CArbon-14 Source Term

CAST

WP2 CIEMAT Final Report on ^{14}C release from steels under aerobic conditions (D2.13)

Author(s): M. Rodríguez Alcalá, E. Magro, J. L. Gascón,

G. Piña, E. Lara, L. Sevilla, G. de Diego and S. Merino

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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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Executive Summary

One of the R&D activities planned in the Spanish context for the next years should provide support and coverage for the drawing up and/or revision of management strategies for the different types of radioactive wastes, based on better understanding of such wastes including the physical, chemical, environmental and radiological properties of the isotopes they contain. Within this framework, the understanding of the ^{14}C behaviour in waste packages with stainless steel could lead to a revaluation of the near surface repository for the disposal of wastes containing this radionuclide in high concentrations.

To achieve these objectives, first the stainless steel was characterised by metallographic analysis using both optical and scanning electron microscopy. According to the results obtained by these techniques, the material is a low content in Ni, 304 or 316 austenitic stainless steel.

Leaching experiments in aerobic conditions have been planned considering two different scenarios, one in which the leaching solution simulates the expected conditions in a cement based repository over long time periods (NaOH solution of pH ca. 12), the other one using an acid solution of 1M H_3PO_4, which has been proved as a high efficiency chemical removal agent. The leaching process was performed in High Pressure Reactors of Stainless Steel with Teflon Insert (material recommended for its chemical inertness) at room temperature and a synthetic mixture of N_2 (79%) and O_2 (21%) was introduced in the containers to assure that the leaching process takes place under aerobic conditions. The gas and the leachate were renewed after 14, 28, 56, 90, 180 and 280 days.

The development of both analytical methods and protocols to measure the release of ^{14}C from the activated steel samples, and the speciation in the aqueous and gaseous phase, have been performed throughout the CAST project.

Analytical methods, suited to identify and quantify low molecular weight organic molecules, comprise Ion Exchange Chromatography and Gas Chromatography coupled to Mass Spectrometry, are described for aqueous and gaseous samples, respectively.

Gas Chromatography analyses indicate that CO was produced in the gas phase of both leaching experiments with NaOH solution of pH ca. 12 and 1M H_3PO_4.

Ion Exchange Chromatography analyses indicate that oxalate has been found as organic carbon dissolved in all steps of the leaching process when H_3PO_4 is used as leachant.

Regarding the first results of the analysis of ^{14}C only the first step of leaching processes presents a value of ^{14}C higher than the detection limit. These values correspond to a 3,6% of total ^{14}C in the case of NaOH and to a 5,7% in the case of H_3PO_4.

The corrosion rate determined in the experiments with NaOH was found to be approximately 2.74E2 nm/year after 281 days and it would be constant in the long run, whereas in the experiments with H_3PO_4 the value obtained was 2.01E4 nm/year after 263 days, and it would be constant in the long run.

List of Contents

1   Introduction

1.1 *Objective*

The disposal of radioactive wastes from nuclear power plants containing ^{14}C implies considerations that are, for several reasons, different from those encountered with other usual isotopes. First of all, its long half-life (5400 years) excludes any significant loss by decay during mid-term storage periods, and secondly, carbon is one of the most commonly encountered elements in living matter occurring in nature in a wide number of chemical forms.

The understanding of the mechanisms by which the ^{14}C can be released from different types of radioactive wastes under its final storage conditions (organic, inorganic, dissolved or gaseous species) can be a crucial aspect in the design of this kind of facilities.

1.2 *Relate to Spanish National Program and the CAST Project*

Since 1984 the management of radioactive waste in Spain has been the responsibility of the Empresa Nacional de Residuos Radiactivos, S.A. (ENRESA), more recently, in the year 2005, ENRESA has been created as a State Business Entity (SBE) in charge of an essential public service: the management of radioactive waste, including spent fuel from the Nuclear Power Plants (NPP's), and the dismantling and decommissioning of nuclear and radioactive facilities.

In Spain radioactive wastes are generated at a number of facilities distributed throughout the country that use radioactive materials and substances as regulated in the specific applicable standards, these being known as Nuclear Facilities (NF's) and Radioactive Facilities (RF's). Radioactive wastes may also occasionally be generated in other areas as a result of specific activities such as uranium mining.

With a view to integral management in Spain, radioactive wastes may be classified in two major groups [1]:

1

- The so-called Low and Intermediate Level Wastes (LILW), which given their characteristics may be temporarily stored, treated, conditioned and definitively disposed of at the El Cabril facility (Córdoba); these include the sub-group of Very Low Level Wastes (VLLW).

- The so-called High Level Wastes (HLW), consisting basically of spent nuclear fuel and other specific high level wastes. This group also includes other Intermediate Level Wastes (ILW) which, in view of their characteristics, cannot be disposed of under the conditions established for El Cabril, specific installations being required for this purpose.

In general, LILW are conditioned by the producers. However, at the majority of the RF's, or in the event of incidents, conditioning is performed in a specific manner and with support from ENRESA on the basis of the available capacities, among which those of the El Cabril installations are fundamental. In all cases the acceptance criteria established by ENRESA for the subsequent management that is foreseen are to be fulfilled.

Before its storage at the Near Surface Repository (El Cabril) producers are required to measure and report ^{137}Cs and ^{60}Co (considered as "easy to measure radionuclides") in their operative wastes, and then ENRESA assesses the content of a number of other radionuclides, including ^{14}C, using scale factors based on statistical studies.

At El Cabril, there is only a limit on the total amount of ^{14}C to be disposed of, and that limit is 20 TBq [2]. Based on that and the room available in the disposal cells, ENRESA derives limits for acceptance of individual waste packages.

Several works and projects at national level aiming to provide data on the content and distribution of ^{14}C in different kind of wastes [3] [4], mainly coming from nuclear reactors ('spent' ion exchange resins or graphite for example), have been carried out over the past years. Because of its mobility, the ^{14}C is considered as a relatively difficult to measure radionuclide in the scale factors calculations.

Due to this limited storage capacity for ^{14}C, radioactive wastes with high concentrations of this radionuclide either are destined for interim storage in a Centralized Temporary Storage (CTS) or for final deep geological disposal together with the spent fuel and the high level wastes. Unfortunately, it should be pointed out that although there is wide agreement in relation to the deep geological disposal option and CTS, there are at present in Spain no facilities of these types and there are considerable delays in its implementation.

A large number of full commercial reactor dismantling projects are now in the execution phase. NPP dismantling and decommissioning activities may be seriously hampered (or even rendered impossible) depending on the availability or otherwise of a sufficient capacity for management of not only the spent fuel but materials of moderate (but appreciable) quantities of radioactive waste containing ^{14}C that, in the Spanish case, require specific temporary storage installations, such as CTS.

Because of the reasons mentioned above, one of the R&D activities planned in the Spanish context for the next years should provide support and coverage for the drawing up and/or revision of management strategies for the different types of radioactive wastes, based on better understanding of such wastes including the physical, chemical, environmental and radiological properties of the isotopes they contain [5].

Within this framework, the understanding of the ^{14}C behaviour in waste packages with stainless steel could lead to a revaluation of the near surface repository for the disposal of wastes containing this radionuclide in high concentrations.

Aiming to achieve these objectives, leaching experiments have been planned considering two different scenarios, one in which the leaching solution simulates the expected conditions in a cement based repository over long time periods (NaOH solution of pH ca. 12) in aerobic conditions, the other one using an acid solution of 1M H_3PO_4, which has been proven as a high efficiency chemical removal agent in graphite within the EU EURATOM FP7 CARBOWASTE program [6].

These particular conditions can facilitate, by conjunction with the anaerobic conditions of experiments undertaken by most of the participants in the CAST project, an understanding of the leaching and speciation processes happening in these experiments.

2   Materials and Methods

2.1 *Activation History of the Material*

The following information has been obtained from the NPP:

1. José Cabrera NPP was operated from 30/06/1968 to 30/04/2006, a total of 13818 days, with 29 cycles of operation.

2. The load factor accumulated during the operational life of the plant is the 70.97%.

3. 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.

4. The degree of maximum spent fuel burning was 45000 MWd/tU and enrichment at least 3.15% in weight of ^{235}U.

5. Finally, the composition was calculated allowing for decay to a reference date of 01/07/2011.

With this information and using the Origen-S software, the radiochemical composition of the samples was obtained. The data, expressed as a fraction of the ^{60}Co content, are shown in Table 1.

The theoretical value corresponding to ^{14}C has been highlighted. This value will be compared with the experimental results.

Table 1. Radiochemical composition of stainless steel as a fraction of ^{60}Co (modelled values with Origen-S for reference date 01/07/2011)

Isotope	/^{60}Co	Isotope	/^{60}Co	Isotope	/^{60}Co
^{3}H	1.45E-03	^{154}Eu	1.13E-04	^{93}Mo	1.29E-05
^{36}Cl	6.42E-06	^{178m}Hf	5.87E-25	^{125}Sb	1.85E-08
^{41}Ca	5.56E-08	^{90}Sr	1.59E-06	^{135}Cs	4.09E-11
^{54}Mn	9.39E-03	^{99}Tc	4.64E-07	^{155}Eu	5.14E-06
^{55}Fe	1.13E00	^{133}Ba	2.58E-08	^{233}U	3.25E-15
^{59}Ni	2.36E-03	^{134}Cs	2.21E-04	^{238}Pu	1.95E-09
^{60}Co	1.00E00	^{137}Cs	1.89E-06	^{239}Pu	1.50E-07
^{63}Ni	2.57E-01	^{151}Sm	5.92E-06	^{214}Am	1.43E-09
^{94}Nb	9.13E-06	^{166m}Ho	2.92E-06	^{244}Cm	8.10E-14
^{110m}Ag	1.82E-05	^{14}C	**6.77E-04**		
^{152}Eu	2.66E-04	^{39}Ar	1.39E-06		

2.2 *Sample preparation*

The pieces used in the leaching experiments on activated stainless steel come from reactor internals of José Cabrera NPP that is being currently dismantled by ENRESA. The pieces, as they arrived at our facilities, and their radiological data, are shown in Figure 1.
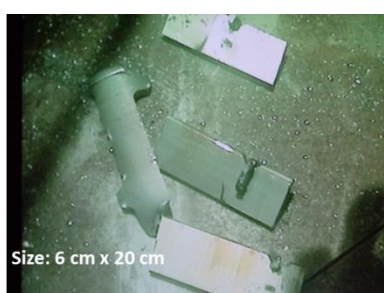
SAMPLES	Contact Dose Rate (mSv/h)	1 Meter Dose Rate (mSv/h)	Co-60 (MBq)
Sample 1 (Guide Tube)	2.12	0.24	7.1
Sample 2 (Guide Tube)	6.6	0.59	22.0
Sample 3 (Guide Tube)	2.5	0.23	8.3
Sample 4 (Support Column)	1.1	0.10	3.7

Figure 1. Pieces and Radiological Data from reactor internals of José Cabrera NPP

These pieces arrived to CIEMAT in April 2014 and due to different inconveniences (described in the point 4.2 of the reports [7-9]) were not transferred to our laboratory until November 2015. The Radiological Protection Department of CIEMAT (RPD) performed wipe tests over the sample surface and detected ^{60}Co and ^{241}Am contamination. As a result

of this, the RPD requested the decontamination of the sample before giving the permission to cut it into smaller pieces compatible with dimensions of the leaching containers. The decontamination was performed (in June 2016) by dipping the piece in a solution with sequestering agent (2%) in an ultrasonic cleaner (35 KHz) for 15 minutes.

The cutting of the pieces was carried out with a cutting machine into a glove box and using a silicon carbide disc (Figure 2). A coolant was used to minimize the alteration of the structure of the material in the cutting area.
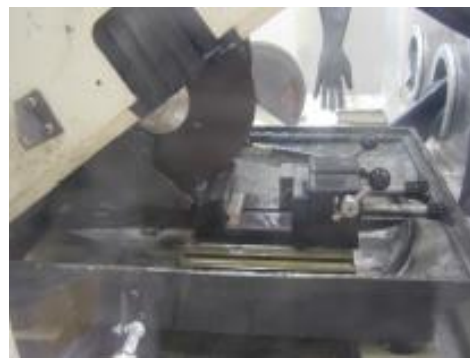
Figure 2. Cutting machine into a glove box

The samples were cut and identified in three directions. The rolling direction of the samples follows the positive z axis direction as shown in Figure 3. 11 pieces were obtained for dissolving in order to characterise the piece, 3 pieces to perform metallographic analysis and 4 pieces for leaching. The contact dose rate ranged between 25 and 60 µSv/h.
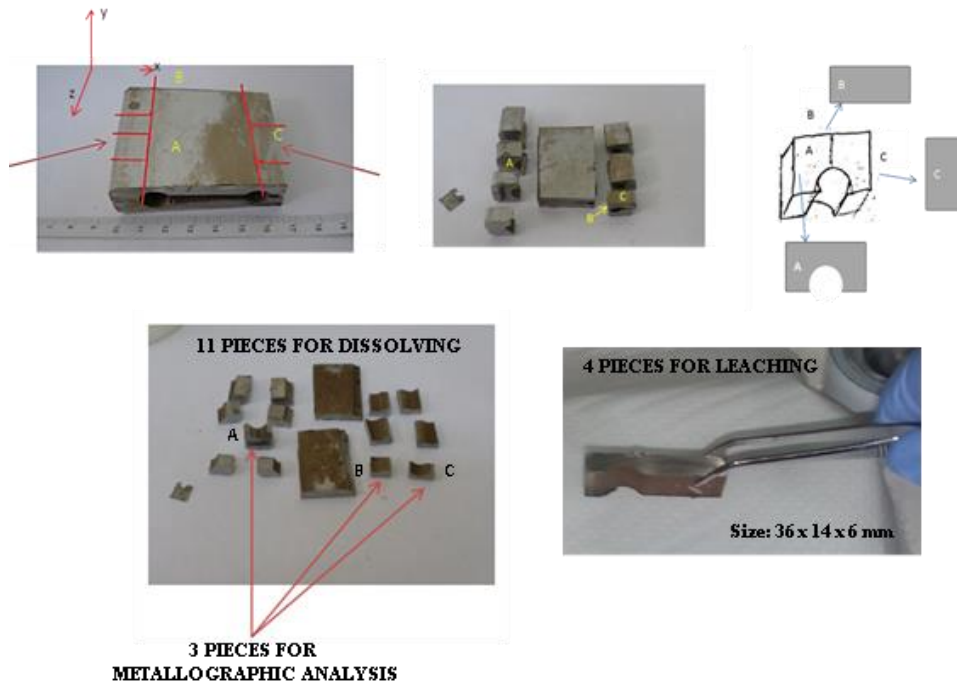

Figure 3. Pieces after cutting

2.3 *Microstructural Characterisation*

Once the irradiated original piece was cut, the preparation of the 3 samples obtained for subsequent analysis with the microscope was carried out through the following steps:

- **Mounting:** The samples were cleaned and embedded in a multipurpose resin EPOMET®G of large grain size. Afterwards, pressure and temperature were applied during 10 min.

- **Grinding and polishing:** The surface preparation was done by applying the following treatments:

    - Silicon Carbide abrasive paper P320 (with water),

- Silicon Carbide abrasive paper P600 (with water),

- Silicon Carbide abrasive paper P1200 (with water) and,

- Polishing with 6 μm diamond paste

The same conditions were maintained in all the steps: rotational speed of 300 rpm for 3 minutes with a pressure of 6 lbs.

- **Chemical attack:** chemical attack of the samples was carried out according to the standard ASTM E407. This attack is of the electrolytic type and its objective is to reveal the limit of grain for further observation under a microscope.

The metallographic analysis of the steel has been performed by the Group of Characterisation of Structural Materials in CIEMAT. The techniques used were:

- Optical Microscopy (OM) to observe the microstructure of the material.

- Scanning Electron Microscopy (SEM) to study the inclusions or precipitates as well as the different crystalline phases in the material. Photomicrographs using a secondary electrons detector (SE) were taken and analysis of chemical elements of inclusions detected with the spectrum of energy dispersive x-ray (EDX) attached to the microscope were performed. In order to identify the extent of these inclusions mapping of x-ray was also carried out.

- Feritscope to measure the ferrite content in austenitic and duplex steel according to the magnetic induction method. All magnetizable structure sections are measured i.e, in addition to delta ferrite also strain-induced martensite, for example, or other ferritic phases.

2.4 *Radiological Characterisation of initial sample*

In order to characterise the stainless steel samples, first it was necessary to dissolve them. The process performed is shown in Figure 4.
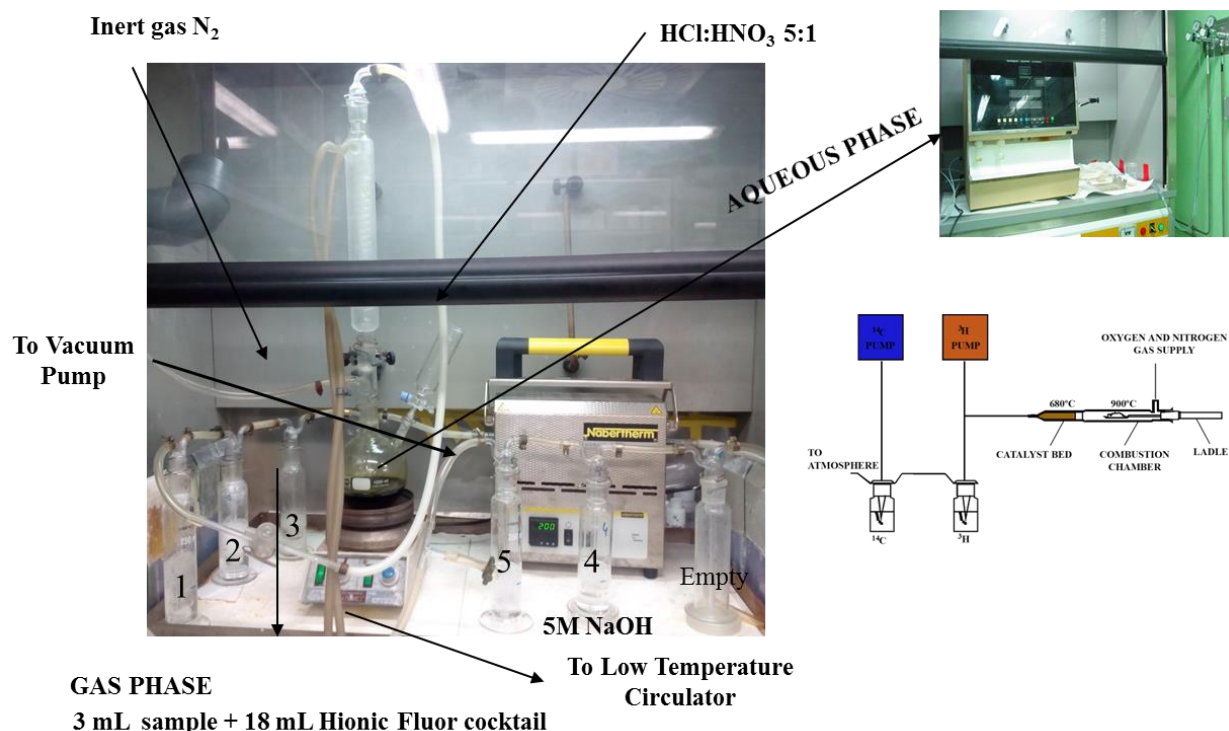
Figure 4. Methodology for the initial steel characterisation

The solubilization of the samples was carried out with a mixture of HCl and HNO_3 acid in a ratio 5:1 at 100ºC. The solution is purged with N_2 and stirred for four hours, in this step the inorganic fraction is released as CO_2 and trapped in washing bottles number 2 and 3 containing 5M NaOH. Other carbonaceous compounds such as CO and CH_4, released during the acid stripping, are oxidised in a catalytic furnace to CO_2 (using Ni_2O_3/Pt as a catalyser and at 200ºC). This CO_2 is trapped in washing bottles number 4 and 5 also containing 5M NaOH. The samples from washing bottles were collected; in this case, 3 mL of sample was mixed with 18 mL of Hionic Fluor cocktail and ^{14}C analysed by LSC using a Quantulus.

To complete the characterization of the initial sample, an aliquot of the solution obtained was introduced in a combustion oven where the sample is burned to 900ºC in an oxygen stream, the gases formed passed through a catalyst bed (CuO, Pt), where the carbon compounds are converted to CO_2, which is trapped in a specific cocktail, and finally the vial obtained was analyzed in the Quantulus equipment. In this process all the interferences coming from beta-gamma emitters different from ^{14}C are removed.

The solution obtained in the process was measured by gamma spectrometry to determine the activity of ^{60}Co present in the initial sample.

2.5 *Speciation*

Throughout the CAST Project and regarding the Analytical Requirements for Speciation, the methodology to determine permanent gases (CO, CO_2), C1 to C5 hydrocarbons, alcohols and aldehydes has been developed using a Gas Chromatograph coupled with a Mass Spectrometer.

Also, the methodology to determine short chain carboxylic acids by an Ion Chromatography System using a conductivity detector has been implemented.

The tests performed to obtain the best conditions to work with these two techniques have been indicated in the point 4.3 of the deliverables [8,9].

2.6 *Leaching process*

After cutting the sample pieces, the leaching process started in June 2016 with two samples and it was performed in High Pressure Reactors of Stainless Steel with Teflon Insert (material recommended for its chemical inertness) at room temperature.

Finally, the procedure has been carried out in the following way:

- The procedure foreseen for developing the leaching tests is based on the standard procedure ISO 6961 [10].

- As leachants NaOH pH = 12 and 1M H_3PO_4 are used.

- The value of the surface area exposed to the leachant is 14 cm^2. The leach tests have been conducted at room temperature and the losses of leachant by vaporization are insignificant.

- The specimen was suspended in 120 ml of leachant by means of a PTFE thread (Figure 5) and surrounded by at least 1 cm of liquid in all directions.
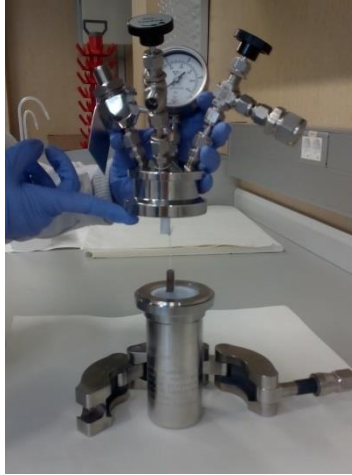

Figure 5. Leaching container

- Before using the containers, these were cleaned with milli-Q water.

- The stainless steel pieces were cleaned with acetone and milli-Q water.

- A synthetic mixture of N_2 and O_2 (21% oxygen, 79% nitrogen) has been introduced in the containers to assure that the leaching process takes place under aerobic conditions. The pressure vessel is 1 bar.

- It was foreseen to renew both the gas and the leachate after 14, 28, 56, 90, 180 and 360 days. However, due to the delay in starting the leaching process, the leachate corresponding to 360 days was not taken, instead of that, the last sample was taken at 280 days.

- After each period, first of all the gas sample (volatile species) was collected by means of a gas tight syringe and immediately injected into the GC-MS system.

- After completing the previous step the container was opened, the specimen was removed from the leachant, and the leachate was transferred to a bottle which was labelled and stored for ulterior analysis.

- After storing the leachate, the PTFE was rinsed with milli-Q water, refilled with fresh leachant, the specimen immersed in the liquid and after purging with synthetic air, the reactor was closed.

The leachate samples corresponding to all steps foreseen have been taken and the following analyses have been performed:

- ^{14}C with a Low Background LSC

- Gamma emitters with a Canberra BEGe 3830 HPGe Detector

- The gas and leachate volatile species with a GC-MS and

- The organic dissolved species (carboxylic acids) with an IC System

3   Results and Discussion

3.1 *Microstructural Characterisation of the initial sample*

3.1.1   Optical Microscopy

All observed areas present a microstructure of austenitic grains with small rounded inclusions in sections A and B (Figure 6). In section C can be observed some elongated inclusions due to the sheet metal forming process (laminated stainless steel) (Figure 7).
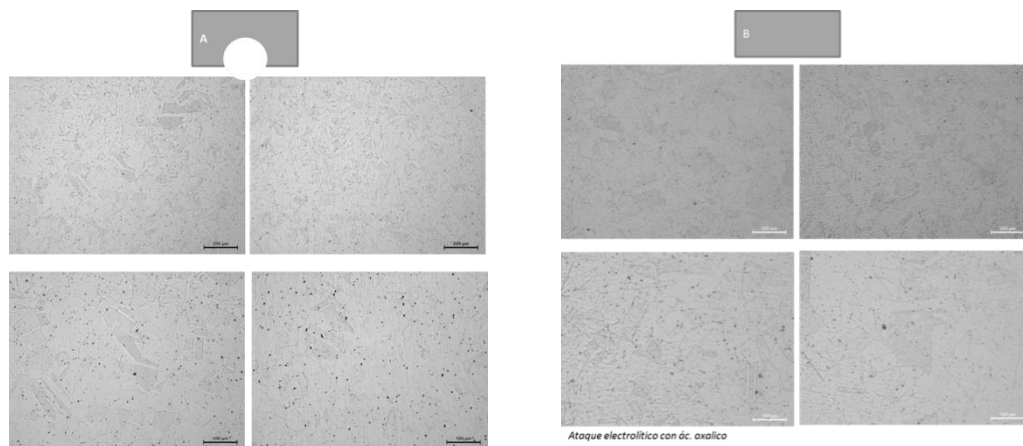

Figure 6. Optical Microscopy in section A and B
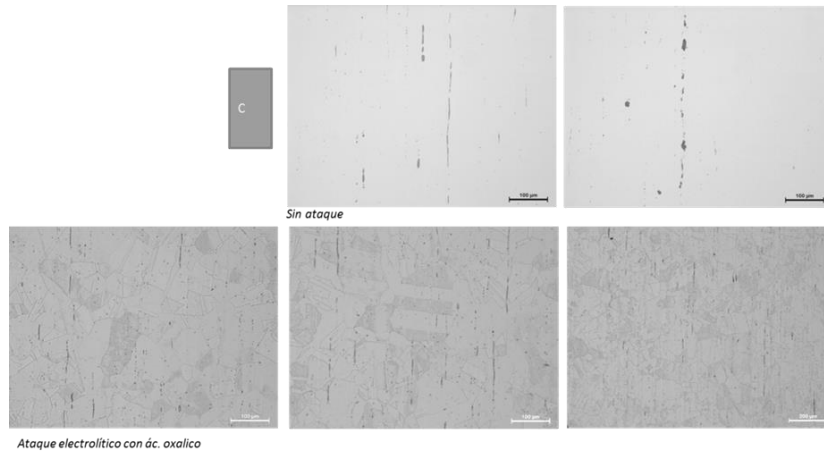
Figure 7. Optical Microscopy in section C

3.1.2 Scanning Electron Microscopy

The inclusions detected are of two types: elongated, which are manganese sulphides, and rounded, which are mainly oxides of titanium, as shown in Figures 8 to 11.
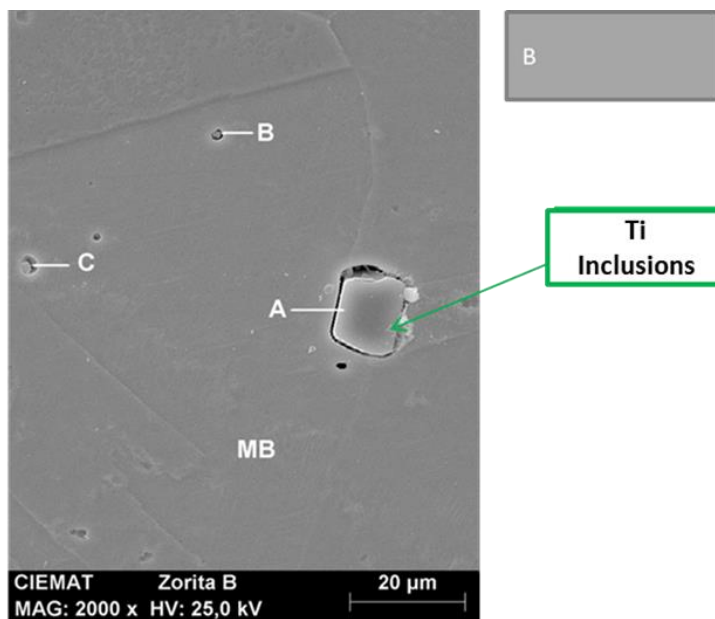
Atomic percent (norm.)	Cr	Mn	Fe	Ni	O	Ti	S	Si	Al
Zorita B (Zona 1) (Edx MB)	20.60	0.00	72.71	6.69	0.00	0.00	0.00	0.00	0.00
Zorita B (Zona 1) (Edx A)	21.00	17.48	0.00	0.00	53.68	6.64	0.00	0.00	1.19
Zorita B (Zona 1) (Edx B)	25.48	6.51	62.39	4.07	0.00	1.19	0.36	0.00	0.00
Zorita B (Zona 1) (Edx C)	18.66	3.85	52.29	3.73	19.10	0.56	0.00	1.81	0.00

Figure 8. Inclusions analysis section B

Atomic percent (norm.)	Cr	Mn	Fe	Ni	O	Ti	S
Zorita B (Zona 2) (Edx A)	24.69	8.46	58.45	4.75	0.00	0.00	3.65
Zorita B (Zona 2) (Edx B)	24.25	10.88	31.37	1.94	29.23	2.33	0.00

Atomic percent (norm.)	Cr	Mn	Fe	Ni	O	S	Si	Ca
Zorita B (Zona 3)	11,10	0,85	37,58	2,56	22,96	0,00	20,93	4,02
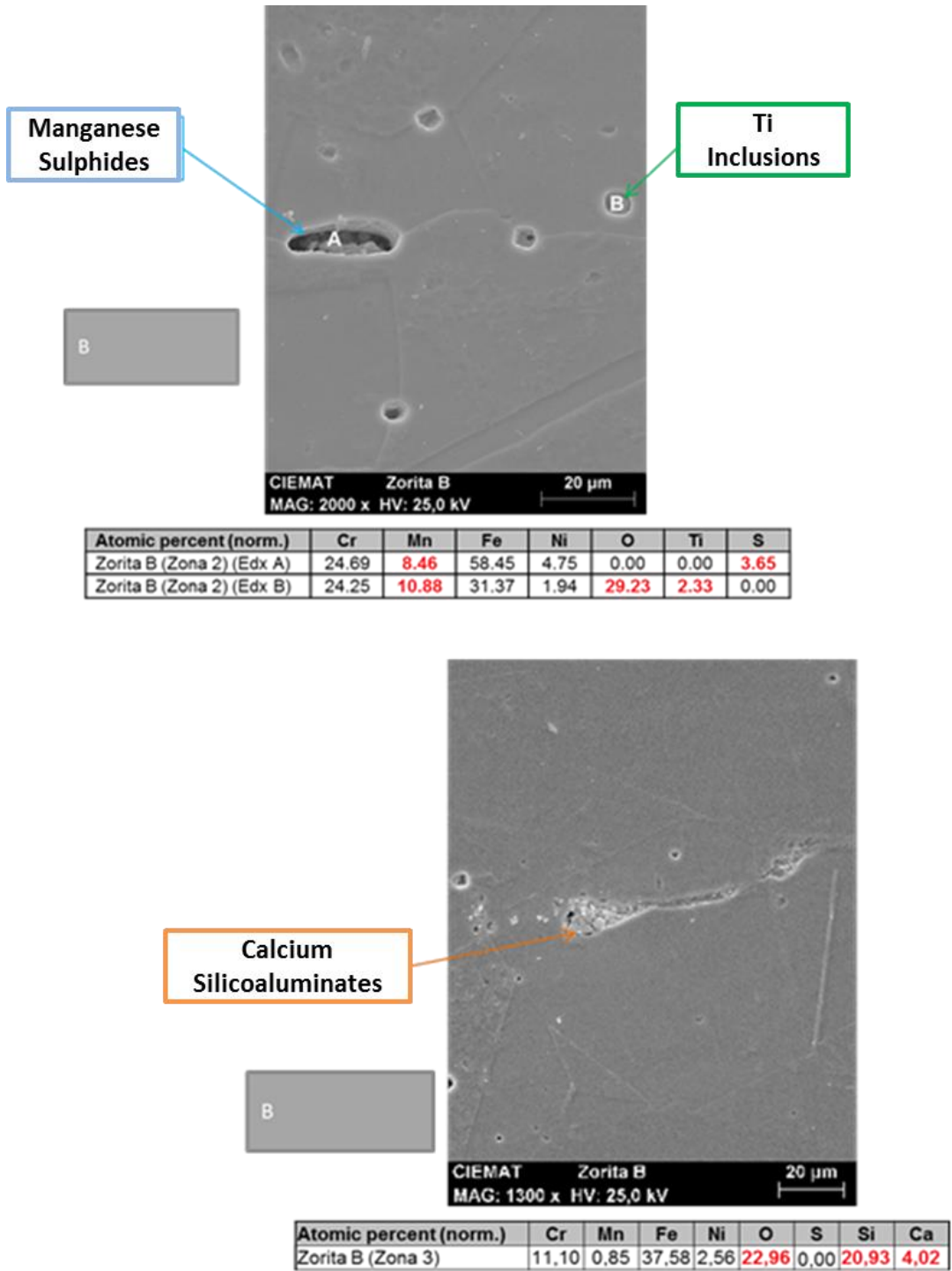
Figure 9. Inclusions analysis section B

Atomic percent (norm.)	Cr	Mn	Fe	Ni	Si
Zorita C-Atacada (C)	25.05	1.54	69.05	3.98	0.38
Zorita C-Atacada (MB)	19.26	1.83	71.46	7.45	0.00

Atomic percent (norm.)	Cr	Mn	Fe	Ni	O	Al	Ti	S
Zorita C (Zona-3)(Edx A)	20.47	16.95	0.00	0.00	51.80	6.74	4.04	0.00
Zorita C (Zona-3)(Edx B)	9.35	29.34	23.94	1.75	0.00	0.00	0.00	35.63

Atomic percent (norm.)	Cr	Mn	Fe	Ni	O	Ti	S
Zorita C (MB)	19.45	1.39	72.41	6.75	0.00	0.00	0.00
Zorita C (Zona-1)(Edx A)	8.52	30.00	22.76	1.42	0.00	0.00	37.30
Zorita C (Zona-1)(Edx B)	10.88	22.84	34.34	3.11	0.00	0.00	28.83
Zorita C (Zona-1)(Edx C)	19.62	12.10	27.37	2.09	33.35	2.69	2.77

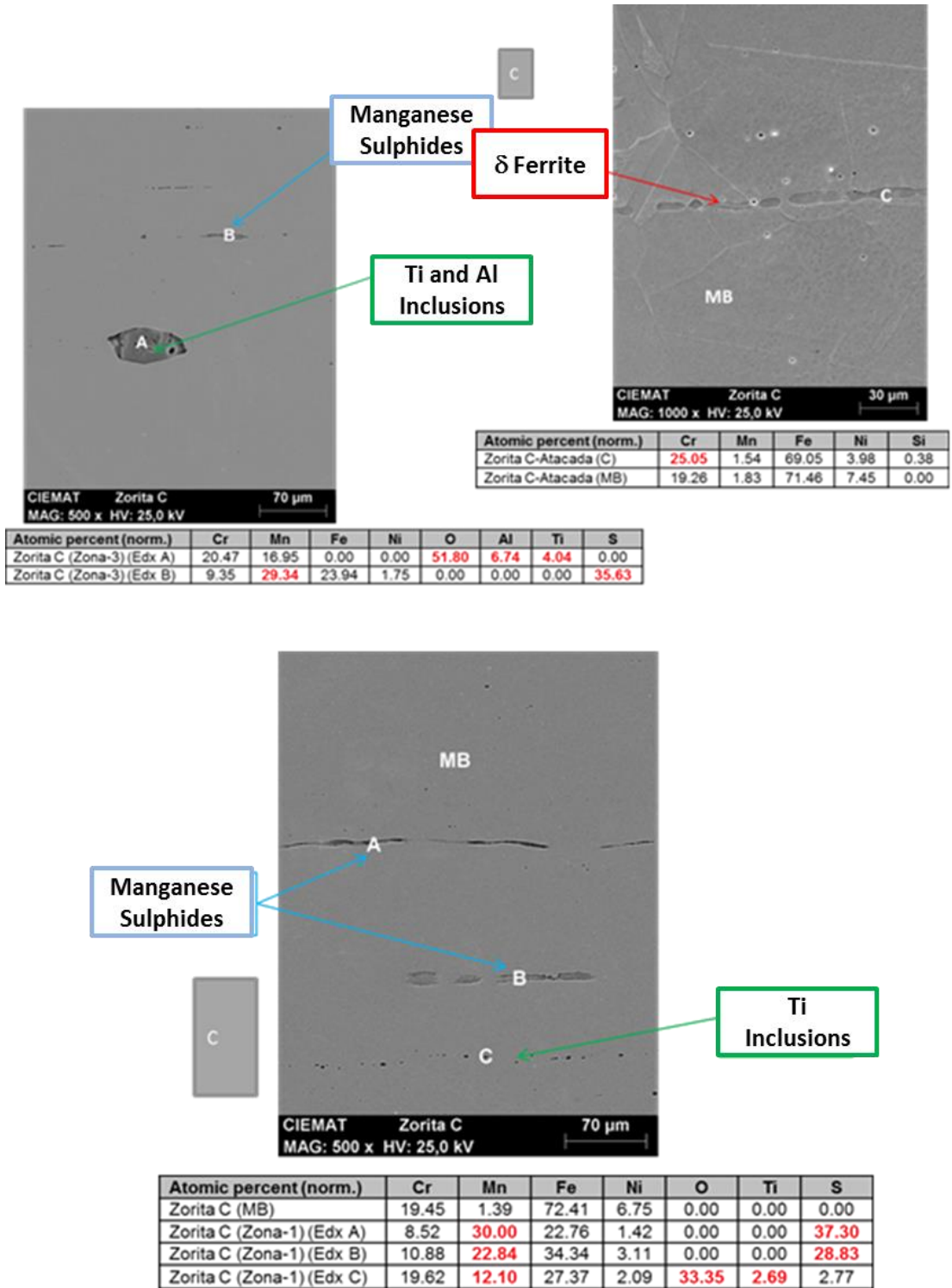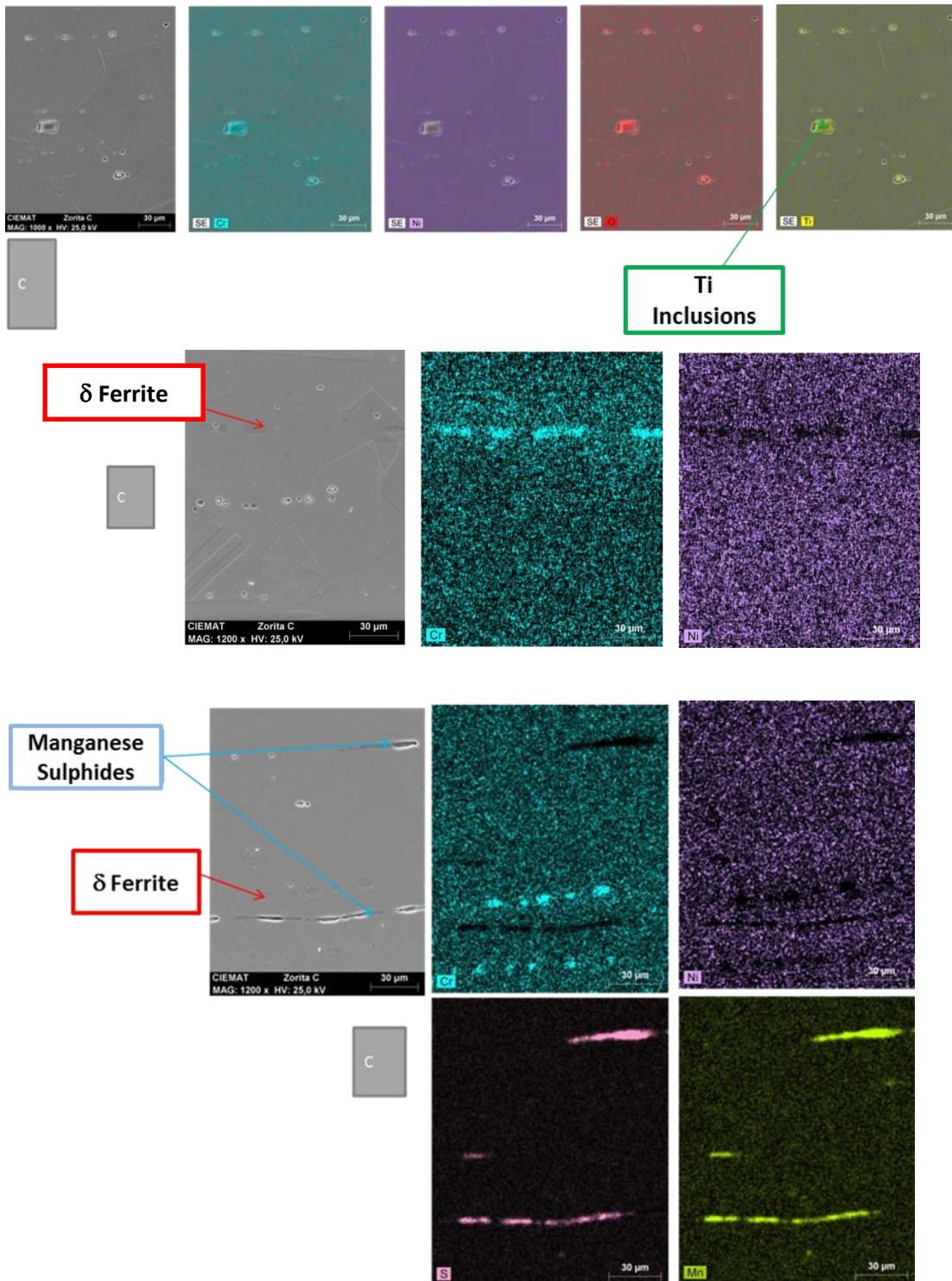**Figure 10. Inclusions analysis section C**

Figure 11. Mapping of X-Ray. Section C

In the Manganese Sulphides, the Mn could be partially replaced by Fe, Cr or Ti.

3.1.3 Feritscope

The measurements obtained (Table 2) correspond to a material with a very low percentage of Delta Ferrite, without deformation and with an annealing treatment.

Table 2. % δ Ferrite in the Stainless Steel

Stainless Steel	A	B	C
% **FERRITE** δ	0,1	0,1	0,1

3.2 *Radiological Characterisation of the Initial Sample*

Having performed the procedure to dissolve the steel samples, the results of ^{14}C obtained in the aqueous and gas phase and the total activity of ^{14}C, corresponding to 5 pieces, are shown in Table 3, where it is observed that ^{14}C practically remains in the aqueous phase as organic carbon, which is concordant with the studies carried out by other authors [11, 12] where they propose the mechanism of hydrocarbon formation through processes similar to those that occur in Fischer-Tropsch synthesis.

The solution of the sample (aqueous phase) was analysed by gamma spectrometry and the value of the activity of ^{60}Co is shown in Table 3. With all these data the ratio between ^{14}C and ^{60}Co has been determined. It can be seen that the experimental ratio (mean value = 6,61E-04) is concordant with the obtained with the Origen-S code (6,77E-04).

Table 3. Results of ^{14}C and ^{60}Co of the stainless steel pieces

Reference	Weight (g)	^{14}C Aqueous Phase Bq ± 2U (%)	^{14}C Gas Phase Bq ± 2U (%)	^{14}C total Bq ± 2U (%)	^{60}Co total Bq ± 2U (%)	Experimental ^{14}C/^{60}Co	Origen-S ^{14}C/^{60}Co
A-CAST-3	12,7745	3,8E1 ± 8	6,0E0 ± 4	4,4E1 ± 8	5,80E4 ± 3	**7,59E-04**	
A-CAST-4	12,2401	3,9E1 ± 8	6,0E0 ± 4	4,5E1 ± 8	5,64E4 ± 3	**7,98E-04**	
A-CAST-5	11,7863	2,7E1 ± 8	6,5E0 ± 4	3,3E1 ± 8	6,18E4 ± 3	**5,34E-04**	6,77E-04
A-CAST-6	20,9352	6,2E1 ± 20	1,4E1 ± 4	7,6E1 ± 20	1,28E5 ± 3	**5,94E-04**	
A-CAST-7	21,0476	6,5E1 ± 10	2,3E1 ± 4	8,81E1 ± 10	1,42E5 ± 3	**6,20E-04**	

The spectra of ^{14}C corresponding to A-CAST-*5* sample are shown in Figure 12.
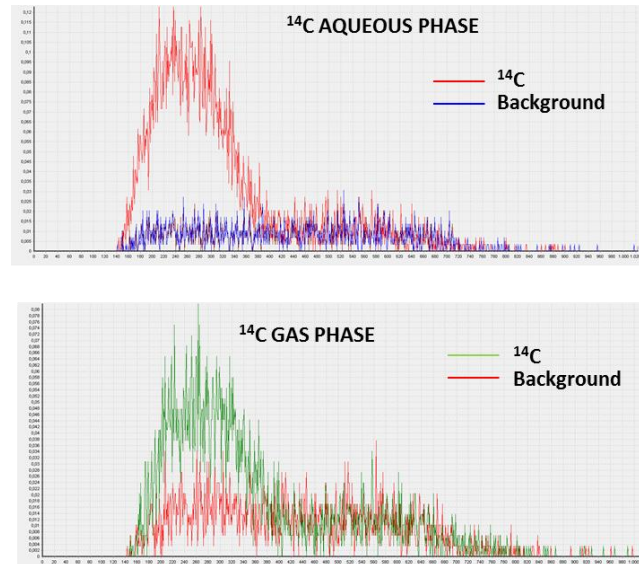

Figure 12. ^{14}C spectra corresponding to the A-CAST-5 stainless steel piece

3.3 *Leaching process and speciation using NaOH pH = 12 as leachant*

3.3.1 ^{14}C and ^{60}Co Results

The ^{60}Co activity of the sample measured by gamma spectrometry, and used for leaching process, is: 6,03E3 Bq/g ± 6%. This datum is in the range of the mean value (5,45E3 ± 9,62E2 Bq/g) obtained from the determinations by dissolution of five pieces next to the sample used for this leaching study. According with these data, it is assumed that the ^{60}Co is homogeneously distributed in the piece.

Therefore, and according with the ratio between ^{14}C and ^{60}Co, the ^{14}C present in the piece of stainless steel would be approximately 4 Bq/g.

The results of ^{14}C and ^{60}Co obtained in the different steps, once the leaching process had finished, are indicated in Table 4. The spectrum of ^{14}C detected in the step corresponding to 15 days is shown in Figure 13.

Table 4. Results of ^{14}C and ^{60}Co in the NaOH pH = 12 leachate (Volume = 120 mL)

Technique	Radionuclide	Day 15 (Bq/mL)	2U (%)	Day 31 (Bq/mL)	2U (%)	Day 59 (Bq/mL)	2U (%)	Day 90 (Bq/mL)	2U (%)	Day 186 (Bq/mL)	2U (%)	Day 281 (Bq/mL)	2U (%)
Combustion Oven + LSC	[14]C	2,39E-02	28	< 4,86E-3	-	< 5,82E-3	-	< 5,84E-3	-	< 5,82E-3	-	< 4,88E-3	-
HPGe Detector	[60]Co	8,25E-02	5	9,04E-03	15	7,71E-03	17	6,07E-03	19	5,25E-03	26	7,82E-3	16

U = Uncertainty
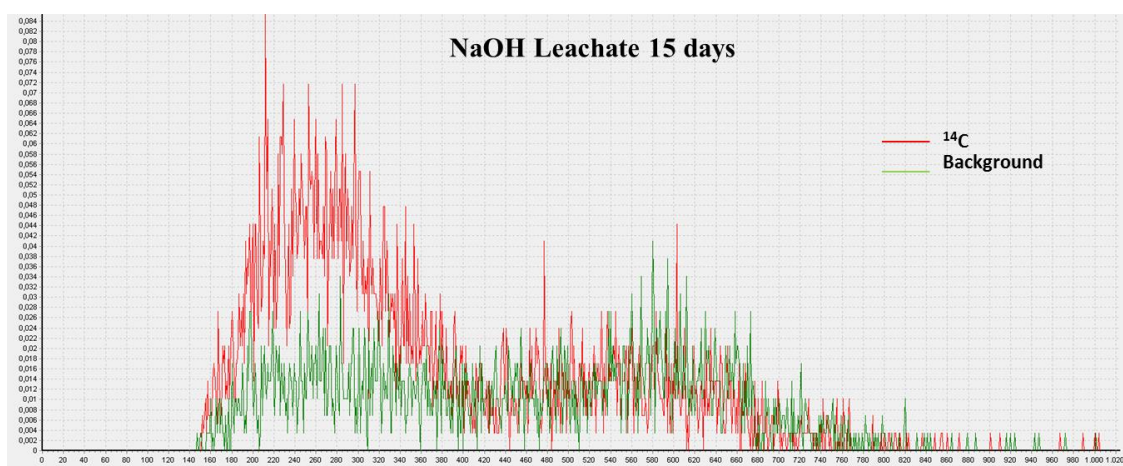
Figure 13. [14]C Spectrum corresponding to the first step of leaching (15 days)

As the weight of the piece is 19.4650 g, in the 120 mL of leachant, if all carbon were leached, it would lead to 6.62E-1 Bq/mL of [14]C. That means that in the first step (15 days) 3,6% of the total ^{14}C in the piece was leached.

Although the value of the first step is higher than Minimum Detectable Activity (MDA), the rest of steps are below MDA. That is to say by this technique at present it is not possible to determine the ^{14}C leachate. In the future and once the procedure to determine ^{14}C in this type of sample is totally developed, all the samples obtained in the leaching process will be sent to the National Center of Accelerators (Sevilla) to analyse them by AMS.

Regarding the results of ^{60}Co, in all steps its activity has been determined. The amount of stainless steel leached has been calculated from ^{60}Co data since it is assumed [60]Co (6,03E3 Bq/g) is homogeneously distributed in the stainless steel piece. To calculate the corrosion rate R_c (nm/year) the equation used is similar to that used by other authors [13,14]:

$$R_c = \frac{A_{SS} \cdot 10^9}{\rho_{SS} \cdot t} \qquad (\textit{Equation } 1)$$

where A_{SS} is the cumulative mass amount of stainless steel leached per unit surface area (g/m^2), ρ is the stainless steel density ($7.9E6$ g/m^3), and t is the test time (years). The surface area of the piece used in the leaching process is $14E-4$ m^2.

The data of the corrosion rate versus the time of leaching are shown in the Figure 14.

The corrosion rate is, approximately, $2.74E2$ nm/year after 281 days and it will be constant in the long run. This value is in a good agreement with the one ($1.00E2$ nm/year) obtained by others authors [15, 16], and therefore the data of ^{60}Co will be adequate to calculate the corrosion rate.
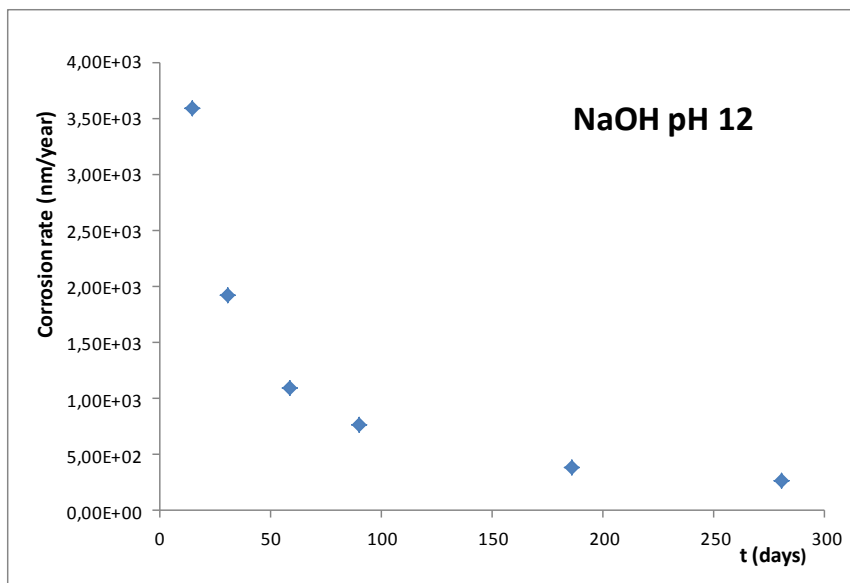

Figure 14. Corrosion rate of stainless steel obtained from cumulative stainless steel leached as a function of time

3.3.2 Organic Carbon Compounds Results

- **Organic Carbon Dissolved Species by Ion Chromatography**

The results of the different leachates, obtained with the column AS-11, with a gradient of concentrations (1.5 mM KOH (0-8 min); 25 mM KOH (8-30 min) and 1.5 mM KOH (30-40 min) and a flow of 1 mL/min, are shown in Table 5.

Table 5. Results obtained in the different steps from NaOH leachates

Compound	Day 15 (mg/L)	Day 31 (mg/L)	Day 59 (mg/L)	Day 90 (mg/L)	Day 186 (mg/L)	Day 281 (mg/L)
Acetate	< 4,0E-2	< 4,0E-2	< 4,0E-2	< 4,0E-2	< 4,0E-2	< 4,0E-2
Formate	< 3,0E-2	< 3,0E-2	< 3,0E-2	< 3,0E-2	< 3,0E-2	< 3,0E-2
Oxalate	< 2,0E-2	< 2,0E-2	< 2,0E-2	< 2,0E-2	< 2,0E-2	< 2,0E-2

As can be abserved all values obtained are lower than Minimum Detectable Concentration, therefore it is not possible to conclude anything.

- **Gas and leachate volatile species by Gas Chromatography-Mass Spectrometry**

The methodology to analyse, in the optimal conditions, CO with a Molsieve 5A column, and alcohols and aldehydes with DB-624UI (L=60 m; ID=0.25 mm and F=1.40 μm), has been developed throughout the project.

The assays to analyse CO have been carried out in isothermal conditions (70ºC) and a Split Flow of 50 mL/min. The calibration curve obtained is shown in Figure 17.

The assays to analyse alcohols and aldehydes have been carried out with the following gradient of temperature: 40ºC (2 min); 1ºC/min to 45ºC (5 min.); 1ºC/min to 50ºC (5 min) and 50ºC (2 min) with a Split 100:1. In this case, the technique of head space sampling was used with 30 seconds of incubation time at 40ºC.

The results of CO and volatile species produced in the different steps of the process are shown in Table 6 and the chromatogram corresponding to 90 days leachates is shown in Figure 15.

Table 6. Results of carbon compounds in NaOH pH =12 leachate (Volume = 120 mL)

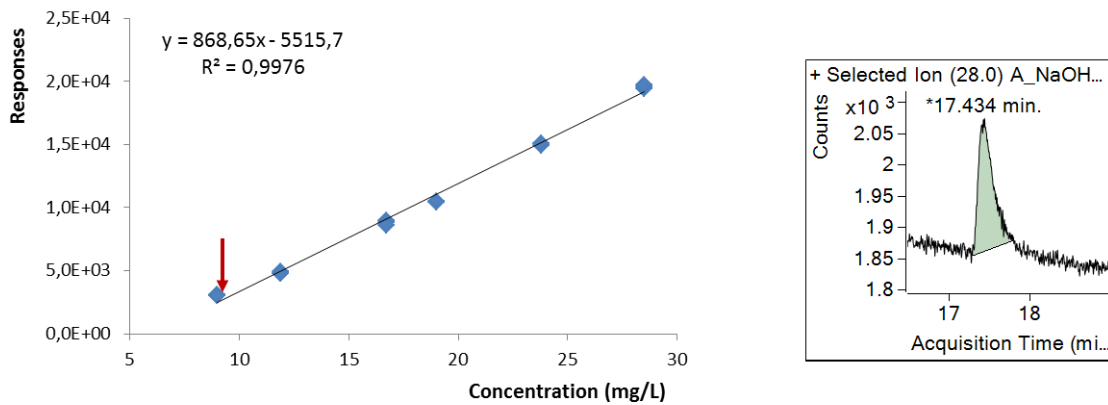| Compound	Day 15 (mg/L)	2U (%)	Day 31 (mg/L)	2U (%)	Day 59 (mg/L)	2U (%)	Day 90 (mg/L)	2U (%)	Day 186 (mg/L)	2U (%)
CO	8,2E0	6	9,6E0	6	7,6E0	6	9,4E0	6	1,6E1	4
Alcohols and Aldehydes	Not detected									

U = Uncertainty

Figure 15. CO Calibration curve and as example a chromatogram corresponding to 90 days

As it can be seen, both alcohols and aldehydes have not been detected in any step of the leaching process. On the other hand, although CO has been detected, it has not been possible to determine the ^{14}C present because the technique to trap the gas samples has not been implemented in our laboratories.

3.4 *Leaching process and speciation using 1M H₃PO₄ as leachant*

3.4.1 ^{14}C and ^{60}Co Results

The ^{60}Co activity of the sample measured by gamma spectrometry and used for leaching process is: 6,32E3 Bq/g ± 6%. This datum is in the range of the mean value obtained as it has been indicated in 3.3.1.

Therefore, and according with the ratio between ^{14}C and ^{60}Co, the ^{14}C present in the piece of stainless steel would be approximately 4 Bq/g.

The results of ^{14}C and ^{60}Co obtained in the different steps, once the leaching process had finished, are indicated in Table 7. The spectrum of ^{14}C detected in the step corresponding to 15 days is shown in Figure 16.

Table 7. Results of ^{14}C and ^{60}Co in the 1M H₃PO₄ leachate (Volume = 120 mL)

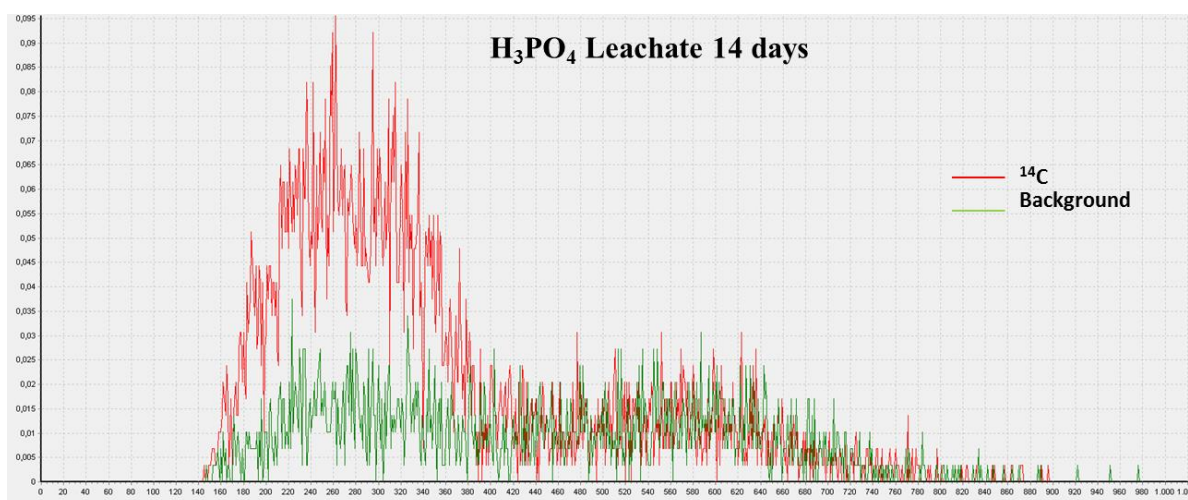| Technique	Radionuclide	Day 14 (Bq/mL)	2U (%)	Day 28 (Bq/mL)	2U (%)	Day 62 (Bq/mL)	2U (%)	Day 93 (Bq/mL)	2U (%)	Day 188 (Bq/mL)	2U (%)	Day 263 (Bq/mL)	2U (%)
Combustion Oven + LSC	^{14}C	3,96E-02	9	< 4,22E-3	-	< 4,92E-3	-	< 4,92E-3	-	< 4,94E-3	-	< 4,22E-3	
HPGe Detector	^{60}Co	4,40E+00	3	9,01E-01	3	1,40E+00	3	7,26E-01	4	4,57E-01	3	1,93E-1	4
U = Uncertainty													

Figure 16. ^{14}C Spectrum corresponding to the first step of leaching (14 days)

As the weight of the piece is 19.5389 g, in the 120 mL of leachant, if all carbon were leached it would lead to 6.97E-1 Bq/mL of [14]C. That means that in the first step (15 days) 5,7% of the total ^{14}C in the piece was leached.

The leaching results of ^{14}C using with NaOH or H_3PO_4 medium could indicate the corrosion behaviour of stainless steels is dominated by the presence of a thin passive film on the surface of the metal [17].

Regarding the results of ^{60}Co, in all steps its activity has been determined. The amount of stainless steel leached has been calculated from ^{60}Co data since it is assumed [60]Co (6,32E3 Bq/g) is homogeneously distributed in the stainless steel piece. The corrosion rate (calculated by equation 1) is, approximately, 2.01E4 nm/year after 263 days, and it will be constant in the long run.

The data of the corrosion rate versus the time of leaching are shown in the Figure 17.
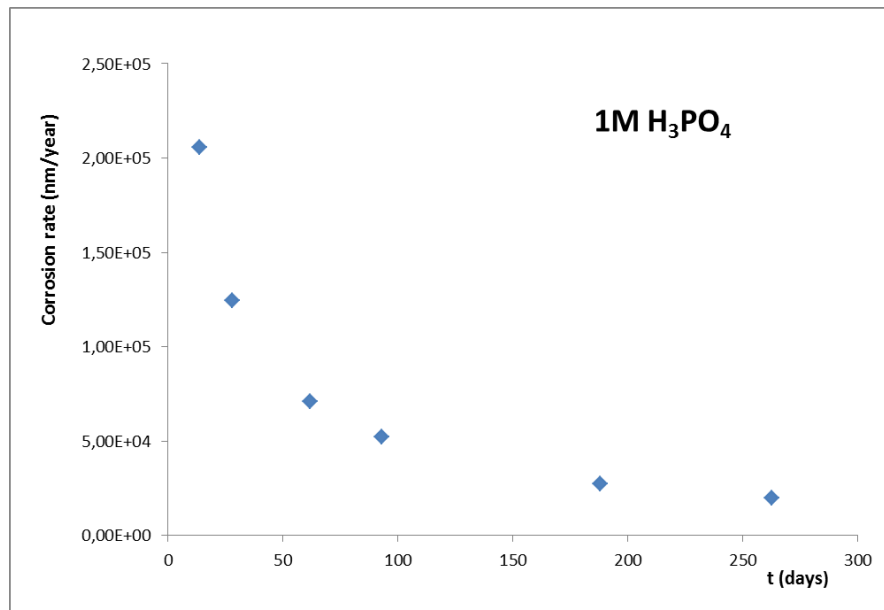

Figure 17. Corrosion rate of stainless steel obtained from cumulative stainless steel leached as a function of time

24

3.4.2 Organic Carbon Compounds Results

- **Organic Carbon Dissolved Species by Ionic Chromatography**

The analyses are performed in the same conditions as mentioned for NaOH leachate. However, in this case it is necessary to prepare a dilution of the sample to be analysed since, due to the high phosphate concentration, this anion interferes in the signal of oxalate. As a consequence of the prepared dilution, although the Minimum Detectable Concentration (MDC) is higher than in the case of NaOH leachate, the oxalate can however be measured since its value is higher than MDC.

The results obtained in the different steps of leaching are indicated in Table 8. Figure 18 shows the chromatogram of the leachate corresponding to 62 days.

Table 8. Results obtained in the different steps from H$_3$PO$_4$ leachates

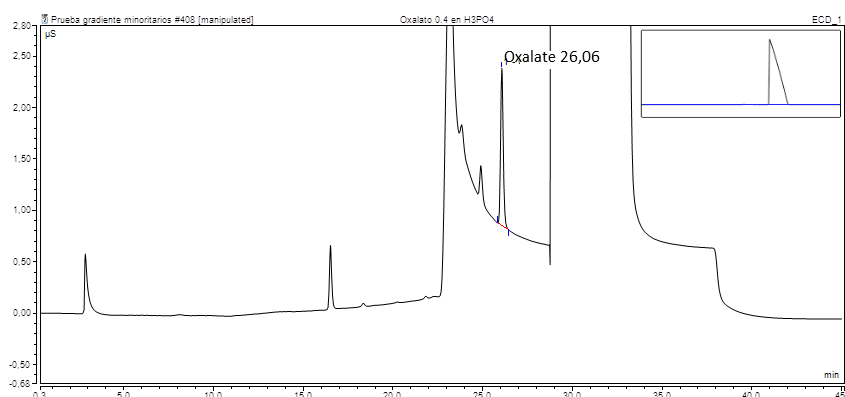| Compound	Day 14 (mg/L)	2U (%)	Day 28 (mg/L)	2U (%)	Day 62 (mg/L)	2U (%)	Day 93 (mg/L)	2U (%)	Day 188 (mg/L)	2U (%)	Day 263 (mg/L)	2U (%)
Acetate	< 5,0E-1	-	< 5,0E-1	-	< 5,0E-1	-	< 5,0E-1	-	< 5,0E-1	-	< 5,0E-1	
Formate	< 5,0E-1	-	< 5,0E-1	-	< 5,0E-1	-	< 5,0E-1	-	< 5,0E-1	-	< 5,0E-1	
Oxalate	6,3E+00	6	6,0E+00	3	1,2E+01	10	7,7E+00	9	4,0E+00	5	6,3E+00	13

U = Uncertainty

Figure 18. Chromatogram of the leachate corresponding to 62 days.

In the first step (14 days) of leaching, the only one where ^{14}C was detected (5,7% of the total ^{14}C), the only carbon compound detected was oxalate (6,3 mg/L).

25

According to the carbon composition data of the 304 Stainless Steel (0,035 and 0,08% C), 3,6% and 1,3%, of the total carbon was leached respectively.

- **Gas and leachate volatile species by Gas Chromatography-Mass Spectrometry**

The analyses are performed in the same conditions as mentioned for NaOH leachate.

The results of CO and volatile species produced in the different steps of the process are shown in Table 9 and the chromatogram corresponding to 62 days is shown in Figure 19.

Table 9. Results of carbon compounds in H_3PO_4 leachate (Volume = 120 mL)

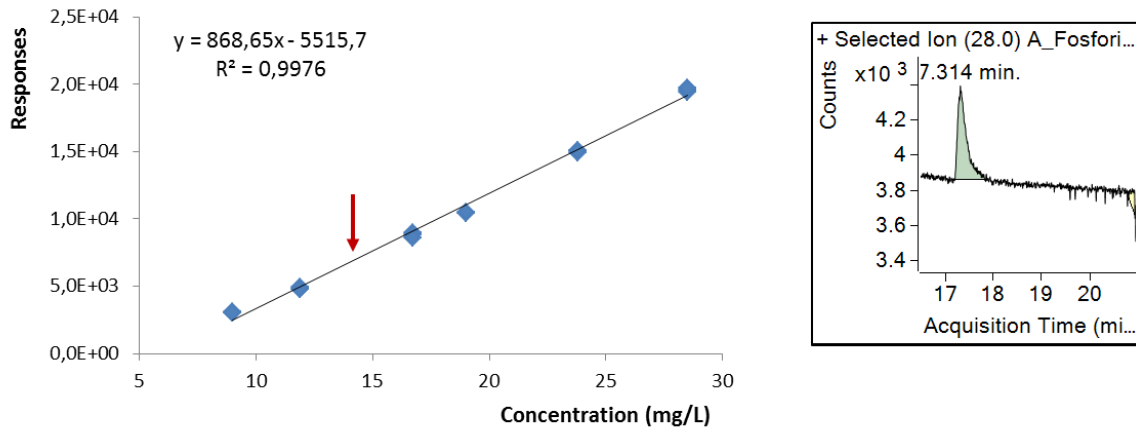| Compound	Day 14 (mg/L)	2U (%)	Day 28 (mg/L)	2U (%)	Day 62 (mg/L)	2U (%)	Day 93 (mg/L)	2U (%)	Day 188 (mg/L)	2U (%)
CO	9,2E0	6	9,8E0	6	1,4E1	4	1,5E1	4	1,5E1	4
Alcohols and Aldehydes					Not detected					

U = Uncertainty

Figure 19. CO Calibration curve and as example a chromatogram corresponding to 62 days

As it can be seen, both alcohols and aldehydes have not been detected in any step of the leaching process. On the other hand, although CO has been detected, it has not been possible to determine the ^{14}C present because the technique to trap the gas samples has not been implemented in our laboratories.

4   Conclusions

- According to the composition of the base material (MB in Figures 8 and 10) and the existence of the inclusions of manganese sulphides and oxides of titanium, as well as the low delta ferrite content, the sample is a low content in Ni, 304 or 316 austenitic stainless steel; this means that the total carbon content in these pieces range between 0,03 % and 0,08 %. As the base material does not have molybdenum, it could be a 304 austenitic stainless steel (AISI 304). To confirm exactly the type of stainless steel a more precise chemical analysis should be made.

- The experimental $^{14}C/^{60}Co$ ratio in the piece is concordant with the ratio obtained with ORIGEN-S code.

- Only the first step of leaching processes presents a value of ^{14}C higher than the detection limit. These values correspond to a 3,6% of total ^{14}C in the case of NaOH and to a 5,7% in the case of H_3PO_4.

- The corrosion rate, calculated by ^{60}Co in the experiments with NaOH, was found to be approximately 2.74E2 nm/year after 281 days and it would be constant in the long run, whereas in the experiments with H_3PO_4 the value obtained was 2.01E4 nm/year after 263 days, and it would be constant in the long run.

- Oxalate has been found as organic carbon dissolved in all steps of the leaching process using H_3PO_4 as leachant.

- Neither alcohols nor aldehydes have been found in the leachates.

- CO has been determined in the gas phase of the leaching process; the methodology to determine ^{14}C in this kind of sample is not implemented in our laboratories.

- It should be indicated that due to the delay with leaching tests, once the process of leaching finished, it has not been possible to carry out either the microstructural characterisation or radiological characterization of the piece.

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