

## **<sup>14</sup>C RELEASE FROM STEELS UNDER AEROBIC CONDITIONS**

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**ABSTRACT.** Radiocarbon (<sup>14</sup>C) is a key radionuclide in the assessment of the safety of underground geological disposal facilities for radioactive wastes, and the understanding of the <sup>14</sup>C behavior in stainless steel may lead to a re-evaluation of the near-surface repository for the disposal of wastes containing this radionuclide in high concentrations. To achieve this objective, leaching experiments were planned for two different scenarios. The first is where the leaching solution, NaOH solution of pH ca. 12 in aerobic conditions, simulates the expected conditions in a cement-based near-surface repository over long time periods. The other one uses an acid solution of 1M H<sub>3</sub>PO<sub>4</sub>, which has been proved as a high efficiency chemical removal agent of <sup>14</sup>C in graphite. The development of both analytical methods and protocols to measure the release of <sup>14</sup>C from the activated steel samples and the speciation in the aqueous and gaseous phase has been undertaken as part of the EC CAST (CArbon-14 Source Term) project. Analytical methods, suitable for identifying and quantifying low molecular weight organic molecules, comprise ion chromatography (IC) and gas chromatography coupled to mass spectrometry (GC-MS); they are described for aqueous and gaseous samples, respectively. In this paper the preparation of leaching experiments to measure the release of <sup>14</sup>C and the results obtained are described.

**KEYWORDS:** <sup>14</sup>C leaching, activated steels, aerobic conditions.

### **INTRODUCTION**

Understanding the mechanisms by which radiocarbon (<sup>14</sup>C) can be released from different types of radioactive wastes under final storage conditions (organic, inorganic, dissolved or gaseous species) can be a crucial aspect in the design of the facilities themselves. The objective of this work is to determine the behavior of <sup>14</sup>C in activated 304 Stainless Steel considering two different scenarios: firstly, one in which the leaching solution, NaOH solution of pH ca. 12, in aerobic conditions, simulates the expected conditions in a cement-based surface repository over long time periods, and secondly, using an acid solution of 1M H<sub>3</sub>PO<sub>4</sub>, which has been proven as a high efficiency chemical removal agent of <sup>14</sup>C in graphite within the EU EURATOM FP7 CARBOWASTE program (Piña et al. 2013).

### **MATERIALS AND METHODS**

#### **Reagents and Standards Solutions**

Ultrapure water: 18.2 MΩcm and total organic carbon (TOC) ≤ 2 ppb

Hydrochloric acid pure, pharma grade, Panreac 37%

Nitric acid technical grade, Panreac 65%

Sodium hydroxide PRS Panreac

Phosphoric acid PRS Panreac 85%

Synthetic air Praxair (21% O<sub>2</sub> and 79% N<sub>2</sub>)

CO standard: 5000 mg/L ± 2%; k = 2

Methanol Fluka GC/MS analysis of volatile organics ≥99.9%

Ethanol Sigma Aldrich G Chromasolv, absolute, for gradient elution ≥99.9%

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Formaldehyde solution ACS reagent, 37wt% in H<sub>2</sub>O, contains 10–15% methanol as stabilizer (to prevent polymerization)

Acetaldehyde Sigma Aldrich ACS reagent, ≥99.5%

Propionaldehyde Sigma Aldrich Reagent grade 97%

KOH Dionex EGCIH eluent generator

Sodium acetate trihydrate Sigma Aldrich PA, >99.5 %

Sodium formate Sigma Aldrich PA, >98%

Sodium oxalate Sigma Aldrich PA, >99.5%

Malonic acid Sigma Aldrich Reagent Pure, >99%

Copper oxide (II), nickel oxide (III), silver vanadate and platinum catalyzers

CO<sub>2</sub> absorber: Oxysolve C-400, Zynsser Analytic

Instagel Plus and Hionic Fluor cocktails, Perkin Elmer

<sup>3</sup>H standard solution supplied by the Ionizing Radiation Metrology Unit (CIEMAT) and <sup>14</sup>C standard solution (DL-Tartaric acid-1,4-<sup>14</sup>C) from Amersham

## Equipment and Analytical Methods

*High-pressure stainless steel reactors* with Teflon inserts (material recommended for its chemical inertness) (Berghof Company).

*Gas chromatograph coupled to a mass spectrometer:* GC-MS instrumentation consisted of Agilent GC serie 7890B/MSD serie 5977A Turbo inert EI with an autosampler CTC Combi-PAL and Headspace. The injector temperature was set at 150°C and injections were made in the split/splitless mode. The GC transfer line was set at 250°C, the MS ion source temperature at 230°C and MS Quadrupole at 150°C. All the mass spectra were collected in scan and sim mode. MassHunter software was used for data acquisition and processing.

The assays to analyze CO were carried out with a Molsieve 5A column, 1 mL of injection volume, in isothermal conditions (70°C) and a Split Flow of 50 mL/min (ratio 43.5:1).

The assays to analyze alcohols and aldehydes were carried out with a DB-624UI (L = 60 m; ID = 0.25 mm and F = 1.40 μm) column, with the following gradient of temperature: 40°C (2 min); 1°C/min to 45°C (5 min.); 1°C/min to 50°C (5 min) and 50°C (2 min) with a Split 100:1. In this case, the technique of headspace sampling was used with 30 sec of incubation time at 40°C.

*Ion chromatograph:* The chromatography system used was Dionex ICS-900 by Thermo Scientific with an AS40 autosampler. Separation was accomplished with a Dionex Ion Pac AS-11-HC anion separator column (4 × 250 mm) and IonPac AG-11-HC guard column (4 × 50 mm). The eluent was KOH at 1 mL/min. The eluent concentration was prepared in situ by an eluent generator by Thermo Scientific Dionex Reagent Free Controller (RFC-30). Suppression was accomplished with a Dionex AERS-500 operated in the auto-suppression recycle mode. The sample size was 50 μL and the separation was performed at room temperature. The AS-11-HC column is specifically designed to resolve a large number of inorganic anions and organic acid anions (short chain carboxylic acids) from a single sample injection in one gradient using hydroxide eluent systems. The detection was

performed with a conductivity detector (digital range: 0–1000 μS/cm). Chromeleon SE Software was used for data acquisition and processing.

The assays to analyze short chain carboxylic acids (acetate, formate and oxalate) were carried out 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.

*OX-500 biological material oxidizer*: an oxidation system for both single and dual radiolabelled samples containing <sup>3</sup>H and <sup>14</sup>C for use in liquid scintillation counting (LSC). This equipment was used for the separation of <sup>14</sup>C in the samples.

*Catalytic furnace Nabertherm (Germany)*: an oxidation system with Ni<sub>2</sub>O<sub>3</sub>/Pt as a catalyzer for the conversion of carbonaceous compounds to CO<sub>2</sub>.

*Liquid scintillation counter*: 1220 Quantulus from PerkinElmer. It is a dedicated environmental counter with proven performance measuring extremely low concentrations of human-made, cosmogenic and other natural radionuclides. Counting efficiency of <sup>14</sup>C for unquenched samples is ≥95%. All samples of <sup>14</sup>C were measured for 300 min.

*Gamma spectrometer*: Gamma spectrometer for high gamma ray measurements. Canberra System BEGe 3830 HPGe detector, typical relative efficiency ≥34%, resolution at 1332 keV: 1.90 keV. The analysis of <sup>60</sup>Co was carried out by gamma spectrometry

### Stainless Steel Samples

The activation history of the stainless steel studied in this paper was obtained via the appropriate authorities from a Spanish nuclear power plant (NPP):

1. José Cabrera NPP was operated from June 30, 1968 to April 30, 2006, a total of 13,818 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 (13,818 days) by the load factor, was 9807.
4. The degree of maximum spent fuel burning was 45,000 MWd/tU and enrichment at least 3.15% in weight of <sup>235</sup>U.
5. Finally, the composition was calculated allowing for decay to a reference date of January 7, 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 <sup>60</sup>Co content, are shown in Table 1. The theoretical value corresponding to <sup>14</sup>C is highlighted.

The samples used in the leaching experiments on activated stainless steel come from reactor internals of José Cabrera NPP, which is being currently dismantled by the Spanish organization ENRESA. The pieces, as they arrived at CIEMAT facilities, and their radiological data, are shown in Figure 1 and Table 2.

The Radiological Protection Department of CIEMAT (RPD) performed wipe tests over the sample surface and detected <sup>60</sup>Co and <sup>241</sup>Am contamination. As a result of this, the RPD requested the decontamination of the sample before giving permission to cut the fragments into smaller pieces

Table 1 Radiochemical composition of 304 Stainless Steel as a fraction of  $^{60}\text{Co}$  (modeled values with Origen-S for reference date 01/07/2011).

Isotope	/ $^{60}\text{Co}$	Isotope	/ $^{60}\text{Co}$	Isotope	/ $^{60}\text{Co}$
$^3\text{H}$	1.45E-03	$^{154}\text{Eu}$	1.13E-04	$^{93}\text{Mo}$	1.29E-05
$^{36}\text{Cl}$	6.42E-06	$^{178\text{m}}\text{Hf}$	5.87E-25	$^{125}\text{Sb}$	1.85E-08
$^{41}\text{Ca}$	5.56E-08	$^{90}\text{Sr}$	1.59E-06	$^{135}\text{Cs}$	4.09E-11
$^{54}\text{Mn}$	9.39E-03	$^{99}\text{Tc}$	4.64E-07	$^{155}\text{Eu}$	5.14E-06
$^{55}\text{Fe}$	1.13E00	$^{133}\text{Ba}$	2.58E-08	$^{233}\text{U}$	3.25E-15
$^{59}\text{Ni}$	2.36E-03	$^{134}\text{Cs}$	2.21E-04	$^{238}\text{Pu}$	1.95E-09
$^{60}\text{Co}$	1.00E00	$^{137}\text{Cs}$	1.89E-06	$^{239}\text{Pu}$	1.50E-07
$^{63}\text{Ni}$	2.57E-01	$^{151}\text{Sm}$	5.92E-06	$^{241}\text{Am}$	1.43E-09
$^{94}\text{Nb}$	9.13E-06	$^{166\text{m}}\text{Ho}$	2.92E-06	$^{244}\text{Cm}$	8.10E-14
$^{110\text{m}}\text{Ag}$	1.82E-05	$^{14}\text{C}$	6.77E-04		
$^{152}\text{Eu}$	2.66E-04	$^{39}\text{Ar}$	1.39E-06		



Figure 1 Fragments of stainless steel.

Table 2 Radiological data from the interior of the José Cabrera NPP reactor (reference date 15/01/2014).

Samples	Contact dose rate (mSv/hr)	1-m dose rate (mSv/hr)	$^{60}\text{Co}$ (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

compatible with dimensions of the leaching containers. The decontamination was performed by dipping the piece in a solution with 2% EDTA in an ultrasonic cleaning bath (35 KHz) for 15 min. The cutting of the pieces was carried out with a cutting machine in a glove box using a silicon carbide disc. A coolant was used to minimize the alteration of the structure of the material in the cutting area. The samples were cut and identified in three directions. 11 pieces were obtained for use in dissolution experiments in order to characterize the pieces, and 4 pieces for leaching experiments. The contact dose rate ranged between 25 and 60 μSv/hr.

### Radiological Characterization of Initial Sample

In order to characterize five stainless steel pieces, first it was necessary to dissolve them. The process is shown in Figure 2.

The dissolution of the samples was carried out with a mixture of HCl and HNO<sub>3</sub> acids in a ratio 5:1 at 100°C. The solution was purged with N<sub>2</sub> and stirred for four hours, in this step the inorganic carbonaceous fraction was released as CO<sub>2</sub> and trapped in washing bottles number 1, 2, and 3 containing 5M NaOH. Other carbonaceous compounds such as CO and CH<sub>4</sub>, released during the acid stripping, were oxidized in a catalytic furnace to CO<sub>2</sub> (using nickel oxide (III)/platinum as a catalyzer and at 200°C). This CO<sub>2</sub> was trapped in washing bottles number 4 and 5, also containing 5M NaOH. Bottle number 1 was discarded due to its acidification and the rest of the washing bottles were collected; in this case, 3 mL of sample was mixed with 18 mL of Hionic Fluor cocktail and <sup>14</sup>C analyzed by LSC. To complete the characterization of the initial sample, an aliquot of the solution obtained was introduced in the OX-500 oxidizer, where the sample was combusted to 900°C in an oxygen stream to constituent water vapor and carbon dioxide; using this process achieved physical separation of <sup>3</sup>H and <sup>14</sup>C radionuclides into two separate counting vials. The gases formed passed through a catalyst bed (copper oxide [II], platinum and silver vanadate), where the carbon

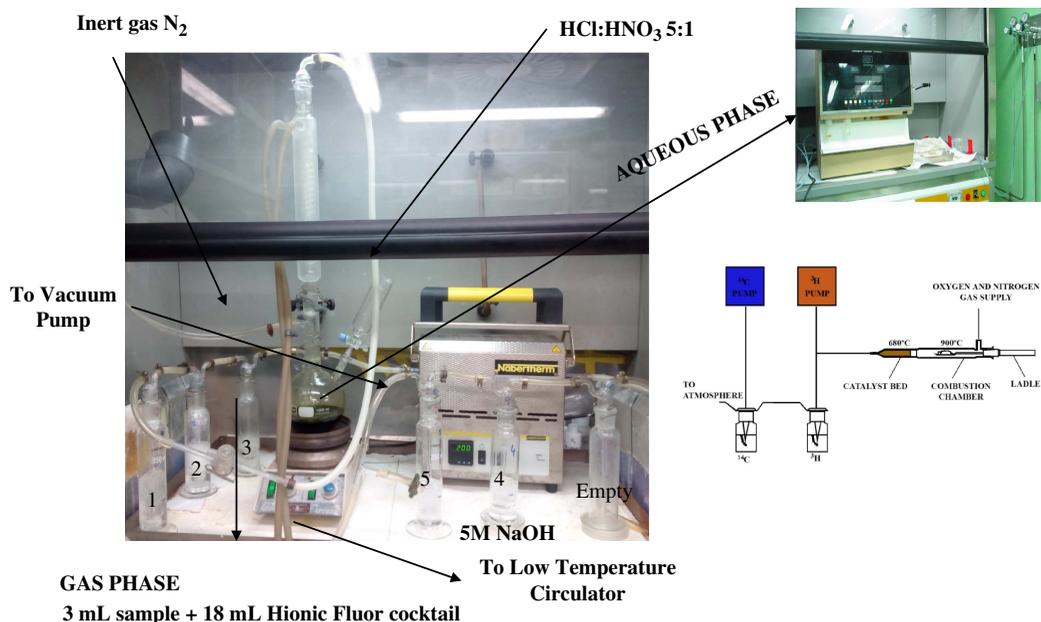


Figure 2 Methodology for the initial steel characterization.

compounds were converted to CO<sub>2</sub> that was absorbed in Oxysolve C-400. Instagel Plus was added as the <sup>14</sup>C liquid scintillator. Finally, the cocktail vial obtained was analyzed by LSC. The solution obtained in the process was measured by gamma spectrometry to determine the activity of <sup>60</sup>Co present in the initial sample.

### Leaching Process

After cutting the sample pieces, the leaching process started with two samples and was performed in high pressure stainless steel reactors with Teflon inserts at room temperature (Figure 3).



Figure 3 High-pressure steel reactors.

The leaching test procedure was based on the standard procedure ISO 6961 (International Organization for Standardization, 1982(E)) and was carried out in the following way:

1. Before using the containers, they were cleaned with ultrapure water and the stainless steel pieces were cleaned with acetone and ultrapure water.
2. The value of the surface area exposed to the leachant was  $14\text{E-}4\text{m}^2$ . The leach tests were conducted at room temperature and the losses of leachant by vaporization were insignificant.
3. The specimen was suspended in 120 mL of leachant by means of a Teflon thread and surrounded by at least 1 cm of liquid in all directions.
4. NaOH pH = 12 and 1M H<sub>3</sub>PO<sub>4</sub> were used as leachants. A synthetic mixture of N<sub>2</sub> and O<sub>2</sub> (21% oxygen, 79% nitrogen) was introduced in the containers to ensure that the leaching process takes place under aerobic conditions. The pressure vessels were 1 bar.
5. The gas and the leachate were replaced after 14, 28, 56, 90, 180, and 280 days. After each period, first of all the gas samples (volatile species) were collected by means of a gas tight syringe and immediately injected into the GC-MS system.
6. After completing the previous step, the containers were opened, the specimens were removed from the leachant, and the leachates were transferred to a bottle, which were labelled and stored for later analysis.

7. After storing the leachates, the Teflon inserts were rinsed with ultrapure water, refilled with fresh leachant, the specimens immersed in the liquid and after purging with synthetic air, the reactors were closed.

The leachate samples corresponding to all steps were analyzed for <sup>14</sup>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.

## RESULTS AND DISCUSSION

### Radiological Characterization of the Initial Sample

The results of <sup>14</sup>C obtained in the aqueous and gas phase and the total activity of <sup>14</sup>C, corresponding to 5 pieces, are shown in Table 3. It is observed that <sup>14</sup>C practically remains in the aqueous phase as organic carbon, which is in agreement with the studies carried out by other authors (Hardy et al. 1996; Deng et al. 1997), who proposed a mechanism of hydrocarbon formation through processes similar to Fischer-Tropsch synthesis.

The solutions of the samples (aqueous phases) were analyzed by gamma spectrometry and the values of the activities of <sup>60</sup>Co are shown in Table 3. The ratio between <sup>14</sup>C and <sup>60</sup>Co was determined for all samples.

The expanded uncertainty, U, of the results is  $k \cdot u_c$ , where  $k = 2$  is the coverage factor that defines an interval having a level of confidence of approximately 95%, and  $u_c$  is the combined uncertainty obtained by the law of propagation of uncertainty.

### Leaching Process and Speciation Using NaOH pH = 12 as Leachant

#### <sup>14</sup>C and <sup>60</sup>Co Results

The <sup>60</sup>Co activity of the sample A-CAST-12 measured by gamma spectrometry, and used for the leaching process, was  $6.03E03 \text{ Bq/g} \pm 6\%$ . This measurement was in the range of the mean value ( $5.45E03 \pm 9.62E2 \text{ Bq/g}$ ) obtained from the determinations by dissolution of five pieces adjacent to the sample used for this leaching study. In accordance with these data, it was assumed that the <sup>60</sup>Co was homogeneously distributed in the piece. Using the ratio between <sup>14</sup>C and <sup>60</sup>Co, the <sup>14</sup>C present in the piece of stainless steel was estimated to be approximately 4 Bq/g.

The results of <sup>14</sup>C and <sup>60</sup>Co obtained in the different steps, once the leaching process finished, are indicated in Table 4.

As the sample weight was 19.4650 g, in 120 mL of leachant, if all carbon were leached, this would lead to  $6.62E-01 \text{ Bq/mL}$  of <sup>14</sup>C. This means that, in the first step (15 days), 3.6% of the total <sup>14</sup>C in the piece was leached. Although the value of the first step was higher than limit of quantification (LOQ), the rest of steps were below LOQ.

Results for <sup>60</sup>Co were determined for all steps. The amount of stainless steel leached was calculated from <sup>60</sup>Co data, since it was assumed <sup>60</sup>Co ( $6.03E3 \text{ Bq/g}$ ) was homogeneously distributed in the stainless steel piece and that the amount of <sup>60</sup>Co present could provide information regarding the amount of <sup>14</sup>C present. To calculate the corrosion rate  $R_c$  (nm/year), an equation used is similar to that used by other authors (Sakuragi et al. 2016a, 2016b):

$$R_c = \frac{A_{ss} \cdot 10^9}{\rho_{ss} \cdot t} \quad (1)$$

Table 3 Results of  $^{14}\text{C}$  and  $^{60}\text{Co}$  of the stainless steel pieces (reference date April 16, 2017).

Reference	Weight (g)	$^{14}\text{C}$ aqueous phase Bq $\pm$ U (%)	$^{14}\text{C}$ gas phase Bq $\pm$ U (%)	$^{14}\text{C}$ total Bq $\pm$ U (%)	$^{60}\text{Co}$ total Bq $\pm$ U (%)	Experimental $^{14}\text{C}/^{60}\text{Co}$	Experimental $^{14}\text{C}/^{60}\text{Co} \pm$ variation coefficient (%)
A-CAST-3	12.7745	3.8E01 $\pm$ 8	6.0E00 $\pm$ 4	4.4E01 $\pm$ 8	5.80E04 $\pm$ 3	7.59E-04	6.61E-04 $\pm$ 17
A-CAST-4	12.2401	3.9E01 $\pm$ 8	6.0E00 $\pm$ 4	4.5E01 $\pm$ 8	5.64E04 $\pm$ 3	7.98E-04	
A-CAST-5	11.7863	2.7E01 $\pm$ 8	6.5E00 $\pm$ 4	3.3E01 $\pm$ 8	6.18E04 $\pm$ 3	5.34E-04	
A-CAST-6	20.9352	6.2E01 $\pm$ 20	1.4E01 $\pm$ 4	7.6E01 $\pm$ 20	1.28E05 $\pm$ 3	5.94E-04	
A-CAST-7	21.0476	6.5E01 $\pm$ 10	2.3E01 $\pm$ 4	8.8E01 $\pm$ 10	1.42E05 $\pm$ 3	6.20E-04	

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

Technique	Radionuclide	Day 15 (Bq/mL) $\pm$ U (%)	Day 31 (Bq/mL) $\pm$ U (%)	Day 59 (Bq/mL) $\pm$ U (%)	Day 90 (Bq/mL) $\pm$ U (%)	Day 186 (Bq/mL) $\pm$ U (%)	Day 281 (Bq/mL) $\pm$ U (%)
Combustion oven + LSC	$^{14}\text{C}$	2.39E-02 $\pm$ 28	< 4.86E-03	< 5.82E-03	< 5.84E-03	< 5.82E-03	< 4.88E-03
HPGe detector	$^{60}\text{Co}$	8.25E-02 $\pm$ 5	9.04E-03 $\pm$ 15	7.71E-03 $\pm$ 17	6.07E-03 $\pm$ 19	5.25E-03 $\pm$ 26	7.82E-03 $\pm$ 16

where  $A_{ss}$  is the cumulative mass amount of stainless steel leached per unit surface area ( $\text{g/m}^2$ ),  $\rho$  is the stainless steel density ( $7.9\text{E}06 \text{ g/m}^3$ ), and  $t$  is the test time (years). The surface area of the sample used in the leaching process was  $14\text{E}-04 \text{ m}^2$ . The data for the corrosion rate obtained from cumulative stainless steel leaching versus the time of leaching are shown in the Figure 4.

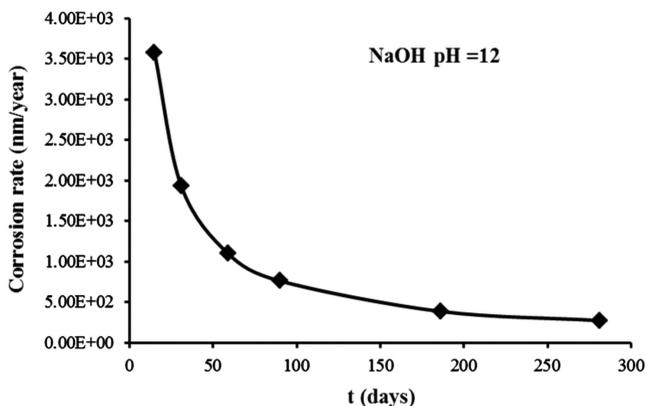


Figure 4 Corrosion rate of stainless steel leached as a function of time.

The corrosion rate was estimated to be approximately 274 nm/year after 281 days, and can be considered constant over time. This value is in a good agreement with a determination (100 nm/year) obtained by other authors (Blackwood 2002; Kursten 2014), and therefore the level of <sup>60</sup>Co will be adequate to calculate the corrosion rate. On the other hand, this value (274 nm/year) obtained in aerobic conditions is higher than the one obtained by Sakuragi et al. (2016a) (0.4 nm/year) using the hydrogen measurement under the anaerobic condition.

### Organic Carbon Compounds Results

- *Organic carbon dissolved species by ion chromatography*

The results of the different leachates are shown in Table 5.

As can be observed, all values are less than LOQ, therefore it is not possible to draw any conclusions.

- *Gas and leachate volatile species by gas chromatography-mass spectrometry*

The CO results produced in the different steps of the process are shown in Table 6. Alcohols and aldehydes were not detected in any step of the leaching process.

### Leaching Process and Speciation Using 1M H<sub>3</sub>PO<sub>4</sub> as Leachant

#### <sup>14</sup>C and <sup>60</sup>Co Results

The <sup>60</sup>Co activity of the sample A-CAST-13 measured by gamma spectrometry, and used for the leaching process, was  $6.32\text{E}03 \text{ Bq/g} \pm 6\%$ . According with the ratio between <sup>14</sup>C and <sup>60</sup>Co, the <sup>14</sup>C present in the piece of stainless steel would be approximately 4 Bq/g.

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-02	<4.0E-02	<4.0E-02	<4.0E-02	<4.0E-02	<4.0E-02
Formate	<3.0E-02	<3.0E-02	<3.0E-02	<3.0E-02	<3.0E-02	<3.0E-02
Oxalate	<2.0E-02	<2.0E-02	<2.0E-02	<2.0E-02	<2.0E-02	<2.0E-02

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

Compound	Day 15 (mg/L) ± U (%)	Day 31 (mg/L) ± U (%)	Day 59 (mg/L) ± U (%)	Day 90 (mg/L) ± U (%)	Day 186 (mg/L) ± U (%)
CO	8.2E00 ± 6	9.6E00 ± 6	7.6E00 ± 6	9.4E00 ± 6	1.6E01 ± 4

The results of  $^{14}\text{C}$  and  $^{60}\text{Co}$  obtained in the different steps, after the experimental leaching process was finished, are indicated in Table 7. On the other hand, although CO was detected, it was not possible to determine  $^{14}\text{C}$  present because a technique to trap the gas samples was not implemented in our laboratories.

As the weight of the piece was 19.5389 g, in the 120 mL of leachant, if all carbon were leached, it would lead to 6.97E-01 Bq/mL of  $^{14}\text{C}$ . This means that in the first step (15 days), 5.7% of the total  $^{14}\text{C}$  in the piece was leached.

The values obtained for the leaching of  $^{14}\text{C}$  using both a NaOH or a  $\text{H}_3\text{PO}_4$  medium were above the LOQ only at the beginning of the leaching process, and it could be a consequence of  $^{14}\text{C}$  distribution in the piece. According to some authors (Sakuragi et al. 2016c; Ueda et al. 2017), in the case of Zircaloy,  $^{14}\text{C}$  specific activity in the external oxide layer that might be activated from nitrogen impurity ( $^{14}\text{N}(\text{n},\text{p})^{14}\text{C}$  reaction) and oxygen ( $^{17}\text{O}(\text{n}, \alpha)^{14}\text{C}$  reaction) was approximately 3 times higher than that in base Zircaloy.

As before, the results of  $^{60}\text{Co}$  were determined. The amount of stainless steel leached was calculated from  $^{60}\text{Co}$  data (6.32E03 Bq/g). The corrosion rate (calculated by Equation 1) is approximately 2.01E04 nm/year after 263 days, and this is expected to be constant over time. The data of the corrosion rate obtained from cumulative stainless steel leaching versus the time of leaching are shown in the Figure 5.

The corrosion rate both in NaOH and  $\text{H}_3\text{PO}_4$  aerobic conditions decreases with time to a low value, as observed in Figures 4 and 5. This behavior is similar to the one observed in anaerobic conditions (Smart et al. 2004) where there is a built-up a layer of corrosion product that controls the corrosion rate evolution.

### Organic Carbon Compounds

- *Organic carbon dissolved species by ion chromatography*

The analyses were performed in the same conditions as mentioned for NaOH leachate. However, in this case it was necessary to dilute the sample to be analyzed due to a high phosphate concentration, which interfered in the signal of oxalate. As a consequence of this prepared

Table 7 Results of  $^{14}\text{C}$  and  $^{60}\text{Co}$  in the 1M  $\text{H}_3\text{PO}_4$  leachate (volume = 120 mL).

Technique	Radionuclide	Day 14 (Bq/mL) $\pm$ U (%)	Day 28 (Bq/mL) $\pm$ U (%)	Day 62 (Bq/mL) $\pm$ U (%)	Day 93 (Bq/mL) $\pm$ U (%)	Day 188 (Bq/mL) $\pm$ U (%)	Day 263 (Bq/mL) $\pm$ U (%)
Combustion oven + LSC	$^{14}\text{C}$	3.96E-02 $\pm$ 9	<4.22E-03	<4.92E-03	<4.92E-03	<4.94E-03	<4.22E-03
HPGe detector	$^{60}\text{Co}$	4.40E00 $\pm$ 3	9.01E-01 $\pm$ 3	1.40E00 $\pm$ 3	7.26E-01 $\pm$ 4	4.57E-01 $\pm$ 3	1.93E-01 $\pm$ 4

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

Compound	Day 14 (mg/L) $\pm$ U (%)	Day 28 (mg/L) $\pm$ U (%)	Day 62 (mg/L) $\pm$ U (%)	Day 93 (mg/L) $\pm$ U (%)	Day 188 (mg/L) $\pm$ U (%)	Day 263 (mg/L) $\pm$ U (%)
Acetate	<5.0E-01	<5.0E-01	<5.0E-01	<5.0E-01	<5.0E-01	<5.0E-01
Formate	<5.0E-01	<5.0E-01	<5.0E-01	<5.0E-01	<5.0E-01	<5.0E-01
Oxalate	6.3E00 $\pm$ 6	6.0E00 $\pm$ 3	1.2E01 $\pm$ 10	7.7E00 $\pm$ 9	4.0E00 $\pm$ 5	6.3E00 $\pm$ 13

Table 9 Results of carbon compounds in  $\text{H}_3\text{PO}_4$  leachate (volume = 120 mL).

Compound	Day 14 (mg/L) $\pm$ U (%)	Day 28 (mg/L) $\pm$ U (%)	Day 62 (mg/L) $\pm$ U (%)	Day 93 (mg/L) $\pm$ U (%)	Day 188 (mg/L) $\pm$ U (%)
CO	9.2E00 $\pm$ 6	9.8E00 $\pm$ 6	1.4E01 $\pm$ 4	1.5E01 $\pm$ 4	1.5E01 $\pm$ 4

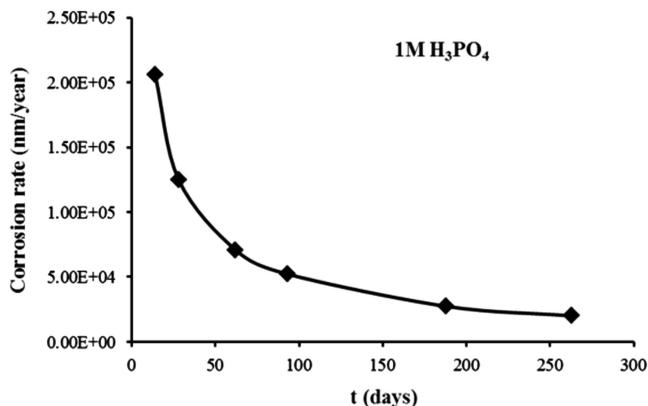


Figure 5 Corrosion rate of stainless steel obtained as a function of time.

dilution, although the LOQ was higher than in the case of NaOH leachate, the oxalate could be measured, since its value was above the LOQ. The results obtained in the different steps of leaching are indicated in Table 8.

In the first step (14 days) of leaching, oxalate was the compound where  $^{14}\text{C}$  was detected (5.7% of the total  $^{14}\text{C}$ ).

According to the carbon composition data of the 304 Stainless Steel (either 0.035 % C max. or 0.08 % C max.), either 3.6% max. or 1.3% max. of the total carbon was leached respectively.

- *Gas and leachate volatile species by gas chromatography-mass spectrometry*

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

The results of CO produced in the different steps of the process are shown in Table 9. Alcohols and aldehydes were not detected in any step of the leaching process. On the other hand, although CO was detected, it was not possible to determine the  $^{14}\text{C}$  present, because the technique to trap the gas samples was not implemented in our laboratories.

## CONCLUSIONS

1. Only the first step of leaching processes presents a value of  $^{14}\text{C}$  higher than the LOQ. These values correspond to a 3.6% of total  $^{14}\text{C}$  in the case of NaOH and to a 5.7% in the case of  $\text{H}_3\text{PO}_4$ .
2. The corrosion rate, calculated by  $^{60}\text{Co}$  in the experiments with NaOH, was found to be approximately 2.74E02 nm/year after 281 days, whereas in the experiments with  $\text{H}_3\text{PO}_4$  the value obtained was 2.01E04 nm/year after 263 days. Both corrosion rates may be constant over time.
3. Oxalate was found as organic carbon dissolved in all steps of the leaching process using  $\text{H}_3\text{PO}_4$  as leachant.
4. Neither alcohols nor aldehydes were found in the leachates.
5. CO was determined in the gas phase of the leaching process; the methodology to determine  $^{14}\text{C}$  in this kind of sample was not implemented in our laboratories.

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## REFERENCES

- Blackwood DJ, Gould LJ, Naish CC, Porter FM, Rance AP, Sharland SM, Smart NR, Thomas MI, Yates T. 2002. The localised corrosion of carbon steel and stainless steel in simulated repository environments. *AEA Technology Report AEAT/ERRA-0318*.
- Deng B, Campbell TJ, Burris DR. 1997. Hydrocarbon formation in metallic iron/water systems. *Environmental Science and Technology* 31:1185–90.
- Hardy LI, Gillham RW. 1996. Formation of hydrocarbons from the reduction of aqueous CO<sub>2</sub> by zero-valent iron. *Environmental Science and Technology* 30:57–65.
- International Organization for Standardization. 1982 (E). *Long-Term Leach Testing of Solidified Radioactive Waste Forms*. ISO 6961.
- Kursten B. 2014. Uniform corrosion rate data of carbon steel in cementitious environments relevant to the Supercontainer design. State-of-the-art report as of December 2013, SCK•CEN Report SCK•CEN-ER-94.
- Piña G, Arsene C, Capone M, Gascón JL, Jones A, McDermott L, Vulpius D. 2013. Decontamination factors by decontamination agents under normal pressure. *Carbowaste Deliverable D-4.3.5*.
- Sakuragi T, Yoshida S, Kato O, Tateishi Y. 2016a. Study of stainless steel corrosion by hydrogen measurement under deoxygenated, low-temperature and basic repository conditions. *Progress in Nuclear Energy* 87:26–31.
- Sakuragi T, Yoshida S, Kinugasa J, Kato O, Tateishi Y. 2016b. Corrosion kinetics of stainless steel by hydrogen measurement under deep geological repository condition. *Proceedings of Waste Management Conference*.
- Sakuragi T, Yamashita Y, Akagib M, Takahashi R. 2016c. Carbon 14 distribution in irradiated BWR fuel cladding and released Carbon 14 after aqueous immersion of 6.5 years. *Procedia Chemistry* 21:341–8.
- Smart NR, Blackwood DJ, Marsh GP, Naish CC, O'Brien TM, Rance AP, Thomas MI. 2004. The anaerobic corrosion of carbon and stainless steels in simulated cementitious repository environments: a summary review of Nirex research. *AEA Technology Report AEAT/ERRA-0313*.
- Ueda H, Sakuragi T, Fujii N and Owada H. 2017. Evaluation of Carbon-14 release from irradiated zircaloy fuel cladding through a long-term static leaching test. *6th East Asia Forum on Radwaste Management Conference*.