

RELEASE AND SPECIATION OF ^{14}C DURING THE CORROSION OF ACTIVATED STEEL IN DEEP GEOLOGICAL REPOSITORIES FOR THE DISPOSAL OF RADIOACTIVE WASTE

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ABSTRACT. Carbon-14 (radiocarbon, ^{14}C) is an important radionuclide in the inventory of radioactive waste in many disposal programs due to its significant dose contributions in safety assessments for geological repositories. Activated steels from nuclear reactors are one of the major sources of ^{14}C . Knowledge of ^{14}C release from steel wastes and its chemical form (speciation) is limited giving rise to uncertainty regarding the fate of ^{14}C and a conservative treatment in assessment calculations. In this work, we summarize and make a synthesis of selected results from Work Package 2 of the EU CAST project aiming to improve understanding of ^{14}C release related to steel corrosion under repository-relevant conditions. The outcome of the experiments is discussed in the context of the long-term evolution of a repository and its potential consequences for safety assessment.

KEYWORDS: activated steel, corrosion, radioactive waste disposal.

INTRODUCTION

In many radioactive waste disposal programs, carbon-14 (radiocarbon, ^{14}C) is an important radionuclide with a potential for significant dose contributions in safety assessments for a geological repository. In nuclear reactors ^{14}C is mainly formed by neutron capture from ^{14}N , ^{17}O or ^{13}C . Little is known, however, of 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. Activated steel from nuclear reactors is one of the major sources of ^{14}C in waste inventories worldwide. The radionuclide is usually assumed to be congruently released during steel corrosion, but with unknown speciation (Swanton et al. 2016). The principal objective of Work Package 2 (WP2) of the EU CAST (CArbon-14 Source Term) project has been to measure the rates and speciation of ^{14}C release from activated steel under repository-relevant conditions to address these uncertainties. The main focus has been on anoxic, high-pH conditions. Such conditions will prevail in a cement-based deep geological repository during the post-closure phase due to the consumption of oxygen by a number of chemical and biological processes (Johnson and King 2008; Diomidis and Johnson 2014) and due to the leaching of alkalis from the cement used for waste conditioning and tunnel backfilling. However, studies have also been performed under oxic conditions at a range of pH values to explore uncertainties related to the evolution of the near field and to different disposal concepts (e.g. near surface repository). The state of understanding of carbon and ^{14}C release from steels during corrosion at the start of the CAST project is summarized briefly below (Swanton et al. 2015).

Steel Corrosion

In general, ^{14}C is assumed to be released from activated steels as the steel corrodes and thus steel corrosion rates are an important input to safety assessments of ^{14}C release. A number of reviews

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of published corrosion data considering the various environments that could be experienced by waste packages containing cement-encapsulated irradiated metal wastes have been published (Smart and Hoch 2010; Diomidis 2014; Swanton et al. 2015). There is a general agreement that uniform corrosion rates of a few 10s nm/a for carbon steel and a few nm/a for stainless steel are expected under anoxic alkaline conditions. It is notable that the very low corrosion rates experienced by stainless steels under these conditions have proved difficult to measure. At the start of the CAST project, new data were emerging from Japan for the successful measurement of sub-nm/a anaerobic corrosion rates for 18/8 stainless steel under high pH conditions (Sakuragi et al. 2016a,b). Further studies to corroborate these very low corrosion rates have been performed under CAST WP2 (Sakuragi 2017).

Chemical Form of Carbon in Steel

The speciation of carbon released from steels during 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 steel wastes of interest (generally <0.3 wt% C), 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). Whereas some alloying components (e.g. niobium, titanium) form very stable interstitial carbide phases that react only slowly with acids releasing methane and hydrogen, transition metal carbides (e.g. iron) may be hydrolyzed by water releasing a range of hydrocarbon species and hydrogen (Cataldo 2003). However, there is considerable uncertainty whether ^{14}C produced by activation of ^{14}N will be present in the same chemical forms in irradiated steels as the carbon present in the steels at the time of their production. At the outset of CAST, only very limited experimental information was available on ^{14}C release from irradiated steels. However, rather more information was available on the release of stable carbon (^{12}C and ^{13}C) from inactive irons and steels to inform the likely speciation of ^{14}C released from irradiated steels.

Chemical Form of Carbon Released by Corrosion

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). In contrast, in experiments on inactive carbon steel and iron carbide, which focused on release to solution, carbon release was reported to arise primarily as soluble organic species, with some of the dissolved carbon being inorganic (Kaneko et al. 2003; Sasoh 2008). 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, a small number of leaching studies on irradiated steel had been performed in Japan. These studies have not been published in detail (and so are difficult to evaluate fully), however, the available information has been collated and summarized by Swanton et al. (2015). In one experiment, in which a sample of irradiated steel was leached in a pH 10 cement-equilibrated water, ^{14}C was reported to be released to the solution phase as a mixture of inorganic (25–34%) and organic (66–75%) species. No gas phase measurements were made. In another

experiment, a small amount of ^{14}C was reported to be released to the gas phase on leaching irradiated steel in pH 12.5 NaOH solution in an ampoule for 42 months. About 25% of the release was to the gas phase with equal amounts of organic and inorganic ^{14}C measured in solution.

Scope of CAST WP2 and of This Paper

The scope of experimental work performed under CAST WP2 included:

- measurement of the long-term corrosion rate of stainless steel under anoxic high-pH conditions (Sakuragi 2017);
- leaching studies of inactive steels, iron and iron carbide to investigate the potential speciation of ^{14}C release from irradiated steels (e.g. Cvetković et al. 2018a);
- the development of compound specific separation and analysis methods for determining the speciation of ^{14}C releases from irradiated steels at the very low concentrations expected in experiments (Cvetković et al. 2018b);
- comparisons of measured ^{14}C inventories for small irradiated steel samples with inventories calculated using activation codes (Mibus et al. 2018); and
- leaching experiments on activated steel samples, principally stainless steels, but also carbon steels, under a range of repository-relevant conditions (Mibus et al. 2018).

In this paper, we focus on the corrosion, the ^{14}C inventory of and ^{14}C release from irradiated stainless steel to develop a deeper understanding of the likely rates of ^{14}C release from steel wastes during storage and disposal and the fate of the ^{14}C released. The paper is structured as follows: first an overview of key experimental studies on stainless steels performed in CAST WP2 is presented, a comparison of the calculated and measured ^{14}C inventories of irradiated steel samples is then described. The results from corrosion and leaching experiments under repository relevant conditions are then presented. The likely evolution of the speciation of ^{14}C release over time and the potential effects of irradiation on the speciation in the experiments are considered. The results of the experiments are then discussed in the context of conditions in a geological repository and the potential implications for safety assessment.

OVERVIEW OF SELECTED EXPERIMENTAL STUDIES

Steel Corrosion

Experimental studies to measure the corrosion rate of 18/8 stainless steel under alkaline anaerobic conditions over a period of 6½ years were performed (Sakuragi 2017). Duplicate tests were performed in dilute NaOH solution of pH 12.5 at 30°C. These studies used a novel gas flow hydrogen monitoring technique to monitor steel corrosion.

Leaching Experiments

The experimental work was focused on the release of ^{14}C from activated steels. An overview of a selection of the experiments, summarizing details of the samples used, the experimental conditions and the analytical techniques applied for quantification of ^{14}C , is given in Table 1.

One study was performed under oxic conditions using stainless steel specimens from the Jose Cabrera NPP, Spain (Rodríguez Alcalá et al. 2017) to simulate aerobic conditions during waste storage or during disposal in a near-surface facility. These studies included pH values ranging from low to high pH.

Table 1 Overview of selected leaching experiments on activated stainless steels and the analytical techniques applied for quantification of ^{14}C releases to the liquid and gas phases.

Sample	Exposure conditions	Analytical techniques	Reference
SS304; Activated Jose Cabrera NPP	0.01M NaOH pH 12 1M H ₃ PO ₄ pH 1 Ambient Temp. Synthetic Air Sampling: 14, 28, 56, 90, 180, 280 days	Liquid: Combustion, LSC; IC, LSC Gas: GC-MS, LSC	Rodríguez Alcalá et al. (2017)
X7CrNiAl17.7 Plenum spring; Activated PWR Gösigen	24% H ₂ SO ₄ + 3% HF pH 1, Ambient Temp. Ar atmosphere Sampling: 1 day	Liquid: Oxidation, LSC Gas: CO ₂ captured in 2M NaOH, LSC	Herm et al. (2017a)
CT specimen, SS316L(N); Activated HFR Petten	0.1M NaOH pH 13 Ambient Temp. N ₂ atmosphere Sampling: 1, 3, 6, 13, 22, 59 weeks	Liquid: Inorganic ^{14}C by acid sep., LSC Gas: Selective oxidation and capture as CO ₂ , CO, hydrocarbons (LSC)	De Visser- Týnová et al. (2018)
SS X6CrNiTi 18-10 or similar; Activated PWR Gösigen	Ca(OH) ₂ pH 12.5 Ambient Temp. N ₂ atmosphere Sampling: 1, 15, 29, 93, 286, 412 days	Liquid: HPIEC-MS, GC-MS, ^{14}C -AMS, NPOC	Wieland and Cvetković (2018)

Key: CT – compact tension; HFR – high flux reactor, NPP – nuclear power plant, PWR – pressurized water reactor; AMS – accelerator mass spectrometry; GC-MS – gas chromatography-mass spectrometry; HPIEC-MS – high performance ion exclusion chromatography-mass spectrometry; IC – ion chromatography; NPOC – non-purgeable organic carbon; LSC – liquid scintillation counting.

One of the studies (Herm et al. 2017a) involved the complete digestion of an irradiated steel plenum spring using a mixture of dilute H₂SO₄/HF to measure the total ^{14}C inventory and also to discriminate the principal forms of ^{14}C release (to gas or to solution as organic or inorganic species) under anoxic, acid conditions. The measured inventory was also used to test the results of activation calculations.

Two of the leaching studies were performed in anoxic high-pH conditions to represent post-closure conditions in a cement-based repository after resaturation, one being performed in 0.1M NaOH solution (pH 13) (De Visser-Týnová et al. 2018), the other in a saturated Ca(OH)₂ solution (pH 12.5) (Wieland and Cvetković 2018).

The irradiated specimens used by De Visser-Týnová et al. (2018) had been stored for a period of almost 20 years in a waste disposal facility and were not subjected to particular pretreatment prior to use in the experiments. The experiment was carried out in duplicate (experiments A and B) in borosilicate glass containers with zirconia liners, in which the specimens were immersed in 600 cm³ 0.1M NaOH solution, with connections for gas and liquid sampling systems. The experiments were performed in a shielded cell with an inert N₂ atmosphere. The experiments were sampled periodically up to 59 weeks leaching. Gas-phase ^{14}C analysis was based on sampling rigs which allowed separation and quantification of ^{14}C released as CO₂, CO

(including volatile oxygen-containing organic species) and gaseous hydrocarbons, in particular CH_4 . A procedure was applied that allowed leached ^{14}C present as carbonate to be quantified in the liquid phase. The total ^{14}C activity in the solution was analyzed after 59 weeks.

The second study was conducted using a 500 mL gas-tight autoclave-type reactor with a PEEK liner emplaced behind a lead shielding (Wieland et al. 2017). Two 1 g stainless steel specimens were immersed in 300 cm³ saturated carbonate-free $\text{Ca}(\text{OH})_2$ solution covered with 200 cm³ N_2 atmosphere at 5 bar pressure. The experiments were sampled periodically up to 412 days. ^{14}C analysis 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 (Cvetković et al. 2018b). No quantification of the ^{14}C carbonate fraction or the volatile hydrocarbons was undertaken. However, the individual stable (^{12}C) carbon compounds (volatile and aqueous species) released from the steel were also separated and quantified using standard analytical techniques, i.e. high-performance ion exchange chromatography and gas chromatography both with mass spectrometry detection.

In a number of the studies, the release of ^{60}Co to the solution phase was measured by gamma spectrometry as a potential proxy for the corrosion of the steel sample. This assumes that ^{60}Co is uniformly distributed through the steel samples and that cobalt dissolves congruently with the corrosion of the steel over the timescale of the experiments. The corrosion rate of the sample can also be estimated from the total ^{14}C release, based on the same assumptions.

^{14}C Inventory Determination

The majority of the samples studied originated from reactor internals or from the reactor vessel of nuclear power plants, while some samples were custom irradiated in research reactors. The irradiation parameters and history are sufficiently well known in most of the cases to estimate the ^{14}C content in the samples. The nitrogen content of the samples, in contrast, an important parameter in determining the amount of ^{14}C generated, is mostly known only 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 sub-sample of the stainless-steel used in the corrosion experiments by Wieland and Cvetković (2018) had been investigated in an earlier study (Schumann et al. 2014). In the other case, the ^{14}C inventory of the stainless-steel plenum spring was experimentally measured after acidic digestion (Herm 2014; Herm et al. 2017a). The activation calculation of the sample employed two independent approaches: (1) simulating the neutron flux using the Monte Carlo N-particle code (MCNP) and subsequently calculating the activation with the CINDER code; and (2) the SCALE/TRITON package was used to develop cladding macro-cross-section libraries, which were applied in the ORIGEN-S code. The full description including further references are given in Herm et al. (2017a). The details of the calculations are compiled in Table 2.

RESULTS

^{14}C Inventory

The model calculations using two different samples and three different approaches estimated the inventory within an uncertainty factor of 2.4 to 4.6. It has to be noted that all calculations underestimated the inventory, while it appears that the most sensitive parameters are the

Table 2 Overview of the activation calculations of ^{14}C specific activities for irradiated steel samples.

	Stainless-steel plenum spring (Herm et al. 2017a)		Guide tube nut (Schumann et al. 2014)
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

Table 3 Comparison of the activation calculation results with measured ^{14}C specific activities for irradiated steel samples.

	Stainless-steel plenum spring (Herm et al. 2017a)		Guide tube nut (Schumann et al. 2014)
Irradiation model	MCNP model of fuel assembly	SCALE/TRITON model of fuel assembly	MCNP reactor model of Gösgen PWR
Experimental ^{14}C inventory [Bq/g]		$2.7(\pm 0.3) \times 10^5$	$17.8(\pm 2) \times 10^3$
Calculated ^{14}C inventory [Bq/g] ¹	$8.5(\pm 0.9) \times 10^4$	$9.5(\pm 1.0) \times 10^4$	$4.5 \times 10^3^*$
Ratio exper./calc. ²	3.2 ± 0.5	2.8 ± 0.4	4.0 ± 0.6

*Uncertainty of 10% assumed.

nitrogen content and the modelled local neutron flux. The comparison between the results of the activation calculation and the experimental values is shown in Table 3.

Steel Corrosion

At the start of the CAST project, new work (Sakuragi et al. 2016b) provided data for the very low corrosion rates experienced by stainless steels under anoxic alkaline conditions. The new data indicated a mean anaerobic corrosion rate of 0.8 nm/a for 18/8 stainless steel at 30°C after two years exposure; they also showed a temperature dependence of the anaerobic corrosion rate that had not been discriminated previously. Further experiments performed as part of the CAST project (Sakuragi et al. 2016a; Sakuragi 2017), over a duration of 6½ years, have confirmed very low corrosion rates for 18/8 stainless steel under these conditions, and measured an even lower steady corrosion rate of 0.4 nm/a at 30°C between 1 and 6½ years.

Release of ^{14}C

Oxic Conditions

304 stainless steel test pieces activated in the Jose Cabrera NPP were used for leaching tests under alkaline (NaOH pH 12) and acidic (1M H_3PO_4) conditions (Rodríguez Alcalá et al. 2017). The leaching test in alkaline solution consisted of several steps over 281 days, with fresh leaching solution used for each step. 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 on ^{60}Co release. 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.

Anoxic Conditions

In the duplicate experiments of 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 leaching. The leaching solution was not refreshed or replaced after each sampling. The results indicate a ^{14}C release rate which is the highest during the first 1–3 weeks and then 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 $520\ \text{nm/a}$. This value is significantly higher than that 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 $3\ \text{nm/a}$ for the period between 3 and 59 weeks. This value is broadly consistent with corrosion rates reported under similar conditions (Sakuragi 2017).

In the experiment of Wieland and Cvetković (2018), corrosion rates were estimated based on ^{60}Co release. The early stage corrosion rate was $\sim 20\ \text{nm/a}$ while $2\ \text{nm/a}$ was 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.

Speciation of ^{14}C

Acidic Anoxic Conditions

The speciation of ^{14}C release in acidic conditions was determined by complete digestion of a stainless steel plenum spring (Herm et al. 2017a, 2017b). 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. The portion of ^{14}C in the inorganic chemical form, both in the aqueous and gaseous phase, was much less than 1%. The individual ^{14}C bearing species were not identified in this study.

Alkaline Anoxic Conditions

In the experiments of De Visser-Týnová et al. (2018), ^{14}C was released primarily to solution as ^{14}C bearing carbonate ($^{14}\text{CO}_2$). Only about $\sim 1\%$ (experiment A) and $\sim 6\%$ (experiment B) of the total ^{14}C was released to the gas phase, mainly in the chemical form of ^{14}C -hydrocarbons ($\sim 90\%$) and some ^{14}CO ($\sim 10\%$). No $^{14}\text{CO}_2$ was detected in the gas phase. Release of the water-soluble ^{14}C containing compounds was fast, initially. The steady state of release was reached after ~ 3 weeks. The activity of the volatile species, i.e. ^{14}C -hydrocarbons and ^{14}CO , increased continuously with time in one experiment (A), while in B, the rate of gas-phase release decreased over time after the initial 3-week phase of faster release. Measurements of total ^{14}C release after 59 weeks were slightly higher than the inorganic ^{14}C measurements indicating that some ^{14}C

was also released as soluble organic species, about 20% in A and 40% in B. Thus, the total ^{14}C release in the experiments at earlier durations are likely to have been underestimated.

In the experiment of (Wieland et al. 2017), ^{14}C -containing acetate, formate and lactate were identified and quantified (Cvetković et al. 2018c). The proportions were as follows: acetate ~32%, formate ~40%, and lactate ~25%. The total concentration of these compounds corresponds to the total organic ^{14}C (TO^{14}C), which was determined by direct analysis of an aliquot of the alkaline solution using ^{14}C AMS. This finding indicates that the three carboxylates are the main water-soluble organic ^{14}C containing compounds. The TO^{14}C content strongly increased within the first 92 days of reaction in accordance with a fast initial release of the carboxylates. After this first phase, however, the rate of release dropped significantly.

The individual stable carbon compounds (volatile and aqueous species) identified, i.e. 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 ^{14}C release from the 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.

DISCUSSION

Effects of Irradiation on Steel Corrosion

The results obtained by Sakuragi (2017) have reinforced earlier findings that the long-term corrosion rates of stainless steels under anoxic, high-pH conditions are below 1 nm/a at 30°C. This indicates that ^{14}C present within the matrix of irradiated stainless steels will potentially be released at a very slow rate. Likewise long-term uniform corrosion rates for carbon steels are generally only a few 10s nm/a, and for carbon steel embedded in unsaturated, anoxic cement corrosion rates as low as 2–4 nm/a have been reported recently (Senior 2017).

It is important to note that the results of Sakuragi (2017) and all of the corrosion data compiled in recent reviews (Smart and Hoch 2010; Diomidis 2014; Swanton et al. 2015) were obtained for unirradiated materials, whereas waste reactor steels will have undergone neutron irradiation. It is known that neutron irradiation can damage the microstructure of steels and has the potential to impact on their corrosion behavior (Was 2007). One form of damage that can arise for stainless steels is the radiation-induced depletion of chromium from the oxide layer at grain boundaries, which can render the steel more susceptible to intergranular corrosion and stress-corrosion cracking (Was 2012). 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, leading 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. These processes lead to some uncertainty concerning the transferability of corrosion rate data from inactive to neutron-irradiated materials.

Most studies of the effects of external 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 1000 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 (5 ppm O_2). Of more relevance to geological disposal, recent work for the Belgian national program (Smart et al. 2009; Winsley et al. 2011) examined the anaerobic corrosion behavior 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 program has shown little effect of radiation at this dose rate on the anaerobic corrosion rate of carbon steel and the long-term corrosion rates have been found to be $<0.1 \mu\text{m/a}$.

It is noted that radiation fields in the repository will decrease over time with the decay of relatively short-lived isotopes such as ^{60}Co . Model calculations for a Swiss ILW (intermediate-level waste) repository consider a time frame of 1000 years to be sufficient to reduce the beta and gamma activity by a factor of 100 (Nagra 2002). Thus any effect of self-irradiation and radiolysis on steel corrosion rates would be limited to relatively short post-closure timescales, relative to safety assessment timescales.

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. 2018; Herm et al. 2017a, 2017b). The proportion of gaseous species is much less, i.e. $\sim 30\%$ 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 A up to 59 weeks. However, in the duplicate experiment (B), 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 B compared to A, so that the gas phase release in B may not have reached a steady-state. The significantly higher initial release rate in B 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 B while a small increase with time was observed in the experiment A (De Visser-Týnová et al. 2018).

Hence, ^{14}C hydrocarbons (in particular $^{14}\text{CH}_4$) may be continuously released during the course of the corrosion process. In contrast, the water-soluble fraction was most likely released almost entirely at the start of the experiment. However, there is also some evidence for slow but continuous increase of the concentration of the water-soluble ^{14}C species with time (De Visser-Týnová et al. 2018). Longer lasting experiments are needed to confirm 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 almost the entire release of the water-soluble ^{14}C species occurred during 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 release of CH_4 during corrosion is also supported by earlier studies using non-irradiated iron powders (Cvetković et al. 2018a).

The proportion of the water-soluble organic and inorganic chemical forms of ^{14}C produced during corrosion of 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 appears that the inorganic chemical form predominantly forms in alkaline conditions (De Visser-Týnová et al. 2018). Further

work is required to obtain confidence on the ratio of water-soluble organic to inorganic carbon.

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 almost 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. 2018a). This interpretation implies that oxidized 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. 2018a). It is further to be noted that instantaneous release is caused by oxidized carbon species being attached to the surface of steel or accommodated by the surface oxide layer. The inventory of the latter species depends on the exposure history of the steel prior to the start of the leaching experiment.

Effects of Irradiation on ^{14}C Speciation

The rate of release of gaseous and water-soluble species with time in the corrosion studies with non-irradiated materials (iron, Fe_3C) 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 irradiation presumably has 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 (De Visser-Týnová et al. 2018; Wieland and Cvetković 2018) quite a different speciation was measured. In the former experiments carbonate (liquid phase) and CH_4 (gas phase) were the dominating species, while the latter reported carboxylic acids (liquid phase) and methane (gas phase). It is interesting to note that the former samples featured an estimated dose rate of 10–20 Gy/h while in the latter case a dose rate 2 orders of magnitude lower was estimated. Here, an effect of radicals formed due to radiolysis on the speciation and hence an influence of the irradiation cannot be excluded.

Chemical Stability of Carbon Species

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 and metastability dominates. In this case reaction mechanisms and kinetic arguments must be used rather than thermodynamic considerations. Hence, although the concept of metastable states has been used in water-rock-organic systems to rationalize field observations and experimental findings (Shock 1988), 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. 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 a cement-based repository, in particular formate and acetate. 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 (Leupin et al. 2016).

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. 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 metallic piece in question in the reactor. Uncertainties in the range of 240–460% were identified between modelled and measured inventories of irradiated steel samples based on two studies. 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, conditioning of the waste in cement or during interim storage.

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 caverns. 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 reported for stainless steel in simulated oxic cement porewater, accompanied by a relatively quick release of ^{14}C species, as CO , in accordance to the prevailing oxidising conditions (Rodríguez Alcalá et al. 2017).

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 encased in the cement pore space is consumed by corrosion and other processes. While there is no experimental information on the release and speciation of ^{14}C under such conditions, corrosion rates for carbon steel embedded in unsaturated, anoxic cement have been reported to be as low as 2–4 nm/a (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, which can lead to precipitation for some solutes, such as carbonate that forms calcite. Gaseous compounds in contrast, may diffuse through the gas filled pore space or even be advectively displaced due to pressure build-up (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 near field remains only partly saturated for at least 100,000 years (Diomidis et al. 2016). This is about 17 half-lives, indicating that any ^{14}C release would occur under unsaturated conditions only. 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 methane go 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 the 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 oxygenated hydrocarbons are, such as carbonate or organic compounds with oxygen-containing functional groups. Radiolysis with subsequent formation of oxidants may enable the formation of these species. However, due to the formation of large amounts of hydrogen due to the corrosion of metallic waste in the repository, 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 might shift towards hydrocarbons without oxygen containing functional groups, such as methane, implying the formation of gaseous species instead of dissolved. Later, the impact of radiolysis on the chemical conditions in the repository will decrease with the decay of relatively short-lived gamma emitters like ^{60}Co . It can be expected that at the latest after 1000 years 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 dominate during the long-term release.

CONCLUSIONS

Under CAST WP2 a series of leaching experiments using samples of activated stainless steels, mild steel and some other, non-activated materials have been undertaken. Most experiments applied alkaline, anaerobic conditions but some tests involved neutral and acidic pH values as well as aerobic conditions. Different experiments provided different but complementary information on the speciation of ^{14}C or ^{12}C releases from steels on leaching, depending on the analytical approaches applied. In general, a fast initial release of both ^{12}C and ^{14}C to the gas and solution phase is observed after immersion of steel samples into the leaching solution with the majority of the release being to solution. Later, within 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 measured speciation of ^{14}C comprises both organic, principally carboxylate species, and inorganic (carbonate) compounds in solution. Hydrocarbons, principally methane, and minor contributions of CO were found in the gas phase. No systematic differences in the behavior of ^{12}C and ^{14}C were observed, although no rigorous comparison of

the behavior of bulk C and ^{14}C could be made. The ^{14}C inventories in selected samples have been estimated based on specified N contents and irradiation histories using different neutron flux and activation models. The measured activities were found to be higher than those calculated within an uncertainty factor of 2.4–4.6. A more extensive comparative study with well-characterized irradiated steel samples is required to further test the calculation of ^{14}C inventories in irradiated steels.

REFERENCES

- Campbell TJ, Burris DR, Roberts AL, Wells JR. 1997. Trichloroethylene and tetrachloroethylene reduction in a metallic iron-water-vapour batch system. *Env. Toxicol. Chem.* 16:625–30.
- Cataldo F. 2003. Organic matter formed from hydrolysis of metal carbides of the iron peak of cosmic elemental abundance. *Int. J. Astrobiol.* 2 (1):51–63.
- 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* 35:447–61.
- Cvetković BZ, Salazar G, Kunz D, Szidat S, Wieland E. 2018b. Analysis of ^{14}C -bearing compounds released by the corrosion of irradiated steel using accelerator mass spectrometry. *Analyst* 143:3059–67.
- Cvetković BZ, Salazar G, Kunz D, Szidat S, Wieland E. 2018c. Quantification of dissolved organic ^{14}C -containing compounds by accelerator mass spectrometry in a corrosion experiment with irradiated steel. *Radiocarbon* (this issue).
- De Visser-Týnová E, Stijkel M, Swanton S, Otlet B, Walker J. 2018. C-14 release and speciation from irradiated stainless steel under alkaline reducing conditions. *CAST Report D.2.8 Issue 2*.
- Deng B, Campbell TJ, Burris DR. 1997. Hydrocarbon formation in metallic iron/water systems. *Environ. Sci. Technol.* 31:1185–90.
- Diomidis N. 2014. Scientific basis for the production of gas due to corrosion in a deep geological repository. *Nagra Arbeitsbericht NAB 14-21*. Nagra, Wettingen, Switzerland.
- Diomidis N, Johnson LH. 2014. Materials options and corrosion-related consideration in the design of spent fuel and high-level waste disposal canisters for a deep geological repository in Opalinus Clay. *JOM* 66:461–70.
- Diomidis N, Cloet V, Leupin OX, Marschall P, Poller A, Stein M. 2016. Production, consumption and transport of gases in deep geological repositories according to the Swiss disposal concept. *Nagra Technical Report NTB 16-03*. Nagra, Wettingen, Switzerland.
- Hardy LI, Gillham RZ. 1996. Formation of hydrocarbons from the reduction of aqueous CO_2 by zero-valent iron. *Environ. Sci. Technol.* 30:57–65.
- Herm M. 2014. Description of the analytical procedure for gaseous and dissolved C-14 species. *CAST Report D3.3*.
- Herm M, González-Robles E, Böttle M, Müller N, Bohnert E, Dagan R, Caruso S, Kienzler B, Metz V. 2017a. Report on ^{14}C release speciation from stainless steel under acidic conditions. *CAST Report D2.11*.
- Herm M, De Visser-Týnová E, Heikola T, Ollila K, González-Robles E, Böttle M, Müller N, Bohnert E, Dagan R, Caruso S, Kienzler B, Metz V. 2017b. Final report on C-14 release from steels under low pH and acidic conditions. *CAST Report D2.16*.
- Johnson L, King F. 2008. The effect of the evolution of environmental conditions on the corrosion evolutionary path in a repository for spent fuel and high-level waste in Opalinus Clay. *Journal of nuclear Materials* 379:9–15.
- Juhas MC, McRight RD, Garrison RE. 1984. Behaviour of stressed and unstressed 304L specimens in tuff repository environmental conditions. *Lawrence Livermore Laboratory Report UCRL 91804*.
- Kaneko S, Tanabe H, Sasoh M, Takahashi R, Shibano T, Tateyama S. 2003. A study on the chemical forms and migration behaviour of carbon-14 leached from the simulated hull waste in the underground condition. *MRS Symposium Proc.* 757: paper II.3.8.
- Leupin OX, Smith P, Marschall P, Johnson L, Savage D, Cloet V, Schneider J, Senger R. 2016. Low- and intermediate-level waste repository-induced effects. *Nagra Technical Report NTB 14-14*. Nagra, Wettingen, Switzerland.
- Mibus J, Diomidis N, Wieland E, Swanton S. 2018. Final synthesis report on results from WP2. *CAST Report D2.18*.
- Nagra. 2002. Project Opalinus Clay – safety report. *Nagra Technical Report NTB 02-05*. Nagra, Wettingen, Switzerland.
- Pastina B, LaVerne JA. 2001. Effect of molecular hydrogen on hydrogen peroxide in water radiolysis. *J. Phys. Chem. A* 105:9316–22.
- Rodríguez Alcalá M, Magro E, Gascón JL, Piña G, Lara E, Sevilla L, De Diego G, Merino S. 2017. CIEMAT final report on ^{14}C release from steels under aerobic conditions. *CAST Report D2.13*.
- Sakuragi T, Yoshida S, Kato O, Tateishi Y. 2016a. Study of stainless steel corrosion by hydrogen measurement under deoxygenated, low-temperature and basic repository conditions. *Progress in Nuclear Energy* 87:26–31.
- Sakuragi T, Yoshida S, Kinugasa J, Kato O, Tateishi Y. 2016b. Corrosion kinetics of stainless steel by

- hydrogen measurement under deep geological repository condition. *Proceedings of Waste Management 2016 Conference*.
- Sakuragi T. 2017. Report on corrosion behaviour of stainless steel. *CAST Report D2.12*.
- Sasoh M. 2008. The study of the chemical forms of C-14 released from activated metals. *Nagra Arbeitsbericht NAB 08-22*. Nagra, Wettingen, Switzerland. p 19–21.
- 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):5448–54.
- Senior N. 2017. Anoxic corrosion of steel in a Swiss L/ILW repository environment. *Nagra Arbeitsbericht NAB 17-19*. Nagra, Wettingen, Switzerland.
- Shock EL. 1988. Organic-acid metastability in sedimentary basins. *Geology* 16(10):886–90.
- Smart NR, Rance AP, Winsley RJ, Fennell PAH, Reddy B, Kursten B. 2009. The effect of irradiation on the corrosion of carbon steel in alkaline media, presented at the NUCPERF 2009 conference on long-term performance of cementitious barriers and reinforced concrete in nuclear power plants and waste management (EFC event 317), Cadarache, France, 30 March–2 April 2009. *RILEM Proceedings*. PRO 64.
- Smart NR, Hoch AR. 2010. A survey of steel and Zircaloy corrosion data for use in the SMOGG gas generation model. *Serco Report SA/ENV-0841*, Issue 3.
- Swanton SW, Baston GMN, Smart NR. 2015. Rates of steel corrosion and carbon-14 release from irradiated steels – state of the art review. *CAST Report D2.1*.
- Swanton SW, Swift BT, Plews M, Smart NR. 2016. Carbon-14 Project Phase 2: irradiated steel wastes. *AMEC Report AMEC/200047/005*, Issue 1.
- Thorstenson DC. 1970. Equilibrium distribution of small organic molecules in natural waters. *Geochim. Cosmochim. Acta* 34(7):745–70.
- Toth LE. 1971. *Transition Metal Carbides and Nitrides*. London: Academic Press.
- Was G. 2007. *Fundamental of Radiation Materials Science*. Springer-Verlag.
- Was G. 2012. Irradiation assisted corrosion and stress-corrosion cracking (IAC/IASCC) in nuclear reactor systems and components. Chapter 6. In: Feron D, editor. *Nuclear Corrosion Science and Engineering*. Cambridge: Woodhead Publishing.
- Wieland E, Cvetković B. 2018. Corrosion of irradiated steel in alkaline conditions: First measurements of the carbon-14 speciation. *CAST Report D2.19*.
- 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* 79:1275–86.
- Wieland E, Cvetković B, Kunz D, Tits J. 2017. Corrosion of irradiated steel in anoxic alkaline conditions: development of the experimental set-up and first results. *PSI Technical Report TM-44-17-01*. Paul Scherrer Institut, Villigen PSI, Switzerland.
- Winsley RJ, Smart NR, Rance AP, Fennell PAH, Reddy B, Kursten B. 2011. Further studies on the effect of irradiation on the corrosion of carbon steel in alkaline media. *Corrosion Engineering, Science and Technology* 46(2):111–16.