advectively displaced due to pressure build-up in the gas phase [Diomidis et al., 2016].

Partly saturated conditions may prevail for many thousands of years as water ingress is counterbalanced by gas generation. For example, for a Swiss repository in Opalinus Clay, the cementitious nearfield remains only partly saturated for at least 100'000 yrs [Diomidis et al., 2016]. This is about 17 half-lives, indicating that any ^{14}C release would be under unsaturated conditions. Upon saturation, corrosion rates are not expected to significantly change and will remain in the range of a few nm per year.

The release of ^{14}C from activated steel in the early phase, i.e. after the first contact of the metal surface with water, will involve the chemical compounds found in the early stage of the leaching experiments. It can be assumed that mainly oxygen containing species like carbonate or carboxylic acids are released to the liquid phase and some smaller amounts of CO and also methane are transferred to the gas phase. These compounds will be released from the metal oxide layer or surface contaminations. The wetting and resaturation process in the waste and the repository near field, which will last over thousands of years, can only poorly be simulated by the sudden immersion of the dry samples into the experimental leaching solution. Hence, the quite fast release process observed in the experiments will, in reality, carry on for a much longer period.

After release of ^{14}C compounds from the metal oxide layer, the ^{14}C from the bulk material will be released upon further steel corrosion. It is still unclear what the source of oxygen for the formation of carbonate or organic compounds with oxygen-containing functional groups will be. From two experiments (s. section 5.5), the conclusion can be drawn that radiolysis with subsequent formation of oxidants may enable the formation of these species. While this may be an explanation for experimental results, it must be considered if this effect may play a role in the real repository. Due to the formation of large amounts of gas, mainly hydrogen due to the corrosion of metallic waste, significantly more oxidants produced by radiolysis would be consumed by dissolved H_2 [Pastina and LaVerne, 2001] compared to the experiments where only one piece of metal slowly produced a small amount of H_2 . This effect would mean that the speciation under real repository conditions will shift towards hydrocarbons without oxygen containing functional groups such as methane implying the formation of gaseous species instead of dissolved.

Later, the impact of irradiation and radiolysis on the chemical conditions in solution in the repository will decrease with the decay of relatively short-lived gamma emitters like ^{60}Co . Model calculations in [Nagra, 2002] consider a time frame of 1'000 years to reduce the beta and gamma activity in a Swiss ILW repository by a factor of 100. It can be expected that at the latest then the influence of radiolysis on the formation of oxygen containing ^{14}C species will be diminished. As a consequence, the formation of gaseous hydrocarbons can be expected to increase during the long-term release.

7 References

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