CArbon-14 Source Term

CAST

WP2 ENRESA Final Report on ^{14}C release from steels under aerobic conditions (D2.14)

Author(s):

Jose Luis Leganés Nieto, Jose Vicente Muñoz Serrano, Carmen María García López

Date of issue of this report: 02/03/2018

The project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no. 604779, the CAST project'		
Dissemination Level		
PU	Public	**X**
RE	Restricted to the partners of the CAST project	
CO	Confidential, only for specific distribution list defined on this document	

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

CAST		
Work Package: 2	CAST Document no. :	Document type:
Task: 2.3	CAST-2017-D2.13	R
Issued by: Enresa		Document status:
Internal no. : Reference to author's internal document number		Final

Document title
WP2 ENRESA Final Report on ^{14}C release from steels under aerobic conditions (D2.14)

Executive Summary

One of the main challenges in demonstrating safety of a radioactive waste repository, relates to post-closure evolution of the engineered barrier system and the quantification of the release rate of radionuclides present in a conditioned wasteform once groundwater has entered. To support understanding of this process, experimental leaching tests have been performed on activated steel samples to measure the Carbon-14 (^{14}C) release under aerobic conditions. This has been the main activity of the Spanish Waste Management Organisation Enresa (Empresa Nacional de Residuos Radiactivos) in the European Commission CAST (CArbon-14 Source Term) project.

Since 2010, Enresa has been dismantling the José Cabrera Nuclear Power Plant (NPP):

- Type:Westinghouse - 1-Loop PWR.
- Net Electrical Power:160 MWe.
- Net Thermal Power:510 MWth.
- Fuel Elements:69 – 14x14.
- Fuel Type:UO_2 – enrichment 3.6% (U-235).
- Mass UO_2 (core)20.76 t.

The removal and cutting process of the upper and lower internals of the reactor was carried out in the period of 2012 - 2013.

As a result of this process, a total of 4 canisters of high activated steel were produced for dry interim storage, in addition to the 12 canisters of spent fuel produced during the pre-dismantling period (2006 – 2010).

In order to save volume in the canisters of High Level Radioactive Waste (HLW), a previous theoretical analysis was developed to assess the actual HLW and Intermediate Level Radioactive Waste (ILW) classification of the reactor internals, an aspect that was verified during the cutting process itself. As a result of the in-situ characterization during segmentation and packaging activities, a total of 7 concrete containers were produced for subsequent deployment to the El Cabril Disposal Centre.

In general, heterogeneous ILW waste has to be disposed of in concrete containers with an internal extra envelope of mortar to meet the release rate Waste Acceptance Criteria that otherwise cannot be fulfilled by the waste, as this heterogeneous waste is generally contaminated.

The analysis of whether this activated steel complies with the release rate criteria, without the necessity of an additional mortar envelope, is an issue of importance for operational cutting and volume saving activities.

The El Cabril laboratory performed a leaching test for the activated item of the upper internals. The test was performed under aerobic conditions and with the objective to determine the release rate of radionuclides, including the release rate of ^{14}C. The preparation of the 7-step leaching experiments to measure the release of ^{14}C is described in this report. The results presented include an activity release rate measured at each step of the leaching process.

List of Contents

1 Introduction

The radiological capacity of every radionuclide at the El Cabril Disposal Centre is derived on the basis of the assessment of the long-term radiological impacts. To limit effective doses and conditional risks, stringent limits are placed on wastes containing long-lived radionuclides, to ensure they contain relatively low levels of activity concentration. This includes limits on the ^{14}C activity at the El Cabril surface repository, due to the radionuclide's long half-life period of 5730 years and due to its limited attenuation with respect to migration through the engineering barriers and the geosphere after facility closure.

Activated steels are generally classified as High Level Waste (HLW), which require Deep Geological Disposal as a final management route.

Enresa is currently licensing a 60 year Centralised Interim Storage Facility for HLW, which includes a programme of waste minimisation and volume reduction as part of the facility optimization. This programme includes consideration of waste minimisation and volume reduction for components of the activated steels which could be separated and reclassified as ILW/LLW and be considered for possible near-surface disposal (e.g. El Cabril).

An important Waste Acceptance Criteria in any repository is the resistance of the waste/wasteform to radionuclide release due to water intrusion, having to fulfil a minimum criterion for the release rate. In the case of that criterion being exceeded, an additional 'safety envelope' should be implemented in the waste conditioning phase, in order to fulfil the release rate criterion.

1.1 *Objective*

The understanding of the mechanisms by which the ^{14}C can be released from different types of radioactive waste under final storage conditions (organic, inorganic, dissolved or gaseous species) can be a crucial aspect in the definition of Waste Acceptance Criteria of a disposal facility.

The goal of this work is to determine the behaviour of activated stainless steel using a standard leach test, performed at El Cabril repository, and to determine the release rate of radionuclides.

The work is focused on the ^{14}C release, but also includes measurement of other radionuclides to determine the total retention capacity of the activated stainless steel. This can then be used to determine if additional waste treatment and/or conditioning is required for the fulfilment of Waste Acceptance Criteria.

For this purpose, a piece of activated steel from the upper internals of the Jose Cabrera NPP was cut to perform a leaching test in aerobic conditions. Figure 1 illustrates the origin of the cut piece.

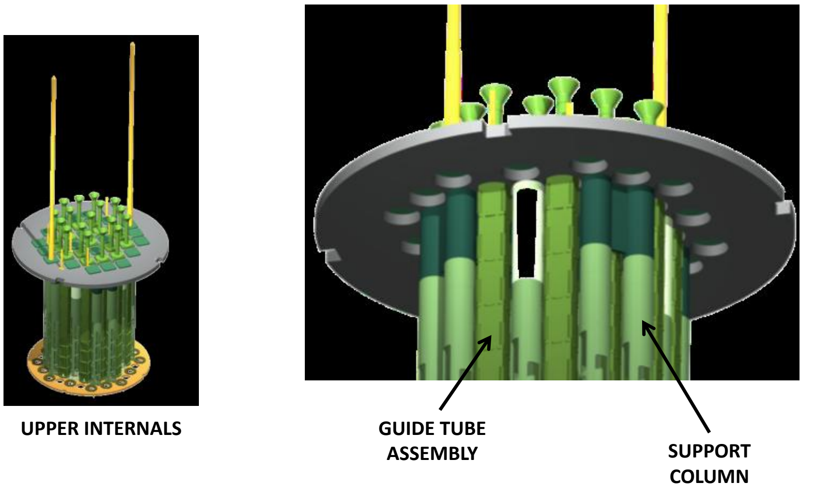

Figure 1: Origin of the piece

1.2 *Relationship to the Spanish National Programme and the CAST Project*

In addition to the aspects indicated in point 1.2 of deliverable D2.13 from Ciemat [RODRIGUEZ et al., 2017], in relation to the Spanish National Waste Management Programme, the behaviour of activated wastes containing ^{14}C and other long-lived radionuclides, is of high importance as it impacts a number of decommissioning projects under development by Enresa.

Vandellos 1 NPP is a Uranium Natural Graphite Gas Reactor, UNGG, it is in its 3rd phase of decommissioning latency period and in 2028 it will start the process of dismantling the reactor building containing the reactor internals and irradiated graphite as the main ^{14}C source term.

In preparation for starting such decommissioning projects in the near future, increased understanding of the chemical speciation of ^{14}C is of high importance for the ongoing development of the Waste Acceptance Criteria for the various disposal facilities, and for supporting the accurate classification of waste as ILW or HLW.

2 Materials and Methods

2.1 *Characterisation of the item*

The $^{14}C/^{60}Co$ ratio in the tested item has been theoretically determined by means of ORIGEN SCALE code [2], whereas the ^{60}Co and other listed radionuclides have been measured by gamma spectrometry. This ratio is very consistent with the $^{14}C/^{60}Co$ measured by Ciemat [3] in another component of the upper internals of José Cabrera NPP that has been subject to analysis.

Table 1: Initial activity of the piece

Isotope	Initial activity Ao (Bq)
^{14}C	7.72E+04
^{60}Co	1.20E+08
^{54}Mn	5.03E+05
^{137}Cs	8.28E+05
^{108m}Ag	< 4.09E+05
^{125}Sb	< 1.27E+06
^{154}Eu	< 4.85E+05
^{155}Eu	< 4.35E+06
^{241}Am	< 2.12E+07

Below are listed the basic irradiation conditions of the internals of Jose Cabrera NPP:

- José Cabrera NPP was operated from 30/06/1968 to 30/04/2006 that means a total of 13818 days, with 29 cycles of operation.
- The load factor accumulated during the operational life of the plant is 70.97%.
- Therefore, the days of irradiation, obtained by multiplying the number of days that the core has been in operation (13818 days) by the load factor, was 9807 days.
- The degree of maximum spent fuel burn-up was 45000 MWd/tU and enrichment at least 3.15% in weight of ^{235}U.
- Finally, the composition was calculated allowing for decay to a reference date of 01/07/2011.
- The item is stainless steel SS304/SS316.

2.2 *Sample preparation*

The upper internal cutting process was carried out underwater on the bottom of the spent fuel pool area, in which a turntable was placed, and by using a disc saw and a band saw in a moving frame. The cutting activities were accomplished in a dynamic and sequential manner.

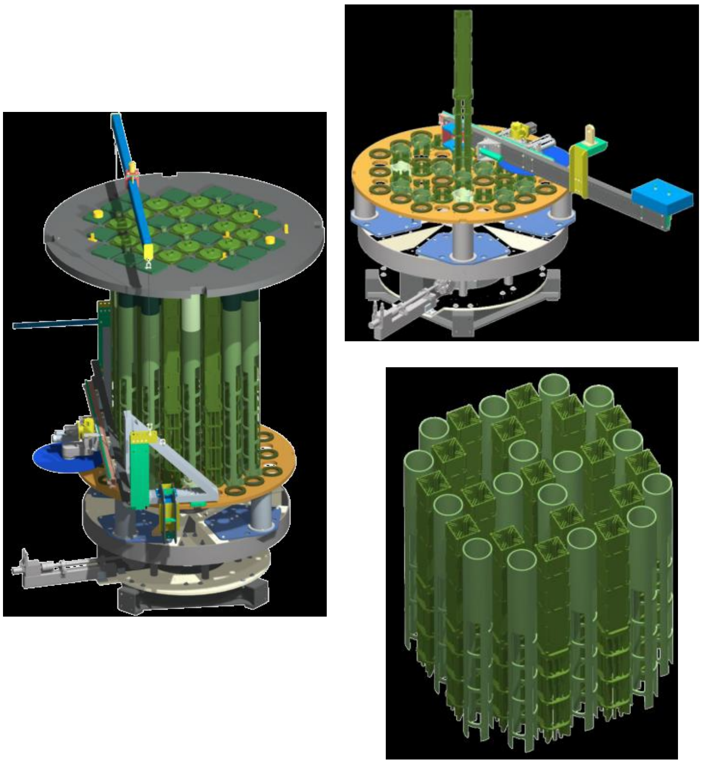

Figure 2: Cutting illustrations

Additional detailed cutting was required in order to create a sample size that met with the requirements for laboratory management and transport.

Figure 3: Detailed further cutting activities and final sample (see Tab. 5.1 for scale)

Table 2: Sample characteristics

Mass (g)	4352
Length (cm)	10
Diameter cm)	20
Apparent Volume (cm^3)	2639
Surface (cm^2)	1407

The dose rate of the sample at the test date was 1.08E+01 mSv/h.

2.3 Description of the test

The leaching test performed is a semi-dynamic process whereby the sample is submerged in deionised water in 7 consecutive steps at set time intervals, during which the total activity release is measured. In each step the leachate is replaced with fresh leachant.

Table 3: Schedule of the test

Leaching step	Step length	Accumulated days	Initial Date	Final Date
1	14	14	14/02/2014	28/02/2014
2	14	28	28/02/2014	14/03/2014
3	28	56	14/03/2014	11/04/2014
4	35	91	11/04/2014	16/05/2014
5	84	175	16/05/2014	08/08/2014
6	189	364	08/08/2014	13/02/2015
7	91	455	13/02/2015	15/05/2015

The leachant characteristics are the following:

- pH = 7±1
- Conductivity σ < 5 µS/cm
- Temperature = 20 ± 3 °C
- Atmosphere: Air

These parameters have been measured in the leachant at every step.

Table 4: Leachant characteristics

Leaching step	Temperature (°C)	Conductivity (μScm^{-1})	pH
1	1.9E+01	1.6E+01	6.8E+00
2	1.6E+01	9.2E+00	7.0E+00
3	2.2E+01	3.7E+00	6.9E+00
4	2.1E+01	2.2E+00	7.2E+00
5	2.5E+01	2.9E+00	6.5E+00
6	2.5E+01	4.5E+00	6.3E+00
7	2.4E+01	3.6E+00	6.1E+00

2.4 *Accelerator Mass Spectrometry*

Due to the expected low quantity of ^{14}C released in the leaching process, an analytical method with a low limit of detection is required in order to quantify release at every step. Accelerator Mass Spectrometry, AMS, has the required low detection limit to achieve this goal.

The standard sample preparation for the measurement of ^{14}C by using AMS techniques consists of:

- Incorporate the carbon of the sample in a carbonate form by precipitation with calcium nitrate $Ca(NO_3)_2$. This procedure mainly accounts for the recovery of inorganic carbon and further development is planned to being able to recover both inorganic and organic carbon.
- Bubbling up the flask with He to remove the CO_2 of the air.
- Hydrolysis of the Calcium Carbonate by phosphoric acid.
- Transport of the produced CO2 to the graphitization system.

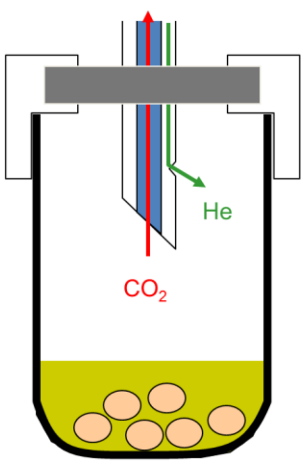

Figure 4 Hydrolysis of Calcium Carbonate sample to produce CO_2 and to send to the graphitisation process

Two approaches are commonly used for sample preparation before the graphitisation process:

1. Carbonate precipitation prior to the hydrolysis step, as indicated.
   No volume restriction is required in this case and the technique allows measurement of low ^{14}C content. This approach takes a relatively long time to implement.
2. Direct hydrolysis of the liquid sample without previous precipitation.
   This technique has a volume restriction and the carbonate concentration has to be above a threshold, but in this case a direct measurement of the sample is possible.

3 Results and discussions

3.1 *Activity released*

In addition to the measurement of the soluble fraction in the leachate, a solid fraction (not soluble) was also found to be released during the leaching test. Both fractions, that dissolved in the leachate and that released as solid have been measured for the different radionuclides considered.

Table 5: Released activity for the measured radionuclides

Days	^{60}Co (Bq)		^{137}Cs (Bq)		^{54}Mn (Bq)		^{108m}Ag (Bq)	
	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid
14	5.20E+04	9.57E+02	<2.16E+02	2.73E+02	<6.91E+00	<1.40E+01	<1.24E+02	<2.65E+00
28	2.41E+04	5.22E+02	<1.04E+02	1.98E+02	<3.60E+00	<3.72E+00	<8.46E+01	<1.39E+00
56	2.53E+04	1.76E+02	<1.50E+02	2.09E+02	<2.27E+00	<4.17E+00	<8.60E+01	1.93E+00
91	2.03E+04	3.39E+02	<9.50E+01	1.42E+02	<3.47E+00	<3.35E+00	<5.45E+01	1.94E+00
175	2.42E+04	1.38E+02	<9.95E+01	2.79E+02	<3.81E+00	<4.01E+00	<5.61E+01	4.48E+00
364	1.48E+04	6.18E+01	<7.93E+01	2.53E+02	<3.06E+00	<3.11E+00	<4.40E+01	1.41E+00
455	3.70E+03	1.56E+02	<2.82E+01	1.31E+02	<4.90E+00	<2.19E+00	<2.41E+01	1.47E+00

Days	^{125}Sb (Bq)		^{154}Eu (Bq)		^{155}Eu (Bq)		^{241}Am (Bq)	
	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid
14	<4.18E+02	1.33E+01	<1.49E+02	<2.18E+00	<2.05E+02	<3.14E+00	<4.01E+02	5.89E+00
28	5.14E+02	7.55E+00	<1.05E+02	<1.15E+00	<1.44E+02	<1.70E+00	<2.83E+02	3.07E+00
56	3.60E+02	6.48E+00	<1.08E+02	1.99E+01	<1.51E+02	1.05E+01	<3.08E+02	7.04E+01
91	<1.90E+02	2.51E+01	<7.19E+01	2.89E+01	<9.32E+01	1.34E+01	5.61E+02	9.46E+01
175	<2.29E+02	4.85E+01	<7.53E+01	1.04E+01	<1.10E+02	5.84E+00	<1.86E+02	5.40E+01
364	<1.99E+02	6.81E+00	<6.07E+01	6.53E+00	<9.10E+01	3.42E+00	<1.46E+02	2.54E+01
455	1.70E+02	4.92E+00	7.59E+01	6.87E+00	<5.54E+01	2.79E+00	4.84E+02	3.69E+01

Table 6: Measured activity for each step for ^{14}C

Days	^{14}C (Bq)
14	<3.38E+02
28	<6.65E+02
56	<6.54E+02
91	<6.61E+02
175	<6.94E+02
364	<6.55E+02
455	<6.75E+02

The only isotope with values above the detection limit for both fractions, i.e. the released solid particles and the released soluble fraction in the leachate, in all of the measurements performed is ^{60}Co, the release rate trend is shown in Figure 5.4.

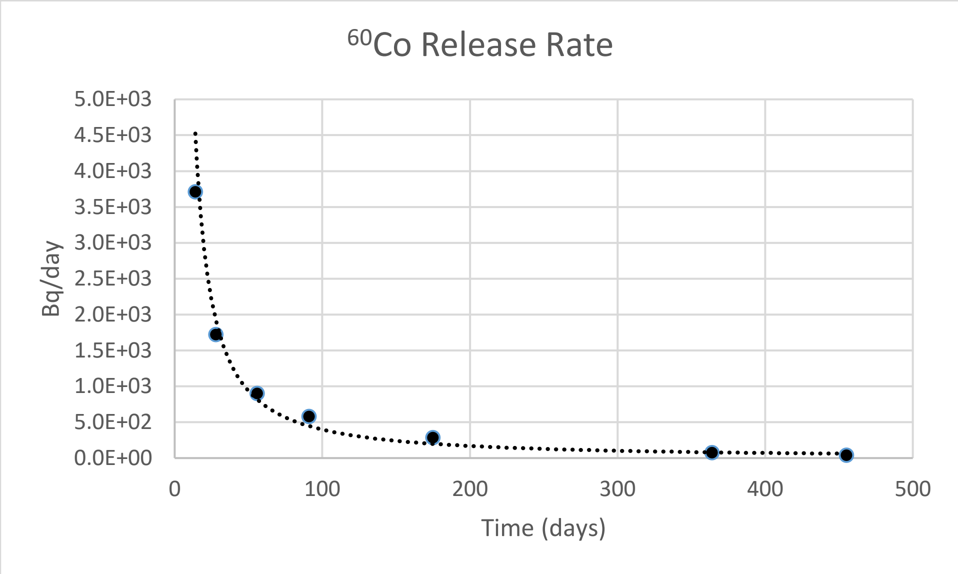

Figure 5: ^{60}Co release rate

A similar trend of released activity is observed for all the radioisotopes. For ^{137}Cs only the solid fraction shows activities above the detection limit in all the steps, and no detection is observed in the liquid fraction.

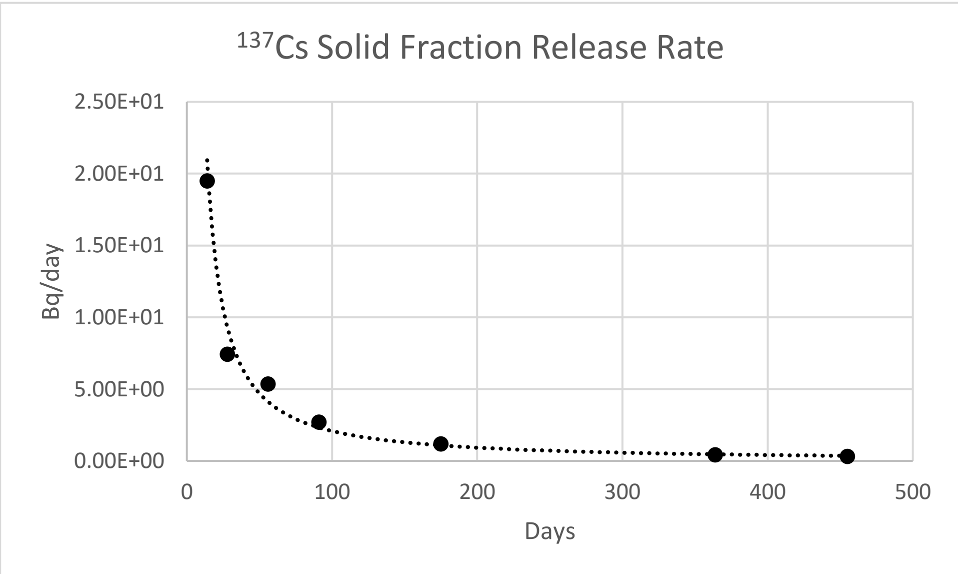

Figure 6: ^{137}Cs release rate of the solid fraction

A regression between ^{60}Co and ^{137}Cs release rates in log scale shows a good correlation coefficient of 0.993, and also that the unit slope is inside its confidence interval, indicating that a Scaling Factor can be applied for the release rate of ^{137}Cs, taking as a reference the release rate of ^{60}Co, namely

$^{137}Cs=5.22E\text{-}03\cdot{}^{60}Co$

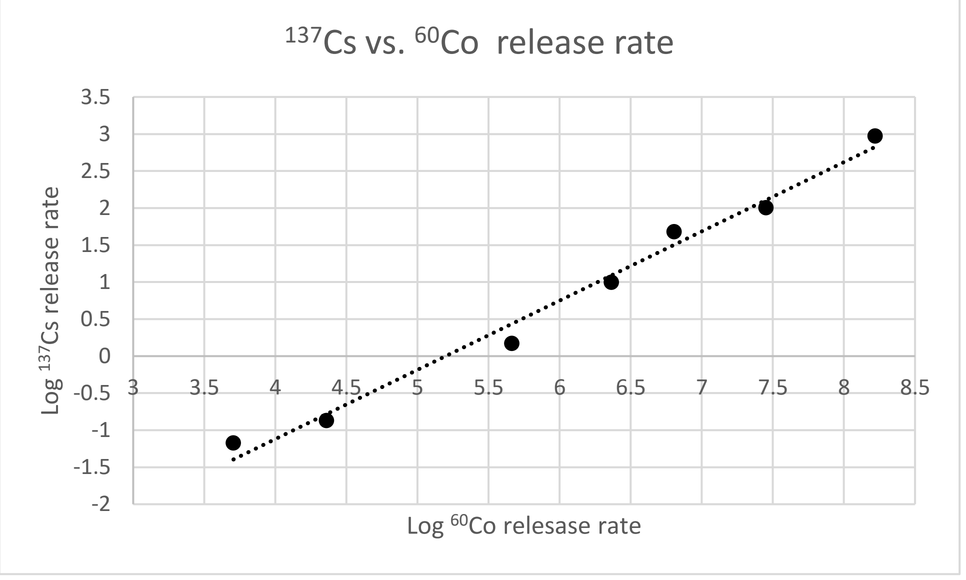

Figure 7: ^{137}Cs vs. ^{60}Co release rate

No ^{14}C activity has been detected above the detection limit (between 0.04 and 0.07 Bq/g) in any of the leachate samples, therefore further analysis is performed for this purpose.

The final ratio of the activity release in relation to the initial activity for each radionuclide are shown in the next table

Table 7: Total Activity Released Ratio

Isotope	Released Activity/Ao
^{60}Co	1.39E-03
^{54}Mn	3.01E-03
^{137}Cs	9.75E-04
^{108m}Ag	2.20E-03
^{125}Sb	1.73E-03
^{154}Eu	1.49E-03
^{155}Eu	2.05E-04
^{241}Am	1.25E-03

The only isotope with all the measured values above the detection limit is ^{60}Co. Taking the release rate values of this radionuclide, in both fractions, as representative of the corrosion rate, the following values are inferred.

Table 8 Corrosion Rate determined from ^{60}Co released fraction

	From Liquid Fraction Data	From Solid Fraction Data	Total
Released Mass (g)	5.96E+00	8.52E-02	6.05E+00
Corrosion Rate (cm/yr)	4.32E-04	6.18E-06	4.39E-04

After 455 days testing, the sample shows evidence of oxidation, as illustrated in Figure 5.5.

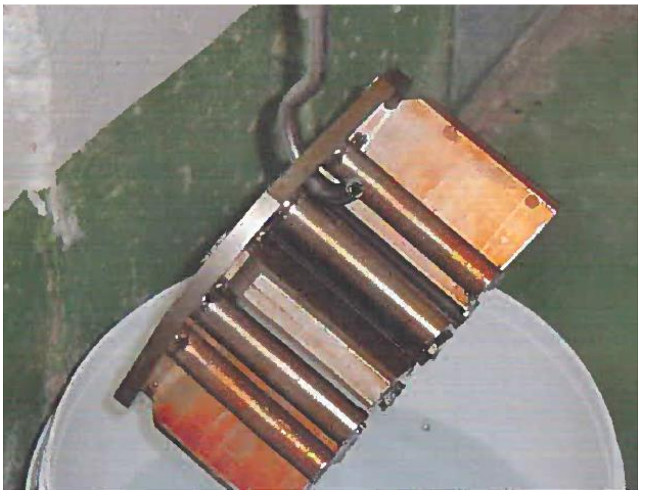

Figure 8 Final aspect of the piece after the test

The final part of this work consists of the measurement of ^{14}C, in the leachate at every step, by means of AMS technique that is currently under development in the National Centre of Accelerators, NCA, in Seville, Spain.

3.2 Accelerator Mass Spectrometry Results

To complement the AMS analysis, a measurement of the total carbon content present (released plus constant background) in every step in this leaching experiment has been performed at the outset, thus allowing values of weight percentage of the leached carbon in comparison with total carbon inventory of the sample to be derived.

Table 9: % of Total Carbon (mainly C-12, organic plus inorganic) in the leached steps.

Step	Subsample	% of C
1	1	1.261
	2	1.444
	3	1.465
2	1	1.057
	2	1.157
	3	1.267
3	1	1.365
	2	0.930
	3	1.125
4	1	1.132
	2	0.919
	3	1.308
5	1	0.975
	2	0.800
	3	0.803
6	1	0.717
	2	0.794
	3	0.825

While waiting for ^{14}C results, from these Carbon data, it could be inferred a total Carbon release rate in the leachate. This assumption supposes that all the carbon comes from the leached piece, something that has to be determined once the ^{14}C or total Carbon due to the background had been measured.

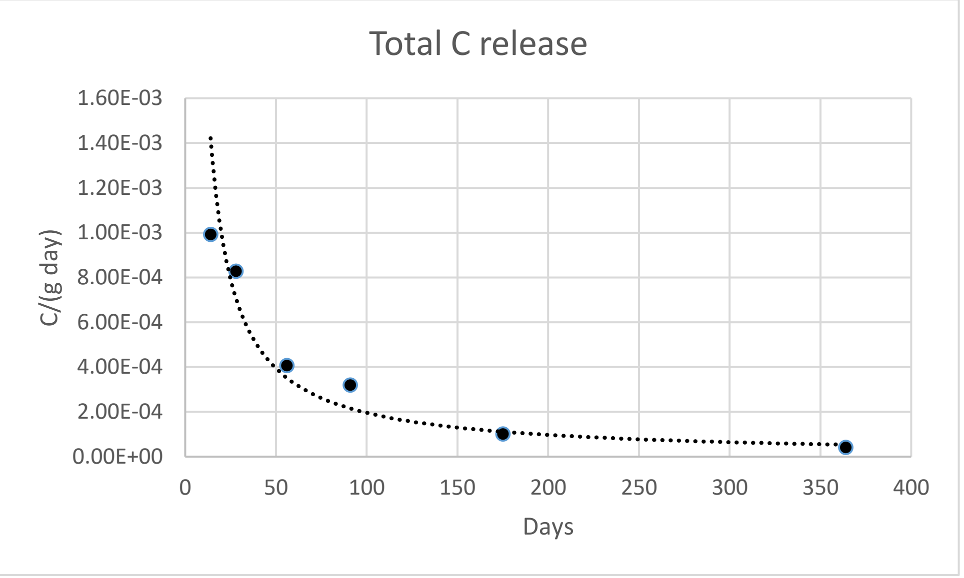

Figure 9: Total Carbon Release Rate

As in the case of the release rate of ^{137}Cs, A good correlation between ^{60}Co release rate and total Carbon release rate is found (r=0,982). In the logarithmic regression, the unit slope is inside the slope uncertainty, meaning that a Scaling Factor for the total Carbon release rate could be derived from the ^{60}Co release rate.

$C=4.26E\text{-}07 \cdot {}^{60}Co$

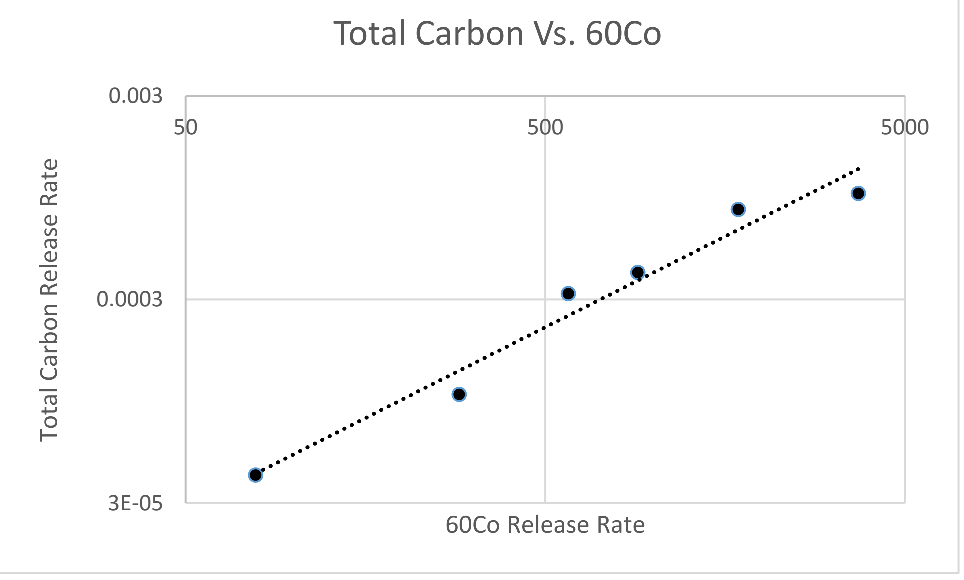

Figure 10: Correlation of Total Carbon Release Rate vs. ^{60}Co Release Rate.

3.3 Conclusions

A standard leaching test that is usually performed in relation to waste packages at El Cabril laboratory has been adapted in order to leach activated stainless steel of type SS304-SS316, with the aim of understanding the release rate of radionuclides from activated steels under aerobic conditions when contacted by deionised water pH7±1.

Although AMS results are awaited, a main conclusion based on Total Carbon analysis and Gamma Spectrometry is the observation of a strong correlation among the release rate of the respective radionuclides detected (including ^{137}Cs and ^{60}Co), in addition to theoretically determined ^{14}C by modelling the $^{14}C/^{60}Co$ ratio using the ORIGEN SCALE code.

In this sense, as ^{60}Co is the easiest of the respective radionuclides to measure, it can be selected as the key nuclide to be used as a basis for scaling the release rates of other radionuclides, and a scaling factor for release rates could be established for every material analysed in this study. The stainless steel corrosion rate could also be scaled with the ^{60}Co release rate.

Although the final values of ^{14}C at every step of the leaching test are not available for this paper (AMS results are outstanding), a release rate of carbon could be inferred from the total carbon measured at every step, which shows a similar trend as for the rest of gamma-emission radionuclides measured.

^{14}C speciation is being addressed in Ciemat studies shown in D2.13.

References

[1] Ministry of Industry, Tourism and Commerce. Sixth General Radioactive Waste Plan (2006).

[2] Ministry of Industry, Tourism and Commerce. Resolution from the Directorate General for Energy Policy and Mines on 21st July 2008 authorized the modification of the design of the facility to include disposal cells specifically designed to store very low-level radioactive

waste, while setting new limits and conditions for nuclear safety and radiological protection associated with the operating permit.

[3] ISO 21238 Scaling factor method to determine the radioactivity of low and intermediate level radioactive waste packages generated at nuclear power plants.

[4] ISO 16966 Theoretical activation calculation method to evaluate the radioactivity of activated waste generated at nuclear reactor.

[5] Ciemat final report on 14C release from steels under aerobic conditions (D2.13).

[6] ORIGEN – The ORNL isotope generation and depletion code. ORNL 1973.

[7] ASTM Standard E1019, 2008. Standard Test Method for Determination of Carbon Sulphur, Nitrogen and Oxigen in Steel, Iron Nickel and Cobalt Alloys by various Combustion and Fusion Techniques. ASTM international, West Conshohocken. PA, DOI: 10 1520/E1019-08.

[8] ISO 11929-Part 1 (elementary application) , Part 2 (Advanced applications), Part 3 (Applications to unfolding methods). “Determination of the characteristics limits (decision threshold, detection limit, and limits of coverage interval) for measurements of ionizing radiation”.

[9] NUREG/CR- 6567 PNNL-11659 “Low Level Radioactive Waste Classification, Characterization and Assessment: Waste Streams and Neutron Activated Metals”.