CArbon-14 Source Term

CAST

Final Report on Carbon-14 release from steels under aerobic and anaerobic conditions (D2.17)

Author(s): M. Rodríguez Alcalá and J.L. Gascón

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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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(D2.17)

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Final Report on Carbon-14 release from steels under aerobic and anaerobic conditions (D2.17)

Executive Summary

CAST Work Package 2 (WP2) addresses the release and speciation of ^{14}C from activated steel during corrosion under conditions of a cement based deep geologic repository. Twelve organisations participate in WP2.

WP2 is subdivided into four tasks; this report is within Task 2.4, which is a summary of the experimental conditions and the comparison of the results obtained for the study on ^{14}C release from steels in alkaline, neutral and acidic media under aerobic or anaerobic conditions (Task 2.3).

The determination of corrosion rates has been carried out by several methods, measuring the concentration of ^{14}C, ^{60}Co and H_2. Measurement of ^{60}Co concentration would be adequate when, in the leaching process, the whole leachate is renewed in each step. However, if the determination of the corrosion rate is carried out by analyses of ^{60}Co concentration, when only a fraction of the leachate is renewed, the results obtained are not consistent.

From the comparison of the results, it is observed that the corrosion rates obtained in aerobic conditions are higher than the ones obtained under anaerobic conditions, so the release rate of any element of the piece would be higher under aerobic conditions.

According to the experimental data obtained in the acid digestion of the pieces of stainless steel, the majority of ^{14}C is as dissolved organic compounds in the aqueous phase.

Regarding the leaching of ^{14}C, the results show that there is an initial fast release of ^{14}C.

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List of Contents

Executive Summary i
List of Contents iii
1 Introduction 1
2 Description of the experimental conditions 1
  2.1 Radiological Characterization (^{14}C) of irradiated stainless steel 1
  2.2 Leaching processes 3
3 Discussion 4
  3.1 Release rate 5
  3.2 Corrosion Rate 6
  3.3 Leaching of ^{14}C 7
  3.4 Organic and inorganic compounds in the gas phase of the leaching process 8
  3.5 Organic and inorganic compounds in the liquid phase of the leaching process 9
4 Conclusions 10
5 References 11

1 Introduction

CAST Work Package 2 (WP2) addresses the release and speciation of ^{14}C from activated steel during corrosion under conditions of a cement based deep geologic repository. In many programmes, activated steel represents the major source of ^{14}C.

WP2 is subdivided into four tasks. This report is focused on Task 2.3, which deals with the corrosion experiments using different materials and a range of experimental conditions. Subsequently, the speciation of ^{14}C is measured in the aqueous and gaseous samples.

Ten organisations have participated in this task: AMEC Foster Wheeler (UK), CIEMAT, ENRESA (ES), JRC (EU), KIT (DE), NRG (NL), PSI (CH), RWMC (JP), SCK·CEN (BE) and VTT (FI).

This report is a summary of the experimental conditions and the comparison of the results obtained for the study on ^{14}C release from steels in alkaline, neutral and acidic media under aerobic or anaerobic conditions.

Due to the delay in starting the leaching processes and the difficulty to set-up the procedures to determine both ^{14}C and organic compounds in a very low concentration in the gas and liquid phase of the processes, only limited conclusions can be drawn.

2 Description of the experimental conditions

2.1 *Radiological Characterization (^{14}C) of irradiated stainless steel*

In order to determine the ^{14}C present in the stainless steel samples, some laboratories used a wet chemistry digestion technique combined with liquid scintillation counting and others carried out an estimation using a computer modelling calculation. The mean values of ^{14}C obtained [1-3, 5, 7-9] are shown in Table 1.

Table 1. Inventory of ^{14}C in irradiated stainless steel

Participant	**Steel type**	**^{14}C Determination**	**^{14}C Activity (Bq/g)**
AMEC/NRG	Stainless Steel 316 L(N) (0.0238% C)	Computer modelling calculation	2.2E5
CIEMAT	Stainless Steel 304/316	Wet chemistry digestion technique	4.0E0
ENRESA	Stainless Steel 304/316	Computer modelling calculation	1.8E1
KIT	Alloy X7CrNiAl17-7	Wet chemistry digestion technique	2.8E5
PSI	One of the following alloys (0.08%C): X6CrNiTi18-10; X6CrNiNb18-10 or X6CrNiMoTi17-12-2	Wet chemistry digestion technique	1.78E4
SCK·CEN	JRQ Carbon Steel (0.1-0.7% C)	Computer modelling calculation	1.75E2
VTT	Ti_Austenitic Stainless Steel (0.023% C)	Computer modelling calculation	2.0E3

The inventory of ^{14}C in each piece depends on both the composition of the stainless steel and the irradiation history. Two of all these laboratories informed about the distribution of the ^{14}C into the aqueous and gas phase as the result of the dissolution of the pieces. In particular, CIEMAT indicated that 81% of the total ^{14}C inventory is dissolved organic compounds in the aqueous phase and 19% in gas phase. KIT indicated that 70% is dissolved organic compounds into the acidic digestion liquor and about 29% as gaseous organic compounds into the gas phase.

2.2 *Leaching processes*

The organisations that have carried out leaching processes and have reported data are presented in Table 2 [1-3, 6-9]. Also, the experimental conditions for the leaching processes are summarised in the same table.

Table 2. Experimental conditions

Participant	Steel type (Active/Inactive material)	Leachant	O_2	Duration
AMEC/NRG	Stainless Steel 316 L(N) (0.0238% C) (Active)	NaOH pH = 13	NO	5 months
CIEMAT	Stainless Steel 304/316 (Active)	NaOH pH =12 1M H_3PO_4	YES	281 days 263 days
ENRESA	Stainless Steel 304/316 (Active)	Deionised water pH =7	YES	455 days
PSI	One of the following alloys (0.08%C): X6CrNiTi18-10; X6CrNiNb18-10 or X6CrNiMoTi17-12-2 (Active)	$Ca(OH)_2$ pH = 12.5	NO	412 days
RWMC	18Cr-8Ni Austenitic Stainless Steel (0.07% C) (Active)	NaOH pH = 12.5 Deionised water	NO	6.5 years 3 years
SCK·CEN	JRQ Carbon Steel (0.1-0.7% C) (Active)	$Ca(OH)_2$ pH = 12.5	NO	231 days
VTT	Ti_Austenitic Stainless Steel (0.023% C) (Active) AISI316Ti Steel (0.3% C) (Inactive) Iron Carbide (Inactive)	Simulated groundwater pH = 8.5 NaOH pH = 12	NO	133 days

3 Discussion

The data calculated for the corrosion rate and release rate, and the results obtained by the analysis of the compounds originated both in gas and liquid phases in the leaching processes of steels in alkaline, neutral and acidic media under aerobic or anaerobic conditions, are shown in Table 3 [1-3, 6-9].

Table 3. Results obtained during the different leaching processes

Participant	Corrosion Rate (nm/y) (Determined by)	Release Rate (fraction/y) (Determined by)	Compounds Gas Phase	Compounds Liquid Phase
AMEC/NRG	1 week: 520 (^{14}C) 22 weeks: 3 (^{14}C)	Not determined	^{14}CO, $^{14}CH_4$	Not determined
CIEMAT	2 weeks: 3580 (^{60}Co) in NaOH pH = 12 40 weeks: 274 (^{60}Co) in NaOH pH = 12	40 weeks: 1.55E-4 (^{60}Co) in NaOH pH=12	^{12}CO	Not detected
	2 weeks: 206000 (^{60}Co) in 1M H_3PO_4 38 weeks: 20100 (^{60}Co) in 1M H_3PO_4	38 weeks: 1.14E-2 (^{60}Co) in 1M H_3PO_4	^{12}CO	$^{12}C_2O_4^{2-}$
ENRESA	65 weeks: 4390 (^{60}Co)	65 weeks: 1.10E-3 (^{60}Co) pH=7	Not determined	Not determined
PSI	Not determined	Not determined	$^{12}CH_4$, $^{12}C_2H_4$,	^{14}Formic acid, ^{14}acetic acid, oxalic acid, malonic acid, glycolic acid and ^{14}l-lactic acid.
RWMC	13 weeks: 1.5 (H_2) 338 weeks: 0.4 (H_2)	Not determined	Not determined	Not determined

Table 3 (Cont.). Results obtained during the different leaching processes

Participant	**Corrosion Rate (nm/y) (Determined by)**	**Release Rate (fraction/y) (Determined by)**	**Compounds Gas Phase**	**Compounds Liquid Phase**
SCK·CEN	33 weeks: 68-117 (Carbon in gas phase)	Not determined	$^{12}CH_4$, $^{12}C_2H_6$, $^{12}C_2H_4$, H_2	Not detected
VTT	No data in active/inactive material	*Data Inactive AISI316Ti Steel (0.3% C):* 90 weeks: 2.9E-3 pH = 8.5 (total C) 90 weeks: 3.7E-3 pH = 12.5 (total C)	Not detected	Total ^{12}C measured in inactive material
		Data Inactive Fe_3C: 90 weeks: 4.8E-4 pH = 8.5 (total C) 90 weeks: 8.4E-4 pH = 12.5 (total C)	*pH = 8.5:* $^{12}C_2H_6$, $^{12}C_3H_8$, $^{12}C_4H_{10}$, $^{12}C_5H_{12}$ *pH = 12.5:* $^{12}C_2H_6$, $^{12}C_3H_8$, $^{12}C_3H_4$, $^{12}C_4H_{10}$, $^{12}C_4H_8$, $^{12}C_5H_{12}$, $^{12}C_5H_{10}$, $^{12}C_6H_{14}$	

3.1 *Release rate*

The values of the release rate obtained in pH = 7 or pH = 8.5 media under aerobic or anaerobic conditions are similar. However, the release rate determined by CIEMAT in alkaline medium under aerobic conditions is lower than the one determined by VTT in alkaline medium under anaerobic conditions; and the release rate in an acidic medium under aerobic conditions is the highest.

3.2 *Corrosion Rate*

According to the data shown in Table 2, the corrosion rates measured under alkaline anaerobic conditions have been between 0.4 and 117 nm/y for a leaching time between 3 weeks and 1 year. On the other hand, in deionised water the corrosion rate given by RWMC laboratory has been approximately 0.4 nm/y for a leaching time of 1 year. The results for the corrosion of stainless steel at room temperature in anaerobic alkaline solutions are concordant with the rate indicated in Table 17 of the report D2.1 (≈100 nm/y) [10].

The results obtained for the corrosion rates under aerobic conditions have been 274 nm/y in an alkaline medium, 4390 nm/y in a neutral medium and 20100 nm/y in an acidic medium for a leaching time of 40, 65 and 38 weeks respectively. The results for the corrosion of stainless steel at room temperature in aerobic alkaline solutions are concordant with the rate indicated in Table 16 of the report D2.1(< 300 nm/y). These results are higher than the ones obtained under anaerobic conditions.

Besides, in all cases, both aerobic and anaerobic conditions and in all media, it is observed that the corrosion rate is higher at the beginning of the leaching test.

AMEC/NRG authors performed analyses of ^{60}Co to determine the corrosion rate value, however, they indicate that the cobalt is being removed from the solution in the different steps either by a precipitation process, due to solubility limitation, and/or a sorption process (e.g. to the vessel walls or onto the surface of the steel samples themselves). As a result, they considered that ^{60}Co is not a suitable marker of the corrosion rate of the steel in their set of experiments [2].

PSI authors gave a corrosion rate value determined by ^{60}Co, however, they indicated in their report [9] that at present they do not understand whether or not ^{60}Co is an adequate measure of the corrosion rate. They considered that re-absorption of ^{60}Co by the surface layer of steel could be one the processes affecting the apparent corrosion rate.

SCK·CEN authors determined a corrosion rate value from the measurement of ^{60}Co but they considered that it was not an adequate method for measuring the corrosion rate [1].

The values of corrosion rate obtained from the measurements of ^{60}Co in the case of AMEC/NRG, PSI and SCK·CEN have not been reported in Table 3.

CIEMAT and ENRESA have given values for corrosion rates determined by ^{60}Co, being the values obtained in a good agreement with the ones obtained by other authors [11-12]. Therefore, CIEMAT and ENRESA consider that will be adequate to calculate the corrosion rate by ^{60}Co.

The discrepancies between the different laboratories could be due to the leaching processes performed by CIEMAT and ENRESA the whole leachate is renewed in each step (all the ^{60}Co is removed) while in the case of AMEC/NRG, SCK·CEN and PSI only a fraction of the leachate is renewed (only part of the ^{60}Co is removed).

3.3 *Leaching of ^{14}C*

According to the data shown in the deliverable reports [1-9], AMEC/NRG, CIEMAT and PSI present results for the leaching of ^{14}C.

In the case of AMEC/NRG, the most of the ^{14}C (0.0004% of the estimated total ^{14}C inventory) is released from the steel during the first week of leaching.

In the case of CIEMAT, ^{14}C has been detected only in the liquid samples of the leaching processes corresponding to the first two weeks, 3.6% of the total ^{14}C inventory in alkaline medium and 5.7% in acidic medium.

In the case of PSI, analyses of the ^{14}C have been carried out in the liquid samples of the leaching process corresponding to 412 days. The ^{14}C bearing individual compounds identified have been formate, acetate and lactate. The ^{14}C content of the compounds agrees well with the total organic ^{14}C content determined in the solution.

The results obtained both under anaerobic and aerobic conditions for the leaching of ^{14}C indicate that there is an initial fast release of ^{14}C from the oxide layer of the irradiated steel samples.

3.4 *Organic and inorganic compounds in the gas phase of the leaching process*

According to the data found in the corresponding deliverables and summarised in Table 3, AMEC/NRG, CIEMAT, PSI, SCK·CEN, and VTT laboratories have determined some organic and inorganic compounds in the gas phase of the leaching process.

The compounds originated and detected under anaerobic conditions are CO, CH_4, C_2H_6, C_2H_4 and H_2.

The AMEC/NRG laboratory has determined that between 1 and 12% of the total ^{14}C inventory is released in the gas phase.

The PSI laboratory has determined methane (^{12}C) 0.99 µM, ethene (^{12}C) 0.06 µM in the gas phase of the leaching process after 412 days.

The SCK·CEN laboratory has determined methane (^{12}C) 10.4 µL/L, ethene (^{12}C) 1.7 µL/L and ethane 0.6 µL/L in the gas phase of the leaching process.

The VTT laboratory has determined small hydrocarbons in the gas phase of Fe_3C experiments at both pH = 8.5 and 12.5. The compounds identified from the pH = 8.5 experiments were ethane, propane, 2-methylpropane and pentane. The compounds identified from the pH = 12.5 were ethane, propane, propylene, butane, 2-buthene, 2-methylbutane, pentane, pentene and hexane (in all cases the carbon determined is ^{12}C). In the case of AISI316Ti Steel (0.3% C) they have not detected any organic compounds.

On the other hand, the CIEMAT laboratory, under aerobic conditions, has determined only ^{12}CO and it has determined that 65% of the ^{12}C released (0.012% of the total ^{12}C inventory) is released in the gas phase in alkaline conditions, while in acidic conditions 1.2% of the ^{12}C released (0.82% of the total ^{12}C inventory) is released in the gas phase.

3.5 *Organic and inorganic compounds in the liquid phase of the leaching process*

Although different laboratories have determined the percentage of organic and inorganic carbon in the liquid phase of the samples used for leaching processes, there are few results related with specific compounds.

The PSI laboratory has analysed organic compounds in the liquid phase of the leaching process of active material in alkaline medium under anaerobic conditions. The concentration of the organic compounds analysed were 44 μM formate, 21 μM acetate and lactate 2.5 μM after 286 days. The concentration of the other carboxylates considered in this study, oxalate, malonate and glycolate, were about one order of magnitude lower. However, the experimentally determined total concentration of the dissolved ^{12}C bearing carbon species is at least three orders of magnitude higher than the ^{12}C concentration estimated based on the ^{12}C content of activated steel specimens and assuming corrosion rates ranging between 10 and 100 nm/y. This finding suggests that activated steel is not the main source of the aqueous carbon species and further implies the present of an additional ^{12}C source in the reactor system.

The SCK·CEN laboratory has analysed, but not detected (< 0.1 mg/L), organic compounds (formate, acetate and oxalate) in the liquid phase of the leaching process of active material in alkaline medium under anaerobic conditions.

The VTT laboratory has analysed organic and inorganic compounds in the liquid phase of the leaching process of an inactive material. In the experiments with AISI316Ti Steel (0.3% C) at pH = 8.5, all ^{12}C released was present in organic form (100%). At pH = 12.5, the majority of the ^{12}C released was present in the organic form (76%), the rest was released in the inorganic form (24%). In the experiments with Fe_3C at pH = 8.5, all ^{12}C released was present in the organic form (100%). At pH = 12.5, the majority of the ^{12}C released was present in the organic form (84%), the rest was present in the inorganic form (16%).

The CIEMAT laboratory has analysed, but not detected (< 0.04 mg/L), organic compounds (formate, acetate and oxalate) in the liquid phase of the leaching process of active material in alkaline medium under aerobic conditions. However, the CIEMAT laboratory has reported, in acidic conditions, values of oxalate above detection limit. The values obtained correspond to 14% of the total ^{12}C present in the piece.

4 Conclusions

- The corrosion rates for stainless steels obtained in aerobic conditions are higher than the ones obtained under anaerobic conditions. In all cases, both aerobic and anaerobic conditions in all media, it is observed that the corrosion rate is higher at the beginning of the leaching test.

- The determination of the corrosion rate via analyses of ^{60}Co release would be adequate if, in the leaching process, the whole leachate is renewed in each step. Determination of corrosion rate with the analyses of ^{60}Co release if, in the leaching process, only a fraction of the leachate is renewed would result in data being generated that could not be further used, i.e. the latter experimental approach is unsuitable.

- According to the experimental data obtained in the acid digestion of the pieces of stainless steel, the majority of ^{14}C is as dissolved organic compounds in the aqueous phase.

- The results obtained both under anaerobic and aerobic conditions in all media for the leaching of ^{14}C indicate that there is an initial fast release of ^{14}C from the oxide layer of the irradiated steel samples.

- According to the results of the leaching processes in aerobic/anaerobic conditions, the $^{14}C/^{12}C$ ratio in the leachate of the first step is different from $^{14}C/^{12}C$ ratio in the next steps, due to the first step leaching the oxide layer of the piece.

- In alkaline anaerobic conditions, in the gas phase of the leaching processes, CO, CH_4, C_2H_6, C_2H_4 and H_2 have been identified. In the liquid phase of the leaching processes formate, acetate, lactate and in a lower concentration oxalate, malonate and glycolate.

- In alkaline aerobic conditions in the gas phase of the leaching processes CO has been identified, while in the liquid phase all organic compounds measured were below the detection limit.

- In acidic aerobic conditions in the gas phase of the leaching processes, CO has been identified.

- In general, it was not possible to extract any significant difference in the ^{14}C speciation under aerobic and anaerobic conditions.

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