CArbon-14 Source Term

CAST

Annual progress report on WP4 – 2014 – (D4.2)

Author(s):

P. E. Reiller, C. Bucur, J. Comte, G. Heisbourg, D. Lebeau, C. Rizzato, A. Rizzo, P. Večerník

Date of issue of this report: 17/10/2014

The project has received funding form the European Union's European Atomic Energy Community's (Euratom) Seventh Framework Programme FP7/2207-2013 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 release 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: 4	CAST Document no. :	Document type: R
Task: all	CAST-2014-D4.2	R = report, O = other
Issued by: CEA		Document status:Final
Internal no. : NA		Draft/Review/Final

Document title
Annual progress report on WP4 – 2014 – (D4.2)

Executive Summary

The first year of the fourth work package (WP4) concerning the study of speciation, source term, leaching, and gaseous release of ^{14}C from spent ion exchange resins, was mostly dedicated to the writing of a state of the art review on sample choice, analytical techniques and current knowledge of release from spent ion-exchange resins. These pieces of information are available in the first deliverable of this work package – D4.1 [RIZZATO *ET AL.*, 2014]. This second deliverable consists in an annual report on the current status of work at the end of September 2014.

List of Contents

Executive Summary i
List of Contents iii
1 Introduction and Context 4
2 Partners Activities 4
  2.1 EDF-CEA 4
  2.2 ENEA 10
  2.3 FZJ 16
  2.4 INR 21
  2.5 SKB 21
  2.6 ÚJV 24
References 26

1 Introduction and Context

The fourth work package (WP4) of the European project CAST is dedicated to the study of speciation, source term, leaching, and gaseous release of ^{14}C from spent ion exchange resins (SIERs). After having recalled reasons for the choice of the SIERs samples within the national program, the general framework of the ^{14}C inventory, analytical problems, and possible release from spent ion exchange resins (SIERs) in the first deliverable [RIZZATO *ET AL.*, 2014], this second deliverable is the annual progress report of the first year of WP4.

2 Partners Activities

2.1 *EDF-CEA*

2.1.1 EDF – Choice and sampling of SIERs within the French program

EDF will provide one sample from 5 different EDF nuclear reactors to CEA in the framework of the CAST project as described in deliverable D4.1 [RIZZATO *ET AL.*, 2014] and recalled in Table 1. The sampling will be made in the storage tanks without any possibility to know the exact SIERs origin – one has to remember that it is a mixture – and thus their detailed history. These samples were chosen for their different origins (power reactor units, nature of the fuels). The characteristics of these samples are summarized in Table 1.

Table 1. Characteristics of the EDF samples.

Name of the sample	Power reactor unit (MWe)	Type of fuel	Provisional delivery date
EDF-A	1450	UOX	01/2014
EDF-B	1300	UOX	07/2014
EDF-C	900	UOX	08/2014
EDF-D	900	MOX	12/2014
EDF-E	1300	UOX	03/2015

EDF SIERs will be sampled during the period from January 2014 to March 2015. The amount of each sample (approx. 10 g) will be defined onsite in compliance with the ADR regulation rules [ADR, 2013], and the Chicade facility (CEA Cadarache Centre, France) acceptance criteria.

The first sample was sent and received by the CEA 06/19/14. It consists of a 10 g sample of wet SIER (Sample EDF-A, sampled 02/18/14). Second and third samples were taken and are still kept on-site.

2.1.2 CEA-LARC – Determination of the ^{14}C content in EDF SIERs

The laboratory of chemical and radiochemical analyses (LARC) in CEA Cadarache will determine the inventory of ^{14}C in SIERs from nuclear power plants (EDF PWR reactors). The objective is to determine the total activity ^{14}C and the distribution among mineral and organic forms of ^{14}C. This first period was devoted to the reception of samples in compliance with the regulations (ADR, INB rules) and preliminary developments for the measurement of the total activity and the distribution of ^{14}C.

2.1.2.1 Reception of samples from EDF

At the date of this deliverable, one sample (EDF-A, see Table 1) was received on 19th June, 2014.

2.1.2.2 Total ^{14}C analysis

The objective is to optimize the total mineralization process with a total recovery of ^{14}C. Developments were performed on virgin IERs. About 0.2-0.5 g of wet IERs is introduced into a little quartz vessel mixed with a “stable carbon” carrier. Mineralization is carried out under O_2 pressure (25 bars) in a closed system (Parr bomb, IKA AOD 1). The combustion of the ion-exchange resin produced CO_2 that is trapped in sodium hydroxide solution as carbonate. To achieve the recovery of ^{14}C, the mineralization system is degasing under a venting station and the gases are flushed into sodium hydroxide bubblers.

Tests on virgin IERs spiked with ^{14}C as ^{14}C-carbonate forms, or ^{14}C-glucose forms, or both, were used to optimize combustion and the concentration of the sodium hydroxide solutions in the mineralization system, or in the bubblers, to trap CO_2. The results show that in all cases – mineral, organic, or both forms – the recovery of ^{14}C is complete (100%). This process will be performed on real sample during the next period.

2.1.2.3 Repartition between inorganic and organic forms of ^{14}C

The study of the distribution of inorganic and organic forms will be carried out by acidic dissolution of the IER. A first step consists in introducing the sample in a glass reactor and mixing it with acidic solutions to provide the degasing of CO_2 and to trap the CO_2 into bubblers with sodium hydroxide solution (mineral form). During a second step, a total oxidation of the IER and the organic forms of ^{14}C was performed by a hot acidic dissolution with oxidizing reagent.

Tests on virgin IERs spiked with ^{14}C as ^{14}C-carbonate forms or ^{14}C-glucose forms or both were used to optimize dissolution parameters to achieve the total recovery of ^{14}C and a good selectivity between mineral and organic forms. The concentration of the acidic solutions, the mass of resin/volume of acidic solutions ratio will be studied in order to quantify and to optimize the chemical yield. The results show that:

- for the mineral form of the ^{14}C, the recoveries in all the cases studied were around 100±10% (included in the uncertainties of the measurements);
- for the organic form the recovery obtained (^{14}C as glucose-form) were in the range of 81% to 91%; based on these results, complementary developments seem necessary to achieve a higher and reproducible recovery of ^{14}C organic forms; this latter point will be studied during the next period.

2.1.3 CEA-LRMO – Determination of the ^{14}C containing molecules

The goal is to determine the source term of ^{14}C and its speciation from resins leaching. The leachates in simulated cementitious environment (NaOH solution, on non-irradiated and irradiated resins) previously presented, will be analyzed to allow detection and quantification of organic compounds in solution. To answer this question, an analytical approach has been defined.

2.1.3.1 Analytical Strategy

In 2014, we established an analytical strategy to answer to different objectives:

- obtain information on the size of the molecules present in the samples
- obtain a semi-quantitative distribution of the different chemical families (alcohols, ketones, carboxylic acids, etc…)

The experimental protocol will be realized as follows:

1) development of a method for quantification of total organic carbon with the aim to determine the carbon mass balance for each leachate solution;
2) development of spectroscopic methods such as infrared analysis to identify the main families of chemical functions (carboxylic acids, aromatic compounds, ketones, alcohols, etc…);
3) development of analytical methods based on chromatographic techniques; the aim is the detection and quantification or semi-quantification of targeted families of molecules, *e.g.*, ion chromatography will be used for the detection of small carboxylic acids and a coupling between gas chromatography and mass spectrometry will be used for detection of small organic compounds with high polarity;
4) development of analytical methods based on mass spectrometry (electrospray-mass spectrometry technique) with the aim to detect and identify molecules with high molecular weights.

This analytical strategy have been already demonstrated for the study of the uranium carbide dissolution [LEGAND *ET AL.*, 2014].

2.1.3.2 Analytical Methods

The sample delivery in the analytical laboratory is dependent on the radioactivity. A first dilution of samples could be necessary to respect the acceptance in α and γ activities and handling in the laboratory.

In a second step, research and analysis of organic targeted molecules will be developed. In this aim, a convenient analytical approach for sample analysis in highly concentrated media such as water cement solution has to be developed as presented in Figure 1.

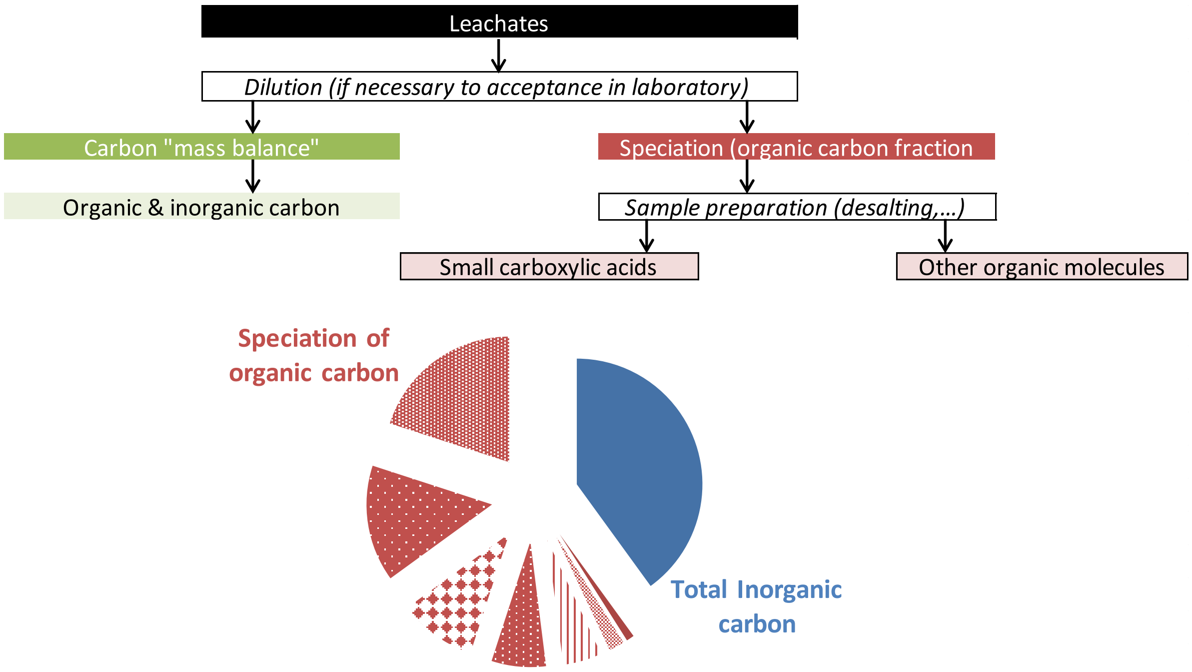

Figure 1. Analytical strategy to be used in CEA/LRMO

2.1.3.3 Carbon Mass Balance

The quantification of total organic carbon is realized to know the quantity of organic matter which was leached in solution. This quantification will also help at the end of the development of the analytical protocol to control the mass balance of each sample.

The measurement is realized by a chemical oxidation. The sample is injected into a chamber with phosphoric acid followed by injection of sodium persulfate. The organic matter is oxidized in CO_2, which is quantified by infrared spectroscopy. A differentiation between organic and inorganic carbon will be realized.

Figure 2: Total organic carbon analyser implemented in active glove box.

2.1.3.4 Sample preparation

Leachates are prepared in simulated cementitious environment (NaOH solution). A desalting and pre-concentration step is needed prior to analysis. For this, IER will be used to exchange Na^+ ions with H^+ from the resin. After washing of the resin, the sample is loaded and eluted with water. The water can then be evaporated under nitrogen atmosphere. At the end of this treatment, the sample can be solubilized in different solvents adapted to the different analytical techniques requirements.

2.1.3.5 Organic carbon speciation

Table 2 summarizes the different objectives of this study and the analytical techniques that have been described in the deliverable D4.1 [RIZZATO *ET AL.*, 2014].

In 2014, a Fourier transformed infrared (FTIR) spectrometer has been installed in the hot lab and can be used for samples analysis in 2015. FTIR spectroscopy enables to identify functional groups of organic compounds present in solution (carboxylic acids, aromatic compounds, ketones, etc…) and can guide the choice of analytical methods to implement thereafter.

The acquisition of a new scintillator counter has been prospected for specific analysis of carbon-14. We are now studying characteristics and costs of this detector for an acquisition at the end of 2014.

Table 2. Analytical Techniques to be used at CEA/LRMO

Aim	**Analytical techniques**
Mass balance	COT
Qualitative analysis for determination of chemical families	FTIR-spectroscopy
Quantification of carboxylic acids	Ion chromatography Gas chromatography-mass spectrometry
Detection of low mass molecule	Gas chromatography-mass spectrometry
Detection of molecules with higher molecular weight	ESI-MS

2.2 *ENEA*

ENEA is committed in three tasks 4.1, 4.2 and 4.3, strictly correlated among each other as the methodological work flows through the logical framework of the task algorithm, starting from the review of the current status, passing through the experimental activities that will lead to some synthesis and elaboration of the final results.

2.2.1 Preliminary and subsidiary activities

ENEA invested a lot of time in reviewing the current status of the scientific research on IERs, trying also to disseminate these pieces of information among the whole team involved in CAST, and to other researchers who could contribute and/or could be interested in this issue.

The main group involved in CAST project is the so-called Fuel Cycle T (FC team) with the support of external expertise.

The scheduling of the planning and training activities is the following

- 24 October 2013 – **preliminary meeting** for the presentation of CAST project to the Fuel Cycle Team

- 4 December 2013 - **official ENEA kick off meeting** of CAST project for the scheduling of the activities of all the CAST Work Packages and with the provision of a specific training event on ^{14}C cycle in nuclear industries for the new staff
- 25 March 2014 – **technical meeting** on the IER sample choice and outcomes of the interaction with Italian WMO (SOGIN)

Before the technical meeting intensive interactions with the Italian WMO organization (SOGIN) were carried out in order to disseminate the objectives of CAST and to reach an agreement for the provision of samples.

A synthesis document on the ^{14}C cycle, useful for basic training on ^{14}C content in nuclear industries, has been edited and distributed as ENEA internal technical document *ENEA-UTFISSM-POOO-016* (in English) which could be requested for access (*send a request by e-mail to antonietta.rizzo@enea.it*).

It was decided for the time being to restrict the sample gathering to the Italian samples and to discuss later with CAST partners, their experiences on sample gathering.

2.2.2 Task 4.1: Current status review of ^{14}C and its release from SIERs (all partners)

A bibliographic review on the IERs and the analytical techniques for the ^{14}C content has been carried out. An extensive description of the state of the art review has been given in CAST deliverable D4.1 [RIZZATO *ET AL.*, 2014].

2.2.3 Task 4.2 – ^{14}C Inventory and speciation in SIERs (CEA, FZJ, ENEA, INR, ÚJV, SKB)

2.2.3.1 Ionic exchange resins

A bibliographic research on the typology of IER and their morphology has been started. The decontamination factor has been identified as an important factor for the assessment of the resin capacity to retain radioactive isotopes and as a consequence, could be proposed also as a target parameter for the prevision on the release properties.

As the decontamination factor is strictly linked to some other chemical-physical parameters we propose to start a review and a selection of these parameters in order to verify their influence on the release mechanism of ^{14}C.

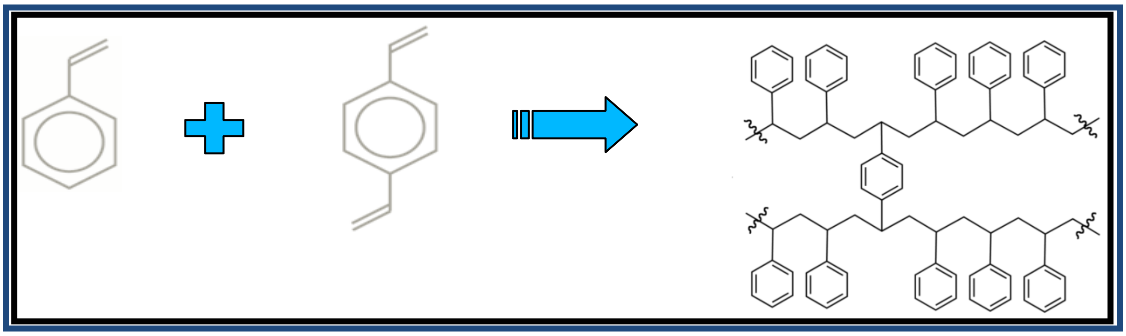

Figure 3. Chemical structure of cross-linked ionic exchange resins

STRONG ACID CATION RESINS (SAC) - gel or macroporous

STRONG BASE ANION RESINS (SBA) – gel or macroporous

MIXED BEDS RESINS - gel/gel or gel/macro or macro/macro or macro/gel

Figure 4. Common physical features of IERs

Decontamination factor (DF)

$$DF = A_{in}/A_{out}$$

where A= activity ; A_{in}= incoming activity A_{out} = outgoing activity

PARAMETERS INFLUENCING THE DF

- Nature of the present radioisotopes
- Concentration of the present radioisotopes
- Density of the functional groups of the resins
- Ion - selectivity

Figure 5. Definition of decontamination factors for the (S)IERs

2.2.3.2 Procurement of IER

ENEA has been in contact with the Italian WMO (SOGIN) and it has received the information regarding the actual inventory of the SIERs. It was possible to get samples only for the PWR Trino NPP. The following situation refers to Trino PWR NPP. The SIERs consist in granulometric particles and their volume (wet samples) is more than 60 m^3 and they are stored in a temporary repository, under the management of SOGIN. The IERs used during the operational phases are both cationic and anionic types and most of them are mixed beds, according to their specific utilization for the purification and treatment processes.

Table 3. Physical parameters of the ENEA IERs

Type of IER	Range of apparent density (kg/L)	Range of granulometry (mm)
Cationic	0.80-0.89	0.30-0.55
Anionic	0.69-0.73	0.30-1.2
Mixed bed	0.72-0.80	0.30-1.25

The total activity of the full amount of SIER is estimated in the range of 1.4 10^{13} Bq.

As most of the SIERs have been already stored, only small amounts are still available to further investigation. ENEA is making arrangements with SOGIN in order to receive 9 samples (3.5-10.0 g for each sample) of their SIERs. These samples are from three different demineralizer vessels and they have been sampled in 2000-2001. It has been planned to have the delivery of the SIERs samples to ENEA laboratory by October 2014.

The samples will undergo to ^{14}C measurement analysis and, if feasible, due to the small amounts, also some morphological characterizations. Because of the old sampling timeframe no gas could be collected but the analysis of the ^{14}C content could allow us to make consideration about the gaseous release rate.

SOGIN has also provided two different samples of fresh IERs that have been stored for almost 10 years in its laboratory. These samples are already in the availability of the ENEA laboratory. Some scanning electron microscopy (SEM) analyses have shown different characteristics of the anionic and cationic resins and the level of degradation could be of some influence for the effective release phenomena for this type of resins. ENEA is investigating if the mechanical degradation is induced by the manipulation of the samples – also during the preparation of the sample for the SEM measurements –, or if they are pre-existent and due to the operations and storage.

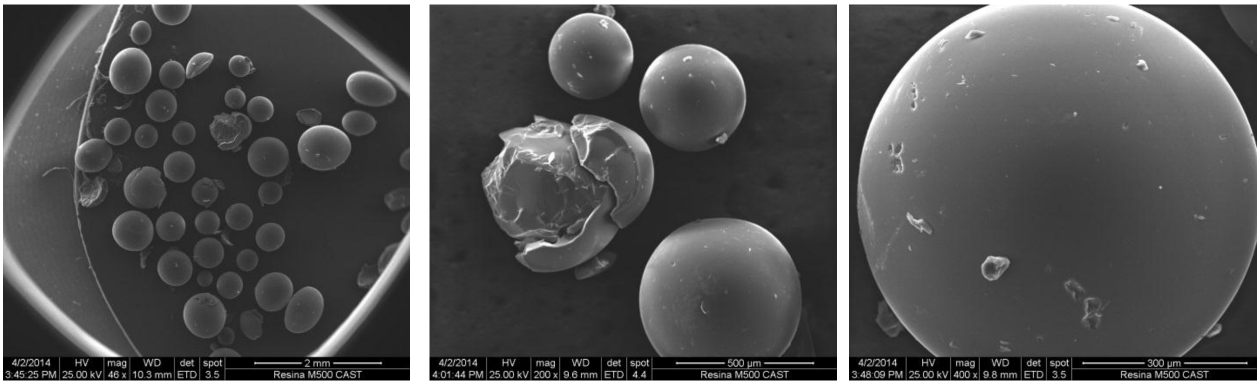

Figure 6. SEM microphotographs of a sample of fresh IERs – anionic.

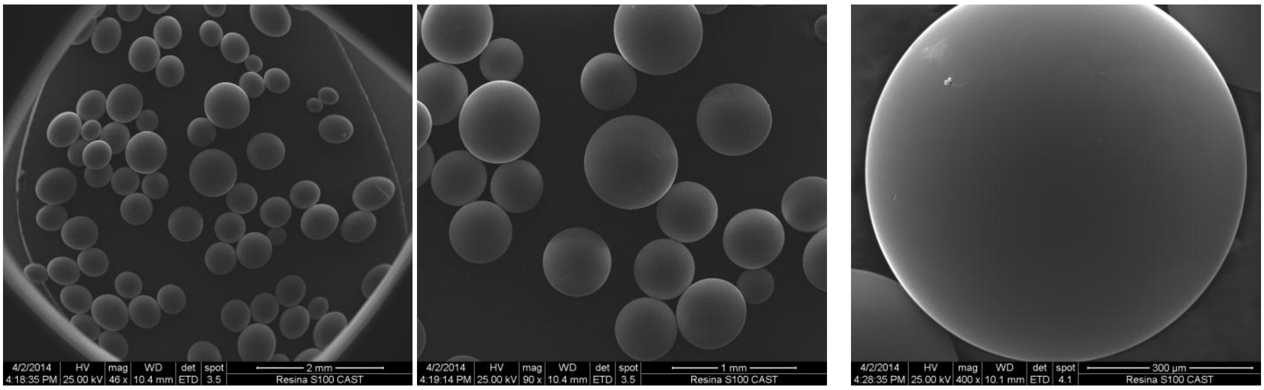

Figure 7. SEM microphotographs of fresh IERs – cationic.

2.2.3.3 Degradation experiment

ENEA is currently investigating the final design of the degradation experiment that will be carried out on the fresh IERs provided by SOGIN, and on some other fresh IERS younger in term of production date. The choice of using “old” fresh IERS and “new” fresh IERS could lead to some consideration about the degradation of the physical structure and the chemical transformation of the resins due to storage conditions.

Some parameters as morphology, elemental content, ^{14}C content *vs*. time of degradation experiment will acquired.

2.2.3.4 Speciation experiment

ENEA is choosing two or three different set-ups of the digestion and combustion system, by designing the whole systems, acquiring the materials, and testing the system (see figures below).

We will start to analyze the ^{14}C content with a very simple process, using an elemental combustor at different temperatures and collecting the fraction separately. The ^{14}C content will be carried out both by ultra-low level LSC and AMS techniques.

A targeted device (Figure 8), with a double chamber combustion cell, has been designed in order to run stepped combustion of IERs samples to obtain different volatile/non-volatile fractions. Qualitative and quantitative measurements of the composition of the fractions will be carried out in order to characterize the resins retention/release phenomenology.

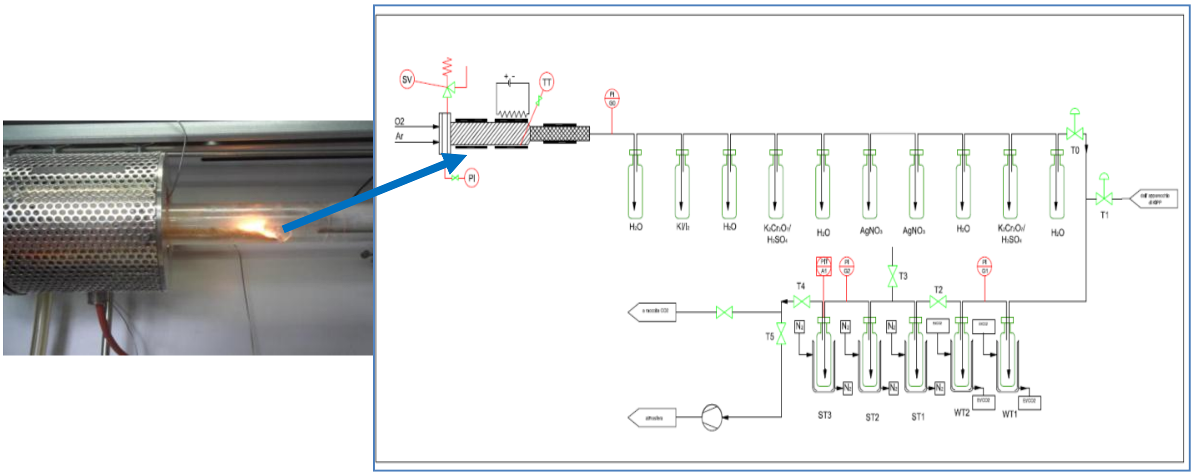

Figure 8. Equipment for the stepped combustion of organic materials for benzene LSC analysis at ENEA ^{14}C laboratory

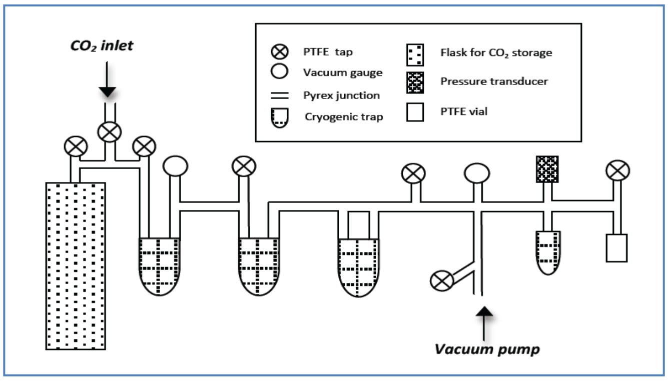

Figure 9. Equipment for the CO_2 direct absorption method at ENEA ^{14}C laboratory

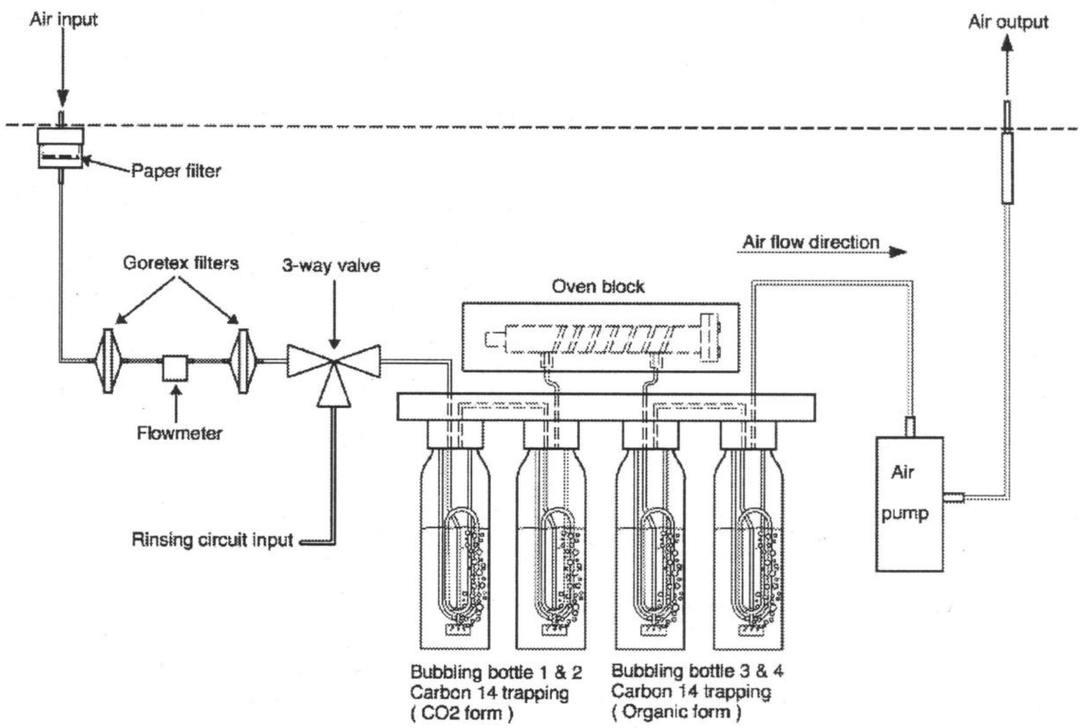

Figure 10. Flow diagram of the inorganic/organic separation equipment at ENEA ^{14}C laboratory

2.2.4 Task 4.4 – Synthesis of experimental data and interpretation – final report (all partners)

An exchange of information and technical details is being carried out with FZJ (Dr. Corrado Rizzato) and we organized an official meeting on 15 April 2014 at ENEA premises. The ENEA presentations used in this meeting could be requested for access to ENEA (mail to antonietta rizzo@enea.it)

2.3 *FZJ*

Forschungszentrum Jülich (FZJ) is involved in all tasks of WP4, in particular focusing the research on ^{14}C on/released by organic BWR (S)IERs, in different conditions. In a first step, the state of the art is drawn from the existing literature by all partners. The knowledge will constitute the basis for optimization of the already-planned investigations. Quantitative evaluations of the total, organic and inorganic ^{14}C on and released by the resins are going to be performed on the specific SIERs, similarly to what has been done in the past – *e.g.* see [MAGNUSSON *ET AL.*, 2008]. More in detail, the ^{14}C-speciation on/released by (S)IERs in different conditions will be sought, evaluating the influencing parameters – as *e.g.* radiolysis, mixed disposal, degradation, rehydration, pH, *etc.*

It has to be noted that the WP4 work at FZJ is part of on-going PhD, Master and Bachelor theses, which are scheduled to be submitted in 2016. Authorisation by the PhD, Master and Bachelor candidates is necessary prior to publication or citing of FZJ’s results.

2.3.1 Progress in Task 4.1

FZJ largely contributed, together with the other partners, to the establishment of the D4.1 [RIZZATO *ET AL.*, 2014]. The criteria for its sample choice are also reported there.

2.3.1.1 Sample choice

FZJ is focusing its research on Ion Exchange Resins (IERs) adopted in water cleaning circuits of BWRs. The work will be part of a PhD thesis. FZJ is in contact with German and other European BWR operators. Following the requests of the operators, in parallel to the agreement within CAST, the samples were anonymized.

The samples used by FZJ and selection criteria are largely discussed in D4.1 [RIZZATO *ET AL.*, 2014]. The choice of SIERs from FZJ is schematically reported in Table 4.

Table 4: Summary of the different samples received/expected by FZJ

BWR	SIERs (CCU)	Water		Gas	
		Primary	Suspension	Treatment Line	Interim Storage
FZJ-A	x	n/a	x	n/a	n/a
FZJ-B	exp	n/a	n/a	n/a	n/p
FZJ-C	exp	exp	exp	exp	n/a
FZJ-D**	exp*	exp*	exp*	exp *	n/a
FZJ-E	exp*	n/a	n/a	n/a	n/a

(exp= expected with high probability; exp*=expected with medium/low probability due to budget limitations; n/a=not available; n/p=not possible; x=received; **several BWRs taken into account: evaluation of samples/costs is still in progress)

2.3.1.2 Analytical techniques

FZJ has largely participated in the writing of deliverable 4.1 [RIZZATO *ET AL.*, 2014] were a particularly complete review of ^{14}C analytical techniques and strategies applied in resins is proposed.

2.3.1.3 Release from SIERs

FZJ has mainly written the chapters of the state of the art report – see deliverable 4.1 [RIZZATO *ET AL.*, 2014] – on the release of ^{14}C from SIERs.

2.3.2 Progress in Task 4.2

The morphology of selected SIERs – see Table 4 and [RIZZATO *ET AL.*, 2014] – is going to be investigated by FZJ as soon as the missing samples will be made available (first samples received in June 2014).

2.3.3 Progress in Task 4.3

Analytical development to lower the detection limits is going on in FZJ, for the ^{14}C-detection/speciation in solution and especially in the gas phase. A strong interconnection and exchange of knowledge with the WP4-partners would accelerate and optimize such a development. In addition, the application of Accelerator Mass Spectrometry (AMS), in particular for gaseous samples, could be the key factor for the detection/speciation of the ^{14}C, or ^{13}C loaded on –and released by – fresh resins. It is recommended that a sample exchange routine should be established with those CAST partners operating AMS capable of measuring also gaseous samples.

Leaching experiments on BWR resins and powder IERs are planned to start in the next months.

The generation of gases during storage and degradation of SIERs from BWR in different waste forms is going to be investigated by FZJ following different approaches.

2.3.3.1 Experiments on the SIERs:

Several samples (see Table 4) are not yet in FZJ and the dedicated equipment needs to be established.

2.3.3.2 Simulation of SIERs with loaded IERs exposed to gamma radiation

A dedicated preliminary gamma irradiation campaign has been established and the relative equipment has been developed. Currently, resin samples, unloaded and loaded e.g. with carbonates and formates, are exposed to gamma radiation in aerobic conditions (see Table 5, Figure 11 and Figure 12). The results obtained from these preliminary tests, together with the results reported in deliverable 4.1 [RIZZATO *ET AL.*, 2014, and references therein], will be utilized for optimization of a larger campaign, including the development and test of the equipment for gas sampling, analytical techniques and concentration methods.

Table 5: List of samples used in the preliminary gamma-irradiation campaign

Sample ID	Sample type	Dose [MGy]
U1	IER-H	0,1
U2	IER-H	0,5
U3	IER-OH	0,1
U4	IER-OH	0,5
U5	IER-OH	1,0
B1	$NaHCO_3$/Water	0,1
B2	$NaHCO_3$/Water	0,5
B3	CH_2O_2/Water	0,1
B4	CH_2O_2/Water	0,5
L1	IER-OH/ $NaHCO_3$/Water	0,1
L2	IER-OH /CH_2O_2/Water	0,5
L3	IER-OH/ $NaHCO_3$/Water	0,5
L4	IER-OH /CH_2O_2/Water	0,1

Figure 11: Sample vial filled with anion exchange resins and water, after closure in controlled atmosphere and pressure, ready for the irradiation campaign

Figure 12: Metallic box used for the irradiation campaign, loaded with sample vials

2.4 *INR*

For this first year of the CAST project, INR has been in contact with representatives of Cernavoda nuclear power plant to establish the ways of SIERs sampling and their transfer to INR Pitesti. Since up to now, no SIERs sampling from the Cernavoda storage tank were performed, INR designed and realized a sampling device that was tested – in the presence of the Cernavoda nuclear power plant representatives – under simulating conditions and it will be tested at Cernavoda – after some modifications to improve the radiological safety of the workers. The SIERs sampled will be transferred to INR to be used in the experimental program developed under CAST project.

If SIERs from storage tanks would not be sampled, fresh SIERs are available – removed from purification systems during routine maintenance work – from different non-fuel contact purification systems of Cernavoda nuclear power plant that will be analysed in the frame of the CAST project. These purification systems were selected since in Romania the SIERs from the fuel contact systems are intended to be disposed of in a near surface disposal and only the non-fuel contact SIERs shall be geological disposed of. Based on literature review, the analytical techniques for the total ^{14}C measurement, and also for organic/inorganic carbon fraction, have been selected – see deliverable D4.1 [RIZZATO *ET AL.*, 2014].

INR has no previous experience in measuring the organic/inorganic fraction of ^{14}C from any type of radioactive waste. Consequently, the components of the experimental set-up for the acid stripping/wet oxidation techniques were ordered and have to be purchased. Once all components assembled, the experimental set-up will be tested using non-radioactive resin labelled with ^{14}C standard in order to determine the recovery of the acid stripping/wet oxidation processes. Also the reproducibility and memory effect of the method will be assessed.

2.5 *SKB*

SKB have finalised the sampling and analysing the ^{14}C content of SIER. The new findings have led to updated uptake factors for almost all Swedish reactors.

The accumulation factors are shown in Table 6, Figure 13 and Figure 14, together with relative standard deviations. The accumulation is shown as Bq/MWh$_{th}$ for total, inorganic and organic ^{14}C. The inorganic ^{14}C consists of species in the carbonate system, mainly, hydrogen carbonate, based on the chemical conditions in the systems. The organic species are most likely simple organic acids, since they have been identified in at least PWR systems during operation.

Table 6. Total accumulation in Condensate Clean-up (BWR) and Reactor Water Clean-up (PWR) as Bq/MWh$_{th}$, with relative standard deviations. The yellow-marked values for F1+F2 and F3 are for dried resins, prior to solidification. All other values are for wet resins

Unit	Accumulation, Bq/MWh$_{th}$			Organic fraction	Relative standard deviation, %		
	Total	Inorganic	Organic		Total	Inorganic	Organic
F1 +F2	2.30E+02	2.26E+02	3.97E+00	1.7%	13%	13%	14%
F3	6.12E+02	6.01E+02	1.06E+01	1.7%	4.9%	4.9%	7.2%
F1 +F2	1.26E+00	1.15E-01	1.15E+00	91%	22%	110%	24%
F3	4.52E+00	3.19E-01	4.21E+00	93%	15%	43%	17%
O1 + O2	1.03E+02	9.73E+01	5.35E+00	5.2%	2.3%	2.3%	9.5%
O3	3.62E+02	3.58E+02	4.13E+00	1.1%	3.4%	3.4%	9.1%
(B1 +) B2	1.54E+02	1.41E+02	1.34E+01	8.7%	20%	22%	51%
R1	9.05E+02	8.81E+02	2.37E+01	2.6%	6.3%	4.3%	15%
PWR	5.42E+02	3.86E+02	1.58E+02	29%	4.4%	5.1%	3.4%

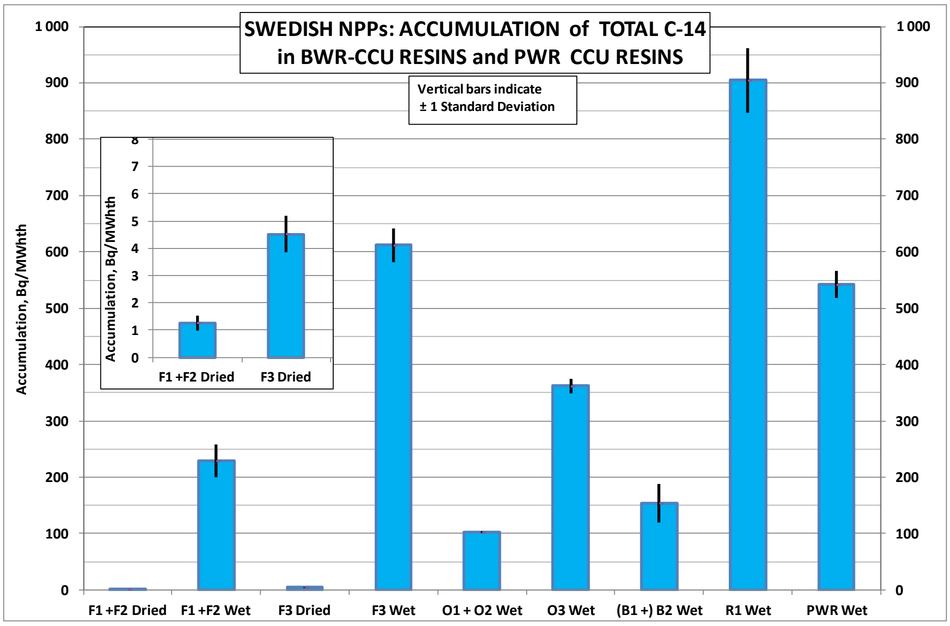

Figure 13 Accumulation of total ^{14}C expressed as Bq/MWhth for the Swedish NPPs. The inset shows the values for dried resins from the Forsmark units. The vertical bars indicate ±1 standard deviation.

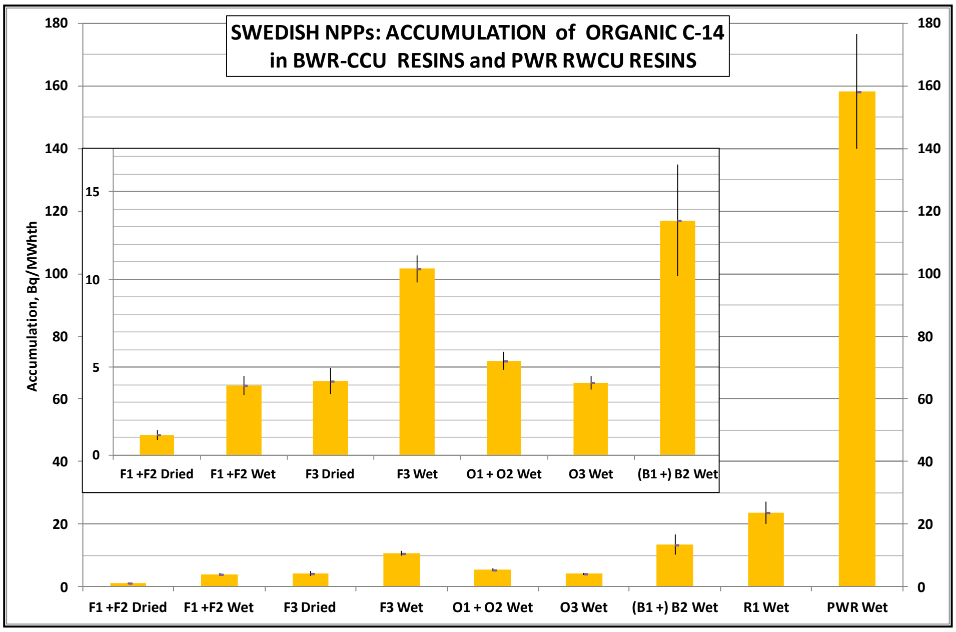

Figure 14. Accumulation of organic ^{14}C expressed as Bq/MWhth for the Swedish NPPs. The inset shows a zoom-in for the units with low accumulations. The vertical bars indicate ±1 standard deviation

The organic fraction of the total accumulation is also given in the table. The standard deviations include the standard deviations in the sample analysis[1] and a 10 % standard deviation in the resin amounts used in the calculations.

Since there are some uncertainties in the calculated production rates of ^{14}C, the accumulation has been expressed as Bq/MWh_{th}.

The results for the accumulation in BWR Condensate Clean-up resins show some results diverging within the units and between the units. Some of these variations can be explained by the ratio between resin mass used and the mass of cleaned water.

The accumulated ^{14}C activity differs between fuel cycles depending on the operational conditions of the reactor. The factor that influences the ^{14}C content in the final waste form the most is the fate of the spent SIERS in the downstream process from the reactor, *i.e.* storage times in different tanks and stirring procedure in the storage tanks. It has been observed that when air bubbling is used as a stirring method lot of the inorganic ^{14}C activity is lost.

2.6 *ÚJV*

2.6.1 Nuclear power plant sample

Specimen of SIERs from Temelín NPP (nuclear power plant) was obtained. By laboratory analysis, the ^{14}C activities of 27 ± 4 kBq/kg for the organic forms and 16 ± 2 kBq/kg for the inorganic forms were determined in the measured sample.

2.6.2 Laboratory sample

Before sorption experiments, analyses of background ^{14}C activity of Amberlite resins specimens (katex in Na^+ form, anex in Cl^- form) and unknown mixed-bed resin were set. Analyses are ongoing and natural background of ^{14}C is expected.

---

[1] The standard deviation used is the maximum of the values obtained in the activity analysis (dominated by the standard deviation in counting) and the scatter between the replicates analyzed for each sample.

2.6.3 Radionuclide solution preparation

As first ^{14}C species, the inorganic bicarbonate (HCO_3^-) was selected for performing the experiments. Sodium bicarbonate was purchased from Perkin Elmer. The package of 1.0 mCi/ml (37 MBq/ml) was diluted into 20 ml of sodium hydroxide solution, sampled for activity verification and now is prepared for experiments.

Activity of ^{14}C samples was determined by Liquid Scintillation Counting (LSC) on Wallac Guardian 1414 device in Central Analytical Laboratory, Chemistry of Fuel Cycle & Waste Management division, ÚJV Řež, a. s.

References

ADR 2013. European Agreement Concerning the International Carriage of Dangerous Goods by Road. *United Nations Economic Commission for Europe*, Available from http://www.unece.org/trans/danger/publi/adr/adr2013/13contentse.html.

LEGAND, S., BOUYER, C., CASANOVA, F., LEBEAU, D., AND LAMOUROUX, C. 2014. Uranium carbide dissolution in nitric acid: speciation of organic compounds. *Journal of Radioanalytical and Nuclear Chemistry,* Vol. 302, 27-39.

MAGNUSSON, Å., STENSTRÖM, K., AND ARONSSON, P. O. 2008. ^{14}C in spent ion-exchange resins and process water from nuclear reactors: a method for quantitative determination of organic and inorganic fractions. *Journal of Radioanalytical and Nuclear Chemistry*, Vol. 275, 261-273.

RIZZATO, C., RIZZO, A., HEISBOURG, G., VEČERNÍK, P., BUCUR, C., COMTE, J., LEBEAU, D., AND REILLER, P. E. 2014. State of the art review on sample choice, analytical techniques and current knowledge of release from spent ion-exchange resins (D4.1). *Carbon-14 Source Term (CAST) Project, N° 604779*, CAST - D4.1.