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CArbon-14 Source Term

CAST

Selected analytical procedures at Armines/Subatech (D2.4)

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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 in underground geological disposal facilities. The project focuses on the release of carbon-14 as dissolved and gaseous species from irradiated metallic materials (steels, Zircaloys), irradiated graphite and from ion-exchange resins.

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 release rate of carbon-14 from the corrosion of irradiated steels and Zircaloys and from the leaching of ion-exchange resins and irradiated graphites under simulated 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

Selected analytical approach at Armines/Subatech (D2.4)

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Executive Summary

This deliverable reports analytical methods proposed by SUBATECH/ARMINES for the characterization of organic acids, in particular carboxylic acids species, which may be released from irradiated stainless steel [Sasoh, 2008; Takahashi et al., 2014]. Such characterizations will be performed thanks to the combination of Ion Chromatography IC and Liquid Scintillation Counting LSC. Despite the fact that the detection limit of IC is not sensitive enough for the detection of the very low concentrations of small carboxylic acids in the leaching solution, this technique will be used for the development of a separation and fractionation technique for the carboxylic acids present in the leachates. Collected carboxylic acids will be transferred to the LSC system for the quantification of ^{14}C activity collected in the fractions. LSC will be used at SUBATECH for the detection of ^{14}C compounds activities**.** For extremely low activity level of ^{14}C collected fractions, signal intensity of ^{14}C could not be distinguished from the LSC background noise; measurement of ^{14}C in the collected fractions using accelerator mass spectrometry (AMS) by an external laboratory will be performed.

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1 Objective of the work

One of the challenges of the CAST project is to identify the speciation of ^{14}C species (organic fraction) released from radioactive waste materials in environmental storage conditions relevant to waste packaging and disposal in underground geological disposal facilities (reducing conditions, alkaline media, groundwater composition). Task 2.2 aims at the development of analytical methods for measuring organic ^{14}C speciation released from irradiated steels during leaching experiments, in particular carboxylic acids species [Sasoh, 2008; Takahashi et al., 2014]. This task is in interaction with the corresponding Task 3.2 of WP3 (Zircaloy).

The objective of SUBATECH is to develop a simple and adapted method for the extraction of the main water soluble radionuclides in the leaching solution using ion exchange resins. The resin treatment stage has several aims: i) the reduction of total activity in leachates to avoid further dilution of the leaching solutions due to activity acceptance limits of the laboratories; ii) get clean and non-contaminated leachates in terms of absence of radionuclides which would limit analytical devices contamination, especially for AMS analyses of ultra-low ^{14}C concentrations; iii) the removal of beta emitter radionuclides which cannot be distinguished from ^{14}C activity by LSC. Indeed, soluble radionuclides like as Sb-125 are negatively charged in the hydroxides or oxo-anions forms and thus may appear in the collected fractions, preventing an accurate quantification of ^{14}C using LSC. This is why a selective extraction of interfering beta emitter radionuclides before the chromatographic separation is required.

Figure 1 shows the outline of the general approach for the characterization of organic ^{14}C.

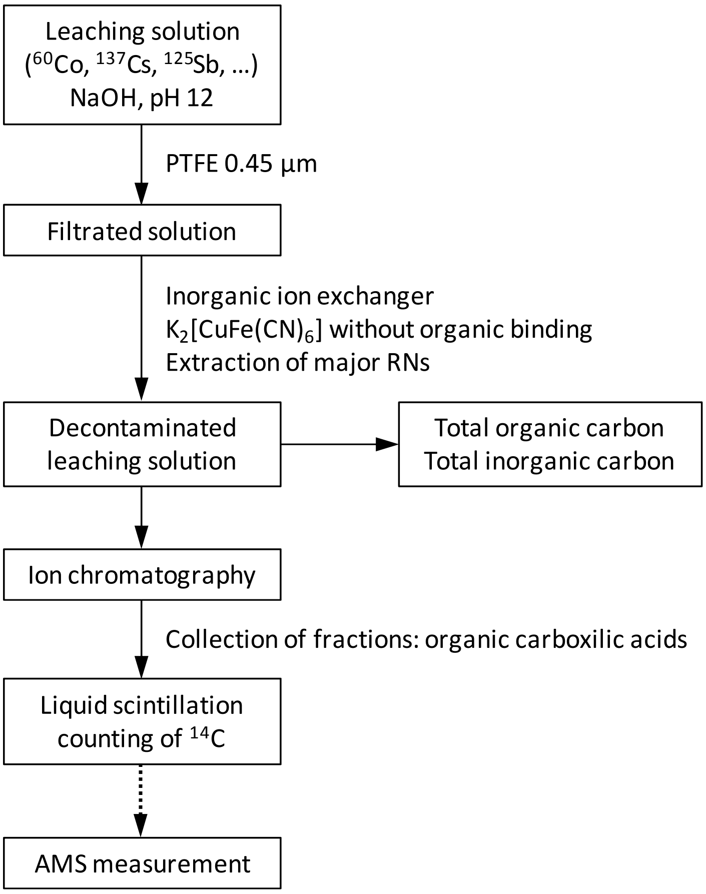

Figure 1: Outline of the general approach

2 Analytical methods

2.1 *Composition of the leaching solution*

The chemical composition of the leaching solution depends on the origin and the nature of the leached irradiated materials. Besides ^{14}C target molecules, the leaching solution contains activation products (e.g. ^{60}Co, ^{63}Ni, ^{55}Fe…), fission products (e.g. ^{137}Cs, ^{99}Tc, ^{90}Sr ^{125}Sb…), and actinides (e.g. ^{235}U, ^{239}Pu), which are present at a significant activity level compared to ^{14}C [Yamaguchi et al., 1999].

Among the cited radionuclides, actinides precipitated or coprecipitated readily in the presence of hydroxides, or other radionuclides as ^{106}Ru and ^{106}Rh, are in a solid state according to Eh-pH diagrams. Therefore their elimination will be ensured during the filtration of the leaching solution. Nevertheless, ionized radionuclides such as ^{137}Cs, ^{134}Cs, ^{125}Sb, ^{60}Co, ^{59}Ni, ^{63}Ni, ^{55}Fe, ^{90}Sr are expected to be present in the filtered leaching solution.

2.2 *Resin treatment: removal of caesium, cobalt, nickel, Iron, strontium and antimony*

Cesium-137 is the main contributor to the total activity of the leaching solution. Its removal can be ensured using a selective extraction method.

In the literature [Collins et al., 1995], potassium hexacyanocobalt (II) ferrate (II) $K_2[CoFe(CN)_6]$ (KCFC), potassium hexacyanonickel (II) ferrate (II) $K_2[NiFe(CN)_6]$ and potassium hexacyanocopper (II) ferrate (II) $K_2[CuFe(CN)_6]$ are good candidates for the fixation of Cs in alkaline media. Extraction experiments of Cs in solution (0.2 – 180 mg/L) give high and homogeneous distribution coefficient of $K_2[CoFe(CN)_6]$ of about 35,000 mL/g compared to resorcinol/formaldehyde resin (SRR) decreasing from 560 to 75 mL/g and crystalline silicotitanate resin (CST) with stable coefficient of about 800 mL/g. As the method aims at measuring the speciation of organic compounds, the chemical conditions during the treatment should not be strongly modified. This justifies the use of KCFC-type resins. The exchange reaction is as follows:

$$K_2[CoFe(CN)_6]_{(sd)} + 2\ Cs^+_{(aq)} \rightarrow Cs_2[CoFe(CN)_6]_{(sd)} + 2\,K^+_{(aq)}$$

The KCFC resin is stable over the entire pH range [Hitoshi Mimura et al., 1997]; the efficiency for Cs removal is ensured for any pH value ranging from acidic to alkaline media.

For removing cobalt, nickel, iron, and strontium, Chelex 100 resin may be used due to its strong attraction for multivalent transition metals and alkaline earth metals. Chelex 100 is typically used for removing trace metal contaminants in natural waters. The interesting characteristics of this resin are the absence of interaction with organic anionic species and the stability over the entire pH range. Furthermore, Chelex 100 is a radiation resistant resin and is currently used for extraction and preconcentration of radionuclides [Alliot et al., 2013; Pakalns, 1980]. The Chelex 100 resin contains iminodiacetate ions acting as chelating groups in binding polyvalent metal ions.

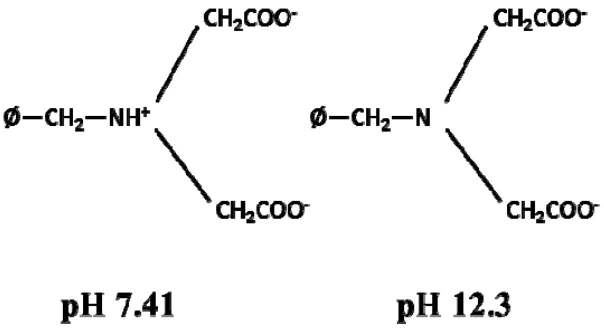

Figure 2: Chelex 100 resin

Chelex 100 in sodium form acts as a cation exchanger and allows the elimination of polyvalent transition metals and alkaline earth metals [Pai, 1988; Pai et al., 1988]. Unlike KCFC, the equilibrium pH value of the batch is a parameter that affects strongly the Chelex-100 efficiency to remove Co, Ni, Fe and Sr. The pH value needs to be adjusted to the neutral range [Pai et al., 1988], to provide free cations, to avoid hydroxide complex formation and to increase the retention efficiency. At this acidification stage, carboxylic acids remain ionized as the equilibrium pH is higher than the pKa values of the carboxylic acids (mostly below 5).

For the antimony removal, Chelex 100 resin needs to be used in the ferric form. According to Chanda and al. work [Chanda et al., 1988], oxoanion species of arsenic (III) and (V) are efficiently removed from aqueous solution by ligand sorption on the Chelex (Fe^{3+}) complex. Due to similarities in the coordinating properties between arsenic and antimony, one could expect an efficient removal of antimony using chelex 100 doped with Fe(III) cations.

Since Chelex (Fe^{3+}) decomposes at both extremely low and high pH, sorption maxima should occur at an intermediate pH depending on the oxidation state and the dissociation constants related to the considered anionic species. Experiments are ongoing to determine the optimal pH value for removing Sb(III) and Sb(V) using Chelex (Fe^{3+}) resin form. Tests on the different resins are performied to validate the optimal pH values allowing a maximal retention of radionuclides and minimal interaction with the target carboxylic acids.

The batch method is used by adding a large excess of resins directly into the sample followed by stirring. Resins are beforehand conditioned in NaOH or KOH, rinsed with copious amounts of MilliQ water and their equilibrium pH is carefully adjusted to the required values, by adding HCl. The solution with radionuclides is given to the resins under agitation for at least 24 hours. After centrifugation, the supernatant is recovered and the remaining activity of each tested radionuclide is quantified by liquid scintillation counting.

2.3 *Ion chromatography*

To implement the analytical strategy described above, a separation of a mixture of carboxylic acids using ion chromatography is carried out. The chromatographic parameters are optimized to enable an individual collection of carboxylic acids fractions. Figure 3 shows the chromatogram related to a mixture of formate, acetate, propanoate and oxalate 1 ppm in NaOH pH 12 solution.

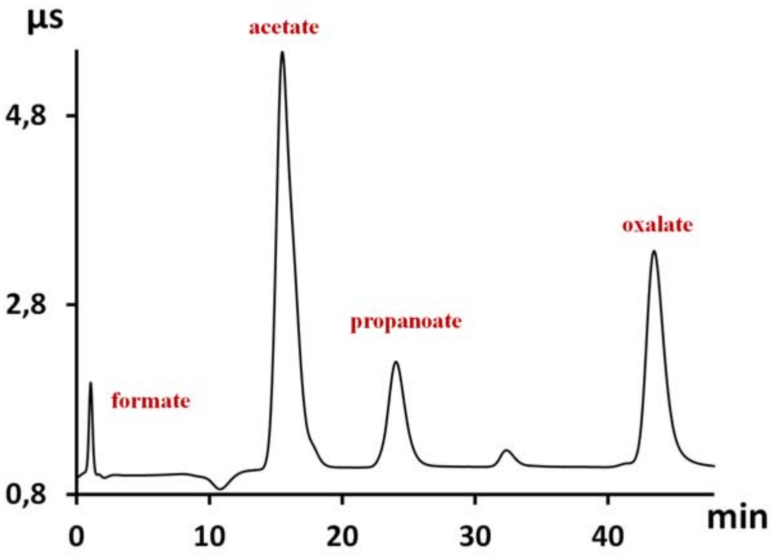

Figure 3: Chromatogram of separation of small carboxylic acid 1 ppm

Analyses are performed with IC Compact 881 Metrohm liquid chromatography equipped with sequential (Metrohm CO_2 suppressor MCS) and chemical (Metrohm suppressor MSM II) suppression modules. In this experiment, a solution comprising Na_2CO_3 (7.5 mM) and NaOH (0.75 mM) is used as the eluent/mobile phase with suppressed conductivity detection.

The separation column used is a Metrosep Asupp 16 250-2.0 column specifically designed for the separation of inorganic and small carboxylic acids anions, the injected volumes are 200 µl. The pump flow is maintained at 0.3 mL/min to maximize the separation peaks; alternatively, one can use a gradient elution to reduce analysis time.

Another feature related to the chromatographic analyses is the detection of carbonates due to the quick carbonation of NaOH solutions. Carbonates coelute and interfere with the quantification of anions of interest i.e. carboxylic acids. To overcome this issue, samples are prepared and kept into a controlled inert gas glove box filled with argon. A separation of a mixture of the six carboxylic acids expected to be produced during steel and iron corrosion [Mibus et al., 2015] is under investigation. After the optimal separation conditions were found, fractions with individual carboxylic acid were collected and their analysis using liquid scintillation counting was performed.

2.4 *Quantification of ^{14}C: Liquid Scintillation Counting*

The quantification of ^{14}C organic compounds can be performed by liquid scintillation counting using a typical Tri-Carb counter or a Quantulus counter for very low level activity. The ^{14}C quantification comes at the end of the process (treatment of leaching solution, ion chromatography separation) to avoid any interferences with beta-emitter. Ongoing tests are conducted to measure the ^{14}C activity in the collected fraction of labelled ^{14}C carboxylic acids. Preliminary tests are performed by separation and quantification of a carboxylic acids mixture spiked with the required activity of ^{14}C of corresponding carboxylic acids, to yield 5 Bq per collected fraction. The collected fractions are mixed with a scintillation cocktail (Hionic Fluor, PerkinElmer) selected to determine the ^{14}C activity in alkaline solutions. The cocktail volume ratio is optimized to have the best counting efficiency. For the oxalate fraction, 83 % of the ^{14}C activity was recovered after the chromatographic separation and fraction collection.

For ^{14}C activities in samples below or close to the detection limit, a more sensitive method is required such as Accelerator Mass Spectrometry (AMS). This technique is highly sensitive and may decrease the detection limit by a factor of 1,000. However, to use this technique one needs to provide decontaminated solution samples to avoid any contamination from other radionuclides since AMS is usually used for archeological samples. Carbon-14 needs also to be in appropriate chemical media to allow the oxidation of organic carbon-14 from aqueous media to gas phase in the form of $^{14}CO_2$(gas).

Figure 5: Tri-Carb analyzer, ^{14}C detection limit: 0.02 Bq/mL

2.5 *Quantification of total dissolved ^{14}C*

Prior to the separation method by ion chromatography, a complementary technique can be used for the quantification of the total dissolved carbon activity by TOC-meter. The device uses a combustion catalytic oxidation method at 680°C to decompose organic compounds in ultra-pure water and even in highly charged water. The value of the total dissolved ^{14}C activity and the deduced concentration of organic compounds in the samples will be determined.

3 Summary

In this work we propose an analytical approach for the analysis of the ^{14}C carboxylic acids released from corrosion of irradiated steels. This approach is based on the use of Ion Chromatography IC for separation of carboxylic acids and Liquid Scintillation Counting LSC for the quantification of ^{14}C in the collected fractions.

We also developed a method for extraction of the main water soluble radionuclides expected in the leaching solution with significant activities. The proposed method is based on the use of ion exchange resins characterized by their selectivity for the major radionuclides and their weak interaction with target ^{14}C carboxylic acids. This analytical strategy combining IC and LSC preceded by a filtration and resin treatment stages of the leaching solution will permit an accurate analysis of the ^{14}C carboxylic acids. Alternatives methods are proposed when the extracted ^{14}C is lower than ranges of detection such as AMS facility.

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