CArbon-14 Source Term

CAST

Influence of material choice on the release and speciation of ^{14}C (D2.15)

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CAST – Project Overview

The CAST project (CArbon-14 Source Term) aims to develop understanding of the potential release mechanisms of carbon-14 from radioactive waste materials under conditions relevant to waste packaging and disposal to underground geological disposal facilities. The project focuses on the release of carbon-14 as dissolved and gaseous species from irradiated metals (steels, Zircaloys), irradiated graphite and 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 Zircaloys and from the leaching of ion-exchange resins and irradiated graphites under geological disposal conditions, its speciation and how these relate to carbon-14 inventory and aqueous conditions. These results will be evaluated in the context of national safety assessments and disseminated to interested stakeholders. The new understanding should be of relevance to national safety assessment stakeholders and will also provide an opportunity for training for early career researchers.

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

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Influence of material choice on the release and speciation of ^{14}C

Executive Summary

In the framework of Work Package 2 of the international CAST project, partially funded by the European Commission, laboratories in Belgium, Finland, Germany, Japan, and the Netherlands each investigated, independently, the release of ^{14}C from steels used in nuclear power plants and its speciation in environments representative for geological disposal. The materials investigated ranged from carbon steels representative for the reactor pressure vessel to stainless steels used as reactor internals. The researchers used a plethora of analytical techniques, including mass spectrometry, gas chromatography, TIC/TOC determination, liquid scintillation counting, ion chromatography, etc. There is a clear distinction in the corrosion rate: the corrosion rate of stainless steel is an order of magnitude lower than that of carbon steel, which confirms literature data. With regards to speciation, for both stainless steel and carbon steel, the main carbon species in the gas phase is methane. For carbon steel, acetate was detected in the liquid phase. Acetate levels in solution are about three orders of magnitude higher than methane levels in the gas phase. When comparing the speciation of ^{14}C released from carbon steel and Zircaloy-4, we find that less methane is released from Zircaloy than from C-steel. On the other hand, Zircaloy releases ethane, while this is not observed for C-steel.

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1 Introduction

In the framework of Work Package 2 of the European CAST project, laboratories from Belgium, Finland, Germany, Japan, and the Netherlands each investigated, independently, the release of ^{14}C from irradiated steels used in nuclear power plants and its speciation in environments representative for geological disposal. The materials investigated ranged from carbon steels representative for the reactor pressure vessel to stainless steels used as reactor internals. The researchers used a plethora of analytical techniques, including mass spectrometry, gas chromatography, TIC/TOC determination, liquid scintillation counting, ion chromatography, etc. Full experimental details and results from each laboratory are given in the individual final reports and are not discussed into detail here. The purpose of the current report is to compare the obtained results and draw conclusions on the influence of the type of material on the of ^{14}C release and the speciation of ^{14}C in a geological disposal environment. Finally, a comparison is made between steels and zirconium alloys, by incorporating the main results from Work Package 3 which focused on Zircaloys.

2 Materials

The main purpose of this report is to investigate the influence of the steel type (stainless steel vs. carbon steel) on the release rate and speciation of ^{14}C, under highly alkaline and anaerobic conditions, because cement-based materials are ubiquitous in disposal galleries and the oxygen in the disposal system is deemed to be depleted after a relatively short lapse of time. Anaerobic tests were performed by SCK•CEN, RWMC, NRG and VTT. The tests performed at ENRESA and CIEMAT were conducted in aerobic environments, so they fall out of the scope of this report. The JRC experiments were not finished in time due to organizational problems, so they are also not included in this report.

2.1 Stainless steels

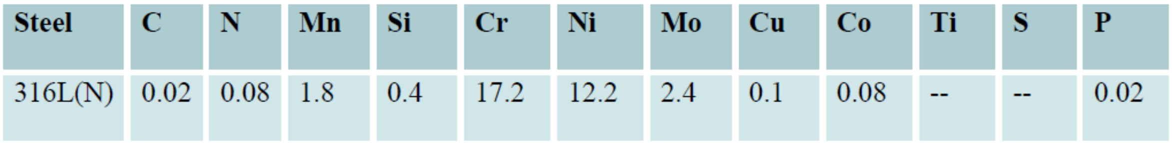
RWMC have investigated a non-irradiated 18Cr-8Ni austenitic stainless steel from Nilako Corporation with a composition shown in Table 1 [Sakuragi 2017]. The average diameter of the grains was approximately 15 µm, and the initial oxide thickness was approximately 3 nm.

Table 1. Chemical composition of the RWMC 18Cr-8Ni austenitic stainless steel (wt.%).

	C	Si	Mn	P	S	Ni	Cr	H(mg/L
Specification	<0.08	<1.00	<2.00	<0.045	<0.030	8.00-10.50	18.00-20.00	-
Specimen	0.07	0.45	0.79	0.028	0.005	8.29	18.14	-

NRG investigated Compact Tensile (CT) specimens of 316L(N) HER-II-type austenitic stainless steels, irradiated in the High Flux Reactor at Petten to a nominal dose of 2 dpa. The composition of the samples is given in Table 2 [De Visser 2017].

Table 2. Chemical composition of the NRG 316L stainless steel samples (wt%).



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

For their tests with irradiated materials, VTT selected the surveillance capsule chains from the Loviisa nuclear reactor. The composition of the material is given in Table 3.

Table 3. Chemical composition of the inactive surveillance capsule material from VTT.

Sample	**Composition (%)**							
Capsule cover	***C***	***Si***	***Mn***	***S***	***P***	***Cr***	***Ni***	***Mo***
	0.023	0.34	1.81	-	0.027	16.7	11.1	2.06
	Cu	***Al***	***W***	***V***	***Ti***	***Co***	***N***	***Fe***
	0.26	0.023	0.02	0.05	0.22	0.07	0.04	(rest)

2.2 *Carbon steels*

The irradiated material was representative for end-of-life conditions in nuclear power plants and as such offered the advantage of providing realistic input data on ^{14}C release into the national safety cases (WP6). The samples we received were irradiated in 1993 in the BR2 reactor at SCK•CEN in the Vestale irradiation loop (290 ± 15 °C; 150 bar). There were different samples for the static and the accelerated tests. The sample for the static tests was rectangular with original dimensions 1 x 10 x 26 mm and had the code 16-6-18/1R. The composition of JRQ steel is given in Table 4. The sample was cut into three subsamples with the dimensions and contact dose rates given in Table 5. The sample for accelerated tests originally was a ½ Charpy-V specimen from which the fissured edge had been cut away. The dimensions of the sample were 10 x 26.1 x 4.5 mm (Figure 1) and its dose rate was 3.6 mSv/h in contact. The sample was manually cut with a metallic handsaw to dimensions fit for the manufacturing of an electrode (the inner cross section of the electrode holder was approximately 25 mm). The final dimensions of the sample for accelerated testing were 10 x 6 x 4.5 mm (Figure 2) and the sample had the code JRQ 16-6-18/AT1. It had a contact dose rate of 920 µSv/h.

Table 4. Chemical composition of JRQ carbon steel.

Element	**C**	**Si**	**Mn**	**P**	**S**	**Cr**	**Mo**	**Ni**
wt.%	0.10-0.17	0.60-0.90	0.50-0.80	0.025	0.035	0.50-0.75	0.15-0.25	<0.25

Table 5. Dimensions and contact dose rates for the subsamples used for static tests.

Sample identification	Dimensions (mm)	Contact dose (µSv/h)
16-6-18/1RA	8.06 x 10 x 1	350
16-6-18/1RB	8.11 x 10 x 1	360
16-6-18/1RC	8.10 x 10 x 1	350

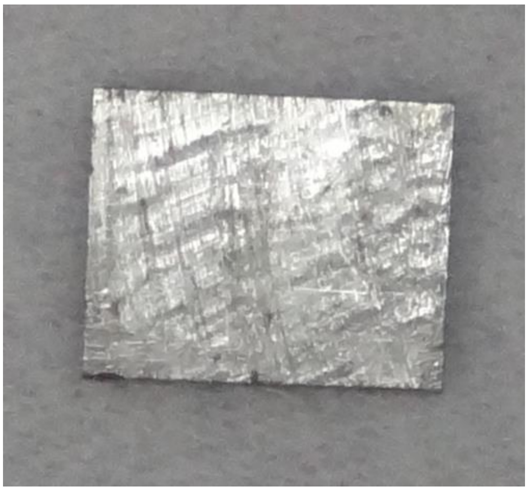


Figure 1. Sample 16-6-18/1RA (for static testing).

Figure 2. Sample JRQ 16-6-18/AT1 for accelerated testing.

3 Experimental techniques

The experiments performed at the different institutes consisted mainly of long-term leaching tests, followed by analysis of the gas and/or the liquid phase. The only exception to this is RWMC, who use mass spectrometry-based online measurement of the evolved gas phase to determine the hydrogen concentration and thus the corrosion rate of the steel.

NRG used glass vials for the leaching experiments (Figure 3), with an inert zirconia crucible serving as an inner container to hold the leachant solution during the leaching experiment. The leaching tests took place in an inert atmosphere and lasted for up to 5 months. VTT had a similar setup, also using zirconia crucibles placed inside glass bottles. SCK•CEN on the other hand, used PEEK-lined stainless steel vials (Figure 4).

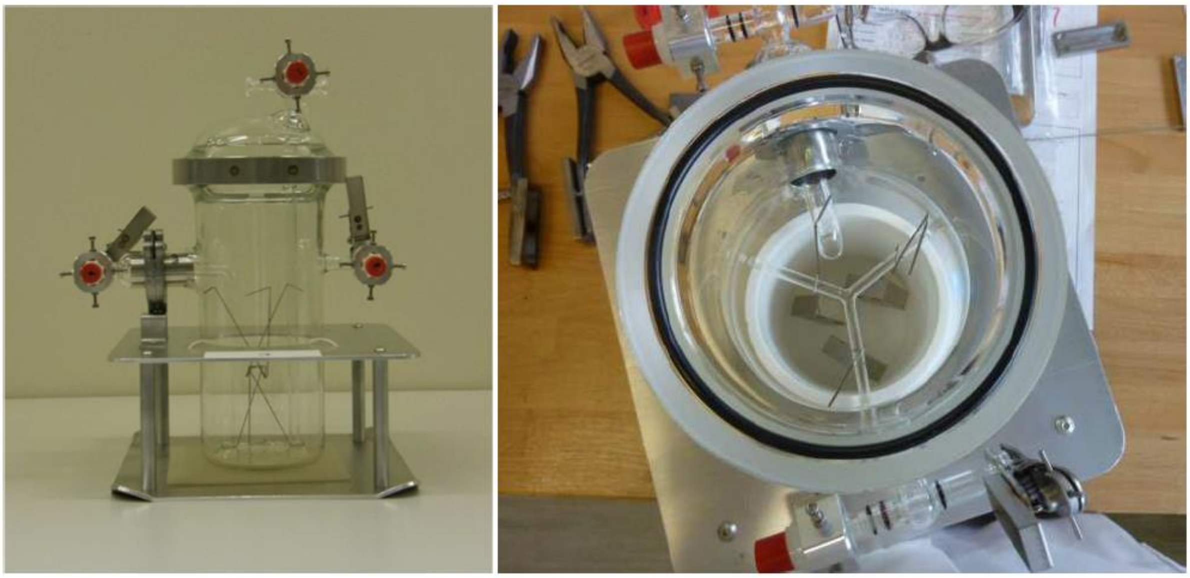


Figure 3. Glass leaching cells used for the leaching tests at NRG.

Figure 4. Leaching vials used for the leaching tests at SCK•CEN.

3.1 *Determination of the corrosion rate*

RWMC used an online measurement of the evolved hydrogen gas during anaerobic corrosion, based on mass spectrometry. Details on the experimental method can be found in [Sakuragi 2017]. NRG used the dissolved ^{14}C measured by liquid scintillation counting to calculate the corrosion rate, assuming that ^{14}C was distributed uniformly throughout the dissolved steel and was released congruently with the corrosion of the steel [de Visser 2017]. SCK•CEN used both the released ^{60}Co measured by gamma spectrometry and the total released carbon species (measured by gas chromatography) to calculate the corrosion rate [Druyts 2017].

3.2 Carbon speciation

In the report by RWMC, the focus was on the corrosion rate, not on speciation. [Sakuragi 2017].

NRG purged the head space of the leaching container with nitrogen and passed the purging gas through a sampling rig. The method involved the selective oxidation and capture of ^{14}C species in the gas stream as $^{14}CO_2$ on soda lime columns. This method allowed the separation and quantification of:

- ^{14}C released as CO_2;
- ^{14}C released as CO; and
- ^{14}C released as volatile hydrocarbons, mainly methane.

Full details of this method are found elsewhere [Swanton 2016].

VTT determined the total amount of dissolved inorganic carbon (DIC) and organic carbon (DOC). In addition, TIC and TOC analyses were performed on the samples with a TOC analyzer (Analytika Jena N/C UV HS) [Heikola 2017].

SCK•CEN used gas chromatography, TIC/TOC analyses, and ion chromatography to determine the speciation of ^{14}C in the gas and the liquid phase [Druyts 2017].

4 Influence of material choice on the corrosion rate

Table 4 gives an overview of the corrosion rates obtained by the participating institutes. It is clear that the corrosion rate of stainless steel is one to two orders of magnitude lower than for carbon steel. This is consistent with literature data (see e.g. [Kursten 2014]). There were no uncertainties reported on these values. In general, it can be said that these measurements are indirect measurements of the corrosion rate, i.e. derived from the measurement of secondary reaction products or radionuclides, except for the measurement made by Sakuragi (2017), which is a direct assessment of the amount of hydrogen gas produced by the anaerobic corrosion of stainless steel. Therefore, the data delivered by RWMC are deemed to be the most reliable.

Table 4. Corrosion rates for stainless steel and carbon steel in highly alkaline, anaerobic solutions.

Institute	**Steel type**	**pH**	**Corrosion rate (nm/yr)**	**Method**	**Reference**
RWMC	Stainless	12.5	0.4	Mass spectrometry	Sakuragi 2017
NRG	Stainless	12.5	3.0	Carbon-14	De Visser 2017
SCK•CEN	Carbon	12.5	7.0	Cobalt-60	Druyts 2017
SCK•CEN	Carbon	12.5	68-117	Gas chromatography	Druyts 2017

5 Influence of material choice on the speciation of ^{14}C

5.1 Analysis of the gas phase

The gas phase after the leaching test with carbon steel was analyzed with gas chromatography by SCK•CEN (Druyts, 2017). This yielded peaks for hydrogen, methane, carbon dioxide, ethene, and ethane. The measured concentrations were low, but well above the detection limit. With the exception of hydrogen, all peaks could be quantified. The peak of carbon dioxide was as intense as during calibration, so the authors assume that no additional carbon dioxide is released during the leaching test. For the other compounds, the average concentrations for C-12 compounds were 10.4 µL/L for methane, 1.7 µL/L for ethene, and 0.6 µL/L for ethane. The concentrations were not measured as a function of leaching time but rather once at the end of the experiment, which lasted for approximately six months.

Gas phase analysis after the leaching tests with stainless steel was also performed by NRG. NRG passed the gas phase through soda lime columns to separate carbon dioxide, carbon monoxide, and methane, as explained in Section 3, and the captured fraction (activity) was measured by liquid scintillation counting (De Visser, 2017). It has to be mentioned that any volatile oxygen-containing organic species (e.g. alcohols, aldehydes and ketones) that escaped from solution into the gas phase would also be collected in the CO fraction. Likewise, any other volatile carbon species that were not be collected by the CO column would be collected in the methane column. Again, we see that the methane fraction is the most important, about one order of magnitude higher than the CO fraction. The CO_2 fraction is negligible. PSI identified formate, acetate and lactate as the main ^{14}C bearing species (Wieland 2018).

These tests show that for both materials, methane and the other volatile carbon species as ethene and ethane dominate the ^{14}C speciation in the gas phase. It is hard to perform a quantitative comparison between both materials because of the difference in setup and methodology to determine the speciation.

5.2 Analysis of the liquid phase

VTT and SCK•CEN measured the distribution of carbon in organic and inorganic form, VTT for stainless steel (Heikola, 2018) and SCK•CEN for carbon steel (Druyts, 2017). The results are presented in Table 5. The VTT results show that in their experiments carbon is mainly released in the organic form, while at SCK•CEN both forms were below the detection limit. Furthermore, VTT used GC/MS to investigate whether toluene, ethyl benzene or xylenes were released from the stainless steels. None of these compounds were detected. SCK•CEN on the other hand were able to measure acetate after one of the leaching tests. In contrast, no formate or oxalate was detected (Druyts 2017). The general conclusion from the liquid phase analysis is that the levels of released carbon compounds is too low to draw definite conclusion on the ^{14}C speciation.

Table 5. Distribution of carbon-12 in organic and inorganic form

Material	**Leaching solution**	**C in organic form (%)**	**C in inorganic form (%)**	**Reference**
AISI 316Ti	pH 8.5	100	0	Heikola 2018
AISI 316Ti	pH 12.5	76	24	Heikola 2018
JRQ C-steel	pH 12.5	Below detection limit	Below detection limit	Druyts 2017

6 Comparison with Zircaloy-4

SCK•CEN have conducted leaching experiments with carbon steel and Zircaloy-4 under identical conditions and an identical experimental setup, making this an ideal starting for a comparison of the ^{14}C release and speciation from both materials [Druyts 2017 and Caes 2017]. Figure 4 shows the analysis of the gas phase by gas chromatography for JRQ carbon steel, Figure 6 shows the analysis for Zircaloy-4. The duration of the leaching experiment was 231 days for carbon steel and 195 days for Zircaloy-4. In both cases, hydrogen, methane, carbon dioxide, and ethene were detected. In addition, in the case of carbon steel, ethane was detected (for Zircaloy-4, ethane may also have been present, but this small peak is hidden by a broad water peak). Hydrogen is produced by the anaerobic corrosion of carbon steel and Zircaloy-4. Table 6 compares the amounts of methane and ethene released by the two materials. The values for carbon steel are higher than for Zircaloy-4, but this can be explained by the longer duration of the leaching test in the case of carbon steel, and the expected lower corrosion rate of Zircaloy-4. As a conclusion, it can be said that individual release rates for ^{14}C compounds are comparable for carbon steel and Zircaloy-4 and that the speciation is identical for the two materials.

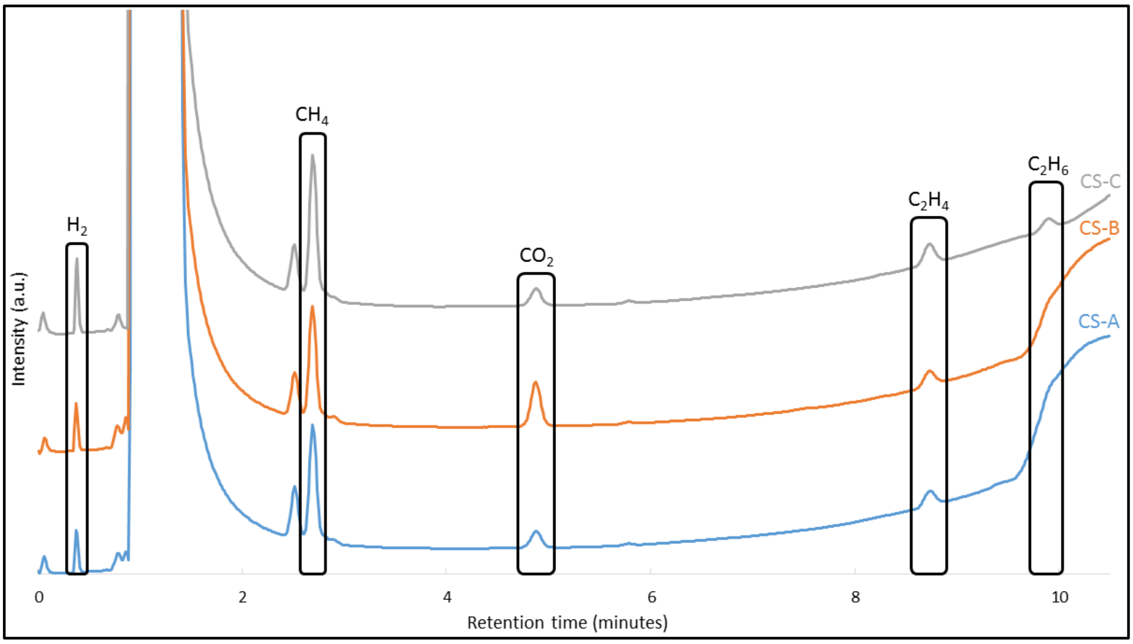


Figure 5. Gas chromatogram for JRQ carbon steel after 231 days of leaching in a pH 12.5 portlandite solution [Druyts 2017].

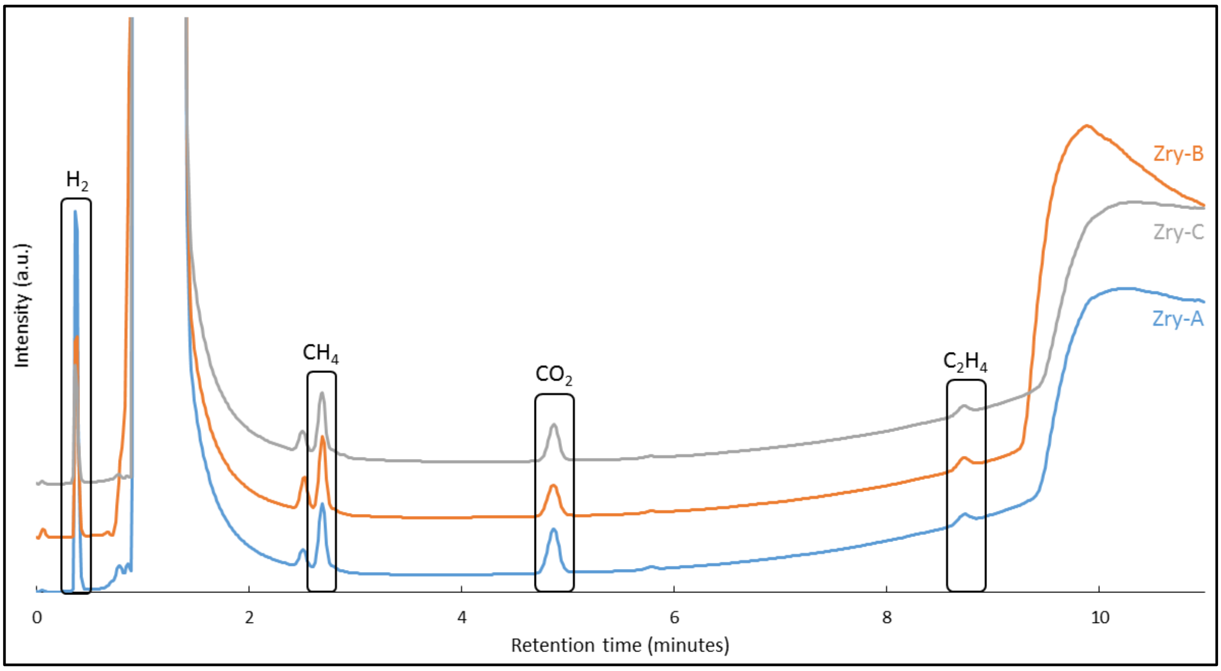


Figure 6. Gas chromatogram for Zircaloy-4 after 195 days of leaching in a pH 12.5 portlandite solution [Caes 2017].

Table 6. Calculated concentration of methane and ethene in the gas phase after leaching tests with JRQ carbon steel and Zircaloy-4 (average values of three tests).

Material	**Methane (μL/L)**	**Ethene (μL/L)**	**Reference**
JRQ C-steel	10.4	1.7	Druyts 2017
Zircaloy-4	6.4	1.0	Caes 2017

7 Conclusions

In the framework of Work Package 2 of the international CAST project, partially funded by the European Commission, laboratories in Belgium, Finland, Germany, Japan, the Netherlands, and Switzerland each investigated, independently, the release of ^{14}C from steels used in nuclear power plants and its speciation in environments representative for geological disposal. The materials investigated ranged from carbon steels representative for the reactor pressure vessel to stainless steels used as reactor internals. The researchers used a plethora of analytical techniques, including mass spectrometry, gas chromatography, TIC/TOC determination, liquid scintillation counting, ion chromatography, etc. There is a clear distinction in the corrosion rate: the corrosion rate of stainless steel is an order of a magnitude lower than that of carbon steel, which confirms literature data.

With regards to speciation for both stainless steel and carbon steel, the main carbon species in the gas phase is methane. For carbon steel, acetate was detected in the liquid phase. Acetate levels in solution are about three orders of magnitude higher than methane levels in the gas phase. When comparing the speciation of ^{14}C released from carbon steel and Zircaloy-4, we find that less methane is released from Zircaloy than from C-steel. On the other hand, Zircaloy releases ethane, while this is not observed for C-steel.

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