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Titolo

EUROPEAN PROJECT “Carbon-14 Source Term” CAST

Deliverable D 4.5

“Final report on the estimation of the source term and speciation”

Descrittori

Tipologia del documento: Rapporto di attività

Collocazione contrattuale: Euratom Seventh Framework Programme FP7/2007-2013 grant agreement no. 604779

Argomenti trattati: Trattamento e stoccaggio dei rifiuti radioattivi

Sommario

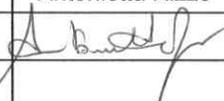
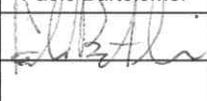
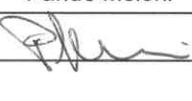
The CAST project (Carbon-14 Source Term) aims to develop understanding of the potential release mechanisms of carbon-14 from radioactive waste materials under conditions relevant to waste packaging and disposal to underground geological disposal facilities. The project focuses on the release of carbon-14 as dissolved and gaseous species from irradiated metals (steels, Zircalloys), irradiated graphite and from ion-exchange materials. This report describes the final results of the CAST activities on the ¹⁴C inventory in the ionic exchange resins and their speciation and has the objective to combine the experiences of all the partners and to show the most significant results they achieve, leading to an improvement of the knowledge of the behaviour of the activated ionic exchange resins. The experimental data are presented, whenever possible, as aggregates in order to make a common picture of the ¹⁴C inventory and speciation in the resins used in the nuclear reactors. Available results on the speciation of ¹⁴C originated from SIERS – partition between inorganic (carbonate) and organic fractions – seem to show that the majority of the ¹⁴C activity comes from the inorganic part. However, results on the partition of inorganic and organic molecules are often contrasting, spanning between 5 and 20% under the form of organic molecules from PWRs and CANDU. The wide range of ¹⁴C inventory values shows that it is not possible to simply estimate the ¹⁴C source term for ionic exchange resins but a dedicated and accurate sampling and analysis programme has to be developed and executed.

Note

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Carbon-14 Source Term

CAST



Final report on the estimation of the source term and speciation (D 4.5)

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The project has received funding from the European Union's European Atomic Energy Community's (Euratom) Seventh Framework Programme FP7/2007-2013 under grant agreement no. 604779, the CAST project.

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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, Zircalloys), irradiated graphite and from ion-exchange materials.

The CAST consortium brings together 33 partners with a range of skills and competencies in the management of radioactive wastes containing ^{14}C , 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 ^{14}C from the corrosion of irradiated steels and Zircalloys 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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CAST		
Work Package: 4	CAST Document no. :	Document type:
Task: 1	CAST-2017-D4.5	R = report
Issued by:	Document status:	
Internal no.: NA	Final	

Document title
Final report on the estimation of the source term and speciation (D 4.5)

EXECUTIVE SUMMARY

This report describes the final results of the CAST activities on the ^{14}C inventory in the ionic exchange resins and their speciation.

The report has the objective to combine the experiences of all the partners and to show the most significant results they achieve, leading to an improvement of the knowledge of the behaviour of the activated ionic exchange resins. The experimental data are presented, whenever possible, as aggregates in order to make a common picture of the ^{14}C inventory and speciation in the resins used in the nuclear reactors.

The wide range of ^{14}C inventory values shows that it is not possible to simply estimate the ^{14}C source term for ionic exchange resins but a dedicated and accurate sampling and analysis programme has to be developed and executed.

Available results on the speciation of ^{14}C originated from SIERS – partition between inorganic (carbonate) and organic fractions – seem to show that the majority of the ^{14}C activity comes from the inorganic part. In particular, for CANDU reactors, the major part is retained in anionic exchange resins under an inorganic form. A minor fraction of ^{14}C -containing species were found in cation-exchange resins and were probably under the form of metal carbonates. However, results on the partition of inorganic and organic molecules are often contrasting, spanning between 5 and 20% under the form of organic molecules from PWRs and CANDU.

The Appendices detail the specific achievement and results of each partner, for references and more in depth specific considerations.

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1. INTRODUCTION AND CONTEXT

In several Reference Cases of disposal systems envisaged by waste management organizations, ^{14}C is one of the most important contributor to the dose – see *e.g.*, JOHNSON AND SCHWYN [2008].

The workpackage 4 of the project CAST deals with one type of radioactive wastes containing ^{14}C : the Ion Exchange Resins (IERS). They are widely used in nuclear facilities for the purification of liquid processes or wastes streams. Particularly, significant amount of IERS are used in water clean-up systems in the reactor coolant. Even if SIERS are not planned to be disposed in deep underground systems but in subsurface storage, the release of ^{14}C from spent ion exchange resins (SIERS) is therefore of a major concern. The localisation of the major contribution of ^{14}C within the plant circuit is determined by the nuclear reactor technology: *i.e.* in pressurized water reactor (PWR) the major contribution of ^{14}C in the resins comes from the clean-up of coolant circuits, in boiling water reactor (BWR) it comes from condensate treatment circuit [YIM AND CARON, 2006].

The chemical form under which ^{14}C is fixed within, or adsorbed to, the IERS will be highly linked with the chemical condition of the reactor, including all its operations.

This report intend to collect all the available information, from the partners of the WP 4 from the EURATOM Project “CAST”, on the content of ^{14}C in the ionic exchange resins, aiming at the elaboration of a comprehensive understanding of the relative source term, including the consideration of its chemical speciation in the waste matrix.

The review of the available information on ^{14}C and its release from SIERS has been completed and released [JOHNSON AND SCHWYN, 2008]. Only very limited information is available on ^{14}C in SIERS [REILLER ET AL., 2014]. Most of the existing ^{14}C determinations for SIERS deal with the maximum activity determination, percentage of recovery, and differentiation between organic and inorganic fractions.

There are a number of challenges in developing a source term for ^{14}C release from SIERS for use in performance assessment, including:

- There is a wide range of SIERS types and locations within the reactor operating circuits;

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- ^{14}C may be lost in the gaseous form during storage, complicating the estimation of the inventory;
- SIERs may age due to gamma irradiation damage, thus potentially affecting the release rate and mechanism [VAN LOON AND HUMMEL, 1999a; VAN LOON AND HUMMEL, 1999b; TRABOULSI *et al.*, 2013];
- SIERs may be grouted with cementitious material, the impact of which will need to be accounted for.

The primary information about the ^{14}C speciation has been acquired determining its repartition between organic and inorganic form; followed by more detailed speciation and content analysis, aimed to determination of the type of contained organic acids, carbonate, etc. The final output of this investigation will be the evaluation of the repartition of molecules potentially fixed and/or released from SIERs during their storage, in order to allow a more realistic performance assessment of the radioactive waste repository. This is considered to be a necessary input for the safety assessment of a repository, going beyond the total activity and partitioning of ^{14}C . Accordingly, this will allow for predictions on the source term with lower uncertainties and, in parallel, for the development of appropriate treatment and conditioning methods to ensure the safe disposal of this specific waste.

The current report is an output of Task 4.2 of the CAST project. The report will firstly describe the type of IERs collected and analysed by the consortium and subsequently it will report the analytical data correlate to them. The Appendices reported the detailed activities for each contributing partners.

2. ^{14}C INVENTORY IN SIERS

The determination of the inventory of ^{14}C in SIERs from nuclear power plants has been achieved by quantification of the total activity of ^{14}C in some selected SIERs samples. The measurements on real samples (SIERs) have been conducted using specifically developed analytical processes that have quantified not only the total activity but also the mineral and organic forms distribution. Preliminary test with non-irradiated IERs have been also conducted in order to set up the better procedure. The partners have been choosing different analytical approaches for their samples, according to the typology of their samples.

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2.1. RESIN SAMPLING METHODOLOGY

The CAST partners have selected samples of irradiated IERs from PWR (including CANDU reactors) and BWR reactors, according to the availability of the samples, the internal procedures for dispatching and the national regulation for the transportation. Some partners could only have access to small quantities of samples, as the main volume was already treated and stored, others had access to old resins, and other to fresh ones, so it was not possible to have very similar samples among the partners, as it was already considered since the beginning of the project. The representativeness of the samples was also questioned among the same batch of samples, as the extraction and storage procedures were developed and applied for the processing and not in view of a sampling strategy. Nevertheless, the availability of a wide variety of samples can allow obtaining some general consideration to support the safety assessment of these wastes. Some samples of non-irradiated IERs were also selected and used to support setting of the analytical procedures and, where applicable, to make comparison analyses.

Generally, purification of the various circuits – *i.e.* primary circuit, secondary circuit and effluent treatment – is ensured by a chain of filters and demineralizers using IERs, which are required to be of high quality nuclear grade in order to remove the undesired ionic species dissolved in the fluid, such as those which can induce corrosion, or radioactive elements that affect local dose rates. A combination of cationic, anionic and/or mixed bed resins are used depending on the circuits' physicochemical conditions and on their specific needs.

At the end, the SIERs discharged from a nuclear facility are a mixture of IERs of different origins and characteristics. Their ionic charge, and activity, depends on the criteria defined to be changed out. The principal criteria are:

- chemical or radiochemical saturation; downstream of the demineralizers, limits are imposed on concentrations of certain substances, the conductivity of the fluid and/or the total γ -radiation measured;
- maximum service lifetime; to avoid degradation products, a maximum lifetime of 7 years has been recommended. This is further reduced to 5 years when the resin is exposed to more aggressive conditions in terms of chemistry or radiochemistry;

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- in rare cases, the bed may need to be changed out due to unusual pressure drop behavior, which is usually an indication of filter or resin degradation;
- along with these criteria, the resin may need to be changed frequently or infrequently depending on the fluid.

When the criteria are reached in a circuit, the SIERs are discharged and stored underwater in storage tanks with the others SIERs of the facility. The storage delay lasts some months until the dose rate is low enough due to the radioactive decay of the very short-lived radionuclides; then the SIERs are conditioned and disposed of.

The sample characteristics, activities, and reception were already described in BUCUR *et al.* [2015] and are summarised in **Table 1**.¹

¹ Not all the samples were used for the scope of task 4.2.

Table 1 – Description of the SIER samples collected by the partner

ORGANIZATION	SIERs type	Notes
EDF-CEA (France)	<ul style="list-style-type: none"> • SIERS from 5 different EDF nuclear reactors (PWR) • Non-irradiated IERs 	Wet and dry beads (mixed anionic and cationic)
ENEA (Italy)	<ul style="list-style-type: none"> • IERS from PWR Trino NPP • non irradiated IERs stored for 10 years and of recent production 	Wet beads (mixed anionic and cationic)
FZJ (Germany)	<ul style="list-style-type: none"> • SIERS from BWR (S) 	Wet and dry beads, powder
ICN (Romania)	<ul style="list-style-type: none"> • SIERS from Cernavoda NPP storage tanks or non-fuel contact purification system 	Wet and dry beads (mixed anionic and cationic)
SKB (Sweden)	<ul style="list-style-type: none"> • SIERS from Condensate Clean-up (BWR) • SIERS from Reactor Water Clean-up (PWR) 	Wet and dry beads (mixed anionic and cationic)
UJV (Czech Republic)	<ul style="list-style-type: none"> • SIERS from PWR 	Wet beads (mixed anionic and cationic)

EDF IERs samples were taken from storage tanks and they were located in different positions in the purification system of different PWR units.

ENEA IERs samples were taken from the purification systems of the PWR units.

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FZJ IERs samples were taken from the Condensed Clean up (CCU) system of BWRs.

RATEN-ICN IERs samples were taken from purification systems of moderator (MOD) and of Primary Heat Transport System (PHTS) of CANDU reactor.

SKB IERS samples were taken from Reactor Water Clean-up systems (RWC) of PWR units and Condensed Clean up system (CCU) of BWR units.

UJV IERS samples were taken from purification systems of the PWR units and LVR research reactor.

SKB partner have analysed a important amount of data, consisting in hundreds of samples collected over 7 years (interval 2008-2015) and belonging to different units of the reactors (334 samples in the Reactor Water Clean-up systems of the PWR units and 335 in the condensate Clean-up systems of the BWR units). The detailed description of the sampling methodology for the sampling campaign is provided in ARONSSON *ET AL.* [2016].

2.2. ANALYTICAL METHODOLOGIES FOR ¹⁴C DETERMINATION

The partners have chosen different analytical approaches, according to the typology of their samples and their past experience.

The two principal methodologies for the collection of the total carbon content of the IERs were the high pressure oxygen combustion and the non-catalytic combustion.

HIGH PRESSURE COMBUSTION (PARR BOMB)

The high pressure combustion (using the *Parr bomb* technique) was chosen by CEA: it was carried out under O₂ pressure (25 bars) in a closed system and the produced CO₂, was trapped in sodium hydroxide solution as carbonate by degassing the system under a venting station and let the gases flushing into sodium hydroxide bubblers (**Errore. L'origine riferimento non è stata trovata.**).

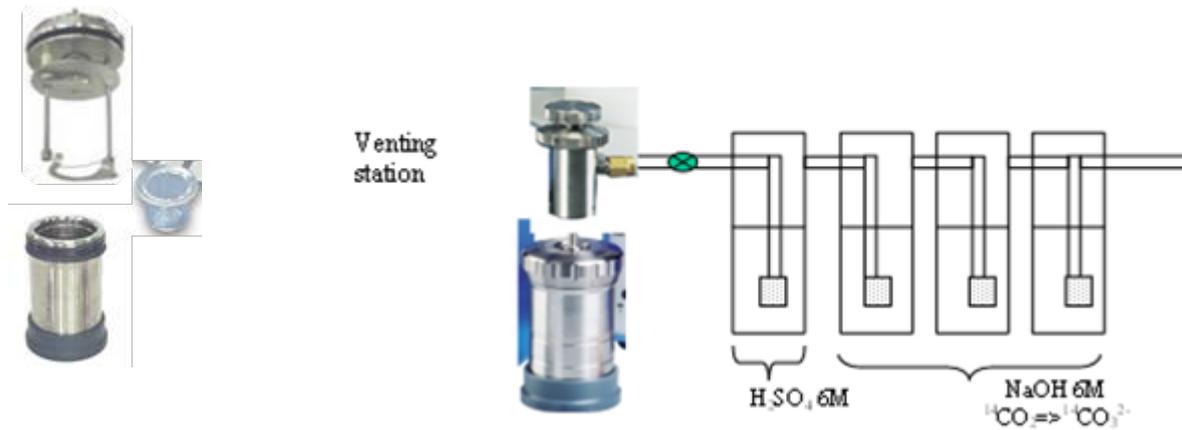


Figure 1. Parr bomb system at CEA

Tests on virgin IERs spiked with ^{14}C (as ^{14}C -carbonate or ^{14}C -glucose forms or both) were used to optimize the combustion and the concentration of the sodium hydroxide solutions. The main achievement was the optimization of the quantity of stable carbon carrier (**Table 2**).

The ^{14}C content was then then measured by Liquid Scintillation Counting Technique.

Table 2. Parameters for total dissolution of SIERs and ^{14}C total measurement by Parr bomb technique

Parameters	Optimum	Maximum
Mass of resin	0.3 g	0.4 g
Mass of the carbon carrier	0.2 g	0.2 g
Trapping solution	NaOH 2M 10 mL	NaOH 2M 10 mL
Trapping gas	Yes	Yes

NON-CATALYTIC OXIDATION

Non-catalytic combustion by flame oxidation method was used by RATEN-ICN partner. By this method, the resins samples are combusted in an oxygen-enriched atmosphere with a continuous flow of oxygen (using Sample Oxidizer equipment) (

Figure 2). By this combustion any hydrogen is oxidized to H_2O and any carbon is oxidized to CO_2 . Since the carbon dioxide readily reacts with compounds containing amines, the Carbo-Sorb® E was chosen to absorb the CO_2 released during combustion process. The carbamide solution was then measured by Liquid Scintillation Counting Technique using a Tri-Carb®

analyser Model 3110 TR., to determine the ^{14}C content. The detailed involved reactions AHN *et al.* [2013] and the specification of the used equipment are described in *Appendix II*.



Figure 2. Non-catalytic oxidation and collection of Carbon for total ^{14}C measurements in liquid samples

The Sample Oxider equipment allowed also the collection of the ^3H containing fraction of the IERs that was measured as an additional information.

Preliminary combustion tests were carried out using ion exchange resin samples spiked with the radionuclides – ^{14}C as sodium carbonate/bicarbonate and sodium acetate, ^3H , ^{60}Co , ^{137}Cs , ^{241}Am and ^{152}Eu – in order to optimize the combustion process and determine the recovery and memory effect of the combustion method. The labelled ion exchange resin sample was placed into a combustor-cone together with different volumes (between 0.1 and 0.5 ml) of combust aide (an agent that enhance the combustion process).

After preliminary combustion tests, the following experimental conditions for measuring the ^{14}C content in SIERs samples were selected (**Table 3**):

Table 3 - Parameters for Combustion of SIERs and ^{14}C total measurement by non-catalytic oxidation technique

Parameters	Optimized values
Mass of resin	0.15 g
Volume of the combustion enhancer (combust aide)	0.2 ml
Combustion time	3 minutes
Trapping solution	Carbo-sorb E

The ^{14}C recovery obtained in these combustion tests was ranging between 93.8 and 99.9%, with an average of 97.5% and standard deviation of 1.24. The memory effect was less than 0.04% and no gamma emitters were identified neither in the counting vial for ^{14}C measurement nor in the ^3H one.

The resins were filtered and dried before being combusted (average water content measured 60.1%). After combustion no other beta-gamma emitters were identified neither in the ^{14}C vials.

Some samples contained impurities, sediments and mud, due to the storage conditions and ageing, therefore it was necessary to separate resins beads from impurities and mud by rinsing and decantation. Rinsing distilled water was analysed to evaluate if any ^{14}C was released during the rinsing and decantation. It was found, that no ^{14}C species were released from spent resin during this process BUCUR *et al.* [2015].

ELEMENTAL COMBUSTION

Elemental combustor has been used by ENEA partner. The total Carbon content has been measured by an elemental combustor. The equipment runs two main chemical steps (**Figure 3**):

1) *Combustion*

- Sample combusts in furnace at 930°C;
- Jet injection of oxygen via lance right over/at sample (turbulent flow).

2) *Gas Separation*

- Helium carrier gas pushes combustion gases through analyzer.

Combustion gases of C, H and S (eventually) are trapped in separate columns, then sequentially released (“purge and trap”). The CO₂ is then measured by a Thermal Conductivity Detector (TCD).

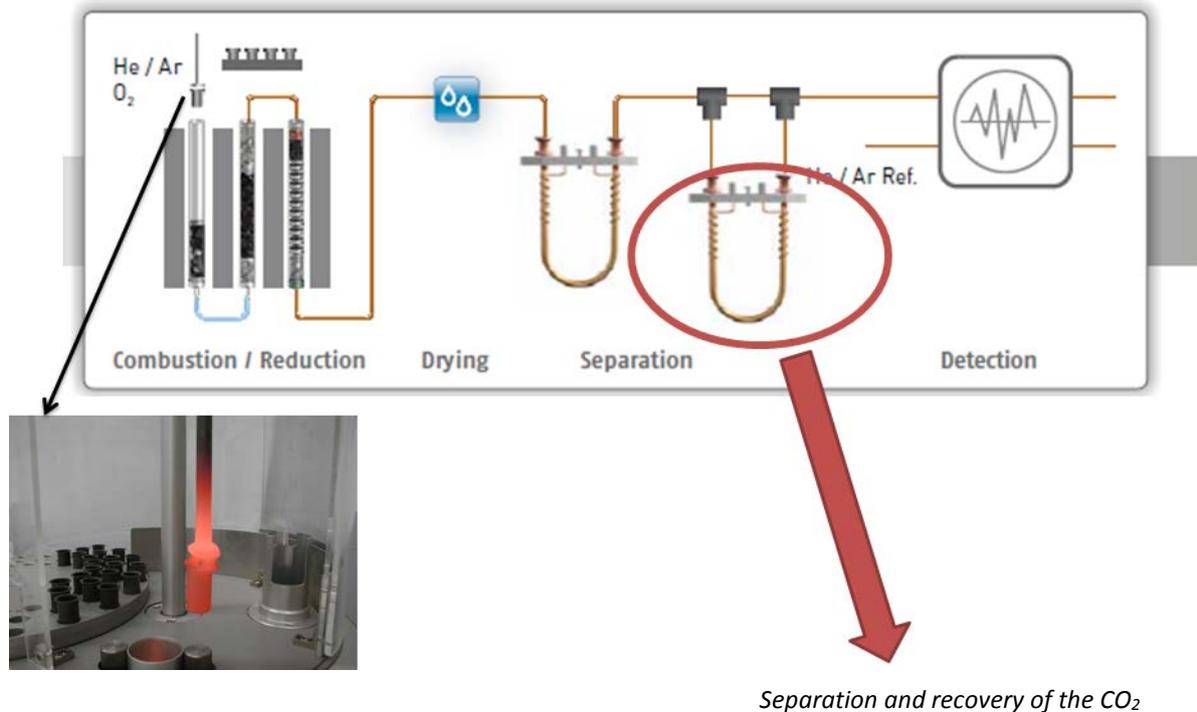


Figure 3. Total Carbon analyser at ENEA

The combustion temperature and the flux of oxygen were optimised in order to have a complete combustion and well separated release peaks on the detector.

3. EXPERIMENTAL DATA OF ¹⁴C INVENTORY

The source term determination by the measurement of the total ¹⁴C content in the SIERS are evidently incomparable among the partners, because of the difference in the reactor type, in the storage condition, in the sampling and the ageing, nevertheless a summary of the results has been given below in order to produce a reference database of the ¹⁴C inventory for some common categories of SIERS; it will provide support for the evaluation of the safety cases and the performance assessment of the radioactive waste repository.

Table 4 summarizes the results obtained by the partners on their analysed SIERS. It is necessary to underline that some partners selected a batch of samples with very similar characteristic, so only the medium average has been reported (CEA *Appendix I*, RATEN-ICN

Appendix II, UJV Appendix IV), on the other hand other partners have analysed a huge amount of samples (315 samples over a period of 7 years) for which ^{14}C inventory interval (min-max) has been reported (SKB, Appendix VI, FZY Appendix III). For all the studies the complete report of the data is attached in the appendices.

Table 4. ^{14}C total determination in SIERS

PARTNER	TYPE OF SIERS	^{14}C total inventory*
CEA	PWR (EDF-A) wet resins	5630 ± 325 Bq/g
CEA	PWR (EDF-A) dry resins†	$10754 \pm 680 \div 10930 \pm 760$ Bq/g (dry) (H ₂ O 40%) (H ₂ O 57%)
CEA	PWR (EDF-B) wet resins	2125 ± 200 Bq/g
SKB	CCU PWR wet resins	1470 Bq/g‡ (dry weight)
SKB	CCU PWR dried resins	$7.9 - 21$ Bq/g§ (dry weight)
SKB	BWR	$2200 - 6200$ Bq/g** (dry weight)
RATEN	CANDU SIERS wet	36500 ± 2220 Bq/g
UJV	PWR SIERS	45 ± 5 Bq/g
UJV	Research Reactor SIERS	2000 ± 280 Bq/g

* Where not specified, the activity is expressed for wet resins weight

† For EDF-A dry resins the range of ^{14}C content has been reported, as the two considered samples have different H₂O content.

‡ Appendix 1 in ARONSSON *et al.* [2016].

§ Appendix 21 in ARONSSON *et al.* [2016].

** Appendix 5 in ARONSSON *et al.* [2016].

The SKB results on wet and dried samples are based on fairly few samples, but they give a strong indication that drying reduces the concentration of ^{14}C and the main part of their ^{14}C activity has been released. This conclusion is supported by measurements of ^{14}C in the ventilation system – see Appendix 18 in ARONSSON *et al.* [2016].

WATER CONTENT IN EDF RESINS

It has been observed that the water content in the EDF resin samples can varies from 40% up to 58%. It seems difficult to have reproducible drying with such small quantities of samples. ^{14}C activities after drying were corrected by taking into account the weight of water to

compare the result without drying. This result have shown that the method developed for the total carbon by combustion under oxygen gives results that are quite close of the reference ($\pm 15\%$). This variation could be due to the water content.

It has been highlighted that the content of water is a critical parameters that affects the statistical calculation of the ^{14}C content for several batch of samples, as it was difficult to calculate average values for samples containing different water contents. The accuracy of the water content is affected by the small amount of samples so further investigation should be planned using a larger amount of SIERs. It is worthwhile to notice that the drying process itself, introduce a modification in the original samples and the possible loss of ^{14}C should be taken into consideration.

TOTAL CARBON CONTENT

ENEA has conducted investigation of the total carbon content on non-activated IERs (new and 12 years old) to provide auxiliary data on the composition of the resins and the effect of ageing, leading to the following results (**Table 5**).

Table 5 – Total Carbon content of ENEA IERs (fresh and aged)

Resin sample	C content %	notes
M500 anionic new	54.4 ± 0.2	Fresh non irradiated anionic resins
M500 anionic old	65.7 ± 0.4	12 years old non irradiated anionic resins
S100 cationic new	47.5 ± 0.6	Fresh non irradiated cationic resins
S100 cationic old	42.8 ± 0.6	12 years old non irradiated cationic resins

The results show that the ageing in closed container caused a decrease in C content in the cationic resins, which could be quantified in 10% of loss, whereas the anionic resins exhibit some anomalies (increase of C content) still to be investigated.

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¹⁴C SPECIATION

The results from MAGNUSSON AND STENSTRÖM [2005] and PARK *et al.* [2008] has showed that the majority of the ¹⁴C activity in SIERS comes from the inorganic (ion exchangeable) compounds. Particularly, in CANDU reactors, most ¹⁴C is retained in anion-exchange resins in inorganic form PARK *et al.* [2008]. A minor fraction of ¹⁴C-containing species has been measured in the cation-exchange resins, after their separation from a mixed bed [MOIR *et al.*, 1994; PARK *et al.*, 2008] probably under form of metal carbonate [MOIR *et al.*, 1994].

An important question, concerning the organic ¹⁴C, relates to its form:

- organic ¹⁴C in ionic form;
- organic ¹⁴C bound to the resins' backbone (non-ionic);
- organic ¹⁴C retained in particulate matter (only for powder resins).

In order to clarify the form of ¹⁴C, CAST partners have adopted different approaches:

- direct measurement of the species released into solution after regeneration of the resins by HPLC (quantification and qualification);
- in reference to the method reported in MAGNUSSON AND STENSTRÖM [2005] and PARK *et al.* [2008], related to the determination of the organic/inorganic ¹⁴C fractions, a slight modification of the procedure could allow the location of the organic ¹⁴C; in particular, after the first step (acidic regeneration), the separation of the solution from the resins, with a subsequent separate wet oxidation of the two fractions (resins/solution), could help understanding whether ¹⁴C is in ionic or non-ionic form;
- indirect measurement by combustion of fully regenerated resins could give information about the fraction of organic non-exchangeable ¹⁴C;
- the ¹⁴C retained in the resins' backbone or in the particulate matter, however, cannot be distinguished with the currently applied techniques; the implication of concentrated sulphuric acid, as reported in MAGNUSSON *et al.* [2008], would attack indistinguishably both materials; a separation of the two materials is rather challenging and requires additional efforts and experimental development.

3.1. ANALYTICAL METHODOLOGY FOR ¹⁴C SPECIATION

The first consideration for the speciation of ¹⁴C content in the SIERS is to differentiate between their organic and inorganic components.

The most used analytical method consists in a sequential extraction of inorganic ^{14}C and organic ^{14}C compounds using acid stripping and wet oxidation, adapted after the method developed by MAGNUSSON *et al.* [2008] for ^{14}C measurement in spent ion exchange resins and process waters.

CAST partners have used slightly different processes in order to collect the organic and inorganic fraction, optimizing their own methods accordingly with the nature of their samples.

“MAGNUSSON” SPECIATION SET UP

The experimental set-up used by RATEN-ICR, CEA and SKB, for release and separation of inorganic and organic ^{14}C is schematically presented in **Figure 4**. It consists in a reaction vessel, a separatory funnel, a nitrogen supply and a vacuum pump, two gas washing lines with a catalytic furnace between them.

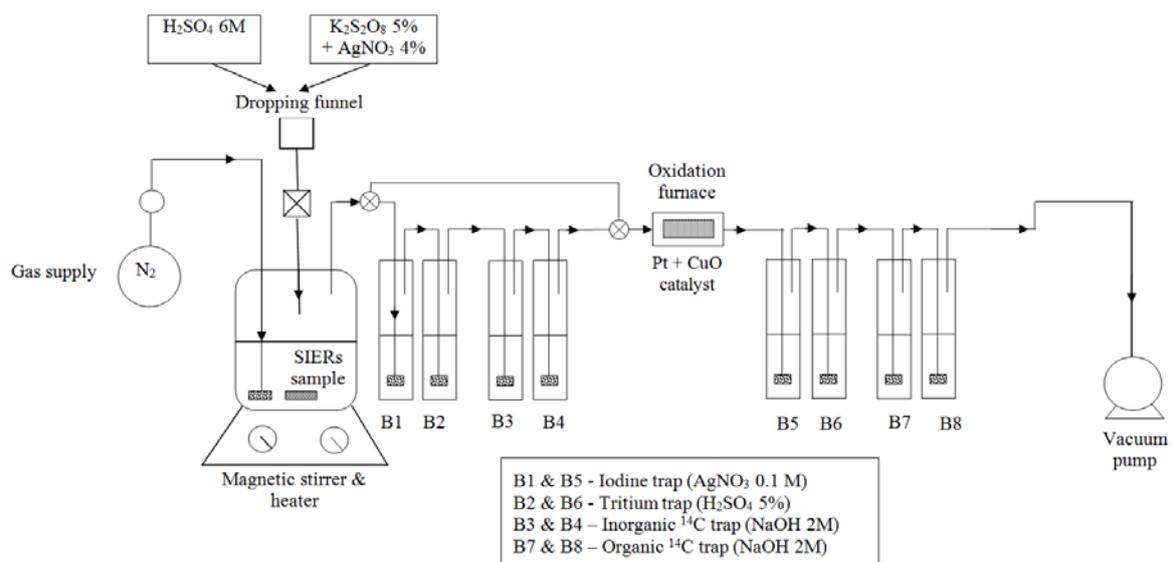


Figure 4. Scheme of experimental set-up for separation and purification of inorganic and organic ^{14}C compounds.

Since the inorganic ^{14}C compounds, *i.e.* carbonates and bicarbonates, are easily transformed by weak acids to carbon dioxide, the inorganic ^{14}C is released during acid stripping step of the analytical method mainly as $^{14}\text{CO}_2$ and the gases released are carried by the carrier gas through the first gas washing line. If any ^{14}C is released during this step as CO or other organic molecules, it passes through the scrubbing bottles of the first gas washing line and is

oxidized to CO₂ in the catalytic furnace and subsequently absorbed in the scrubbing bottles of the second gas washing line. After the acid stripping step is accomplished the first gas washing line is isolated from the system by means of three ways valves placed before the first scrubbing bottle and the fourth one.

Because the organic compounds have high bounding energies between atoms they are decomposed by strong oxidants such as potassium persulphate (K₂S₂O₈). Presence of a catalyser such as silver nitrate (AgNO₃) enhances the decomposition of the organic compounds. During the wet oxidation step the temperature of the solution in the reaction vessel is slightly increased to 90°C.

The mechanism of ¹⁴C-labelled organic compounds decomposition is based on the OH^(*) radicals [AHN *et al.*, 2013] and has been fully reported in *Appendix II*.

FZJ SPECIATION SET UP

During the CAST project FZJ partner has optimized the sequence of washing bottles for the radioanalytical analyses of ¹⁴C released in the gas phase, allowing a lower dilution of the ¹⁴C activity and an optimal volume for the ³H and ¹⁴C absorption. In particular, miniaturized washing bottles have been developed and tested, with a reduced volume and, accordingly, a reduced dilution of the activity – see D4.3 [BUCUR *et al.*, 2015].

The employment of CuO-Pt/Al₂O₃ in the oxidation furnace, has been abandoned due to the activity retention (memory effect) experienced during leaching tests with graphite. As an output of these tests , only CuO has been employed for the catalyser see D4.4 [COMTE *et al.*, 2017].

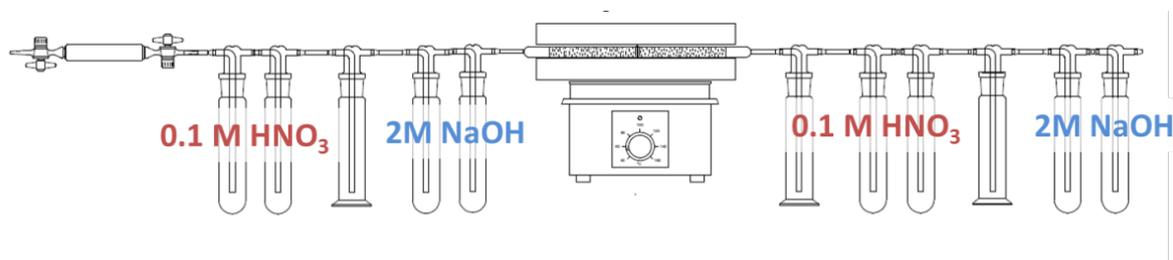


Figure 5. Experimental setup for the analysis of ¹⁴C designed by FZJ, with a catalyser to convert HT to HTO, CO to CO₂ and organics to CO₂.

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3.2. CHARACTERISATION OF THE SPECIATION SYSTEM

Preliminary acid stripping/wet oxidation tests were carried out using aqueous solutions spiked with the radionuclides of interest: inorganic ^{14}C (under the form of $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$), organic ^{14}C (sodium acetate and lauric acid), ^3H , and gamma emitters (^{60}Co , ^{137}Cs , ^{241}Am and ^{152}Eu).

For the ^{14}C -labelled sodium carbonate/bicarbonate component, the ^{14}C recovery was between 94.8 and 98.3%, and no gamma emitters were identified in any of the scrubbing bottles. The entire activity of ^{60}Co , ^{137}Cs , ^{241}Am and ^{152}Eu were found in the solutions sampled from the reaction vessel – with average recovery higher than 96%.

For ^{14}C -labelled sodium acetate component, it has been noted that the recovery of ^{14}C was quite low and a major amount was found in the gas washing after the acid stripping step, where we should expect to recover only the inorganic portion of the sample.

It was supposed that the sulphuric acid used in the acid stripping step could reduce part of the ^{14}C -labelled sodium acetate conducting at its release as $^{14}\text{CO}_2$ in the acid stripping step, as it was part of the inorganic component.

To assess how much from the ^{14}C under the form of sodium acetate is released in the acid stripping step two more tests were carried out only with ^{14}C -labelled sodium acetate solution. Only scrubbing bottles with alkaline solution were used for these tests – three before the catalytic furnace and two after it. The first two alkaline gas washing bottles were isolated by three ways valves placed before and after them (**Figure 6**) after the acid stripping step of the analytical method.

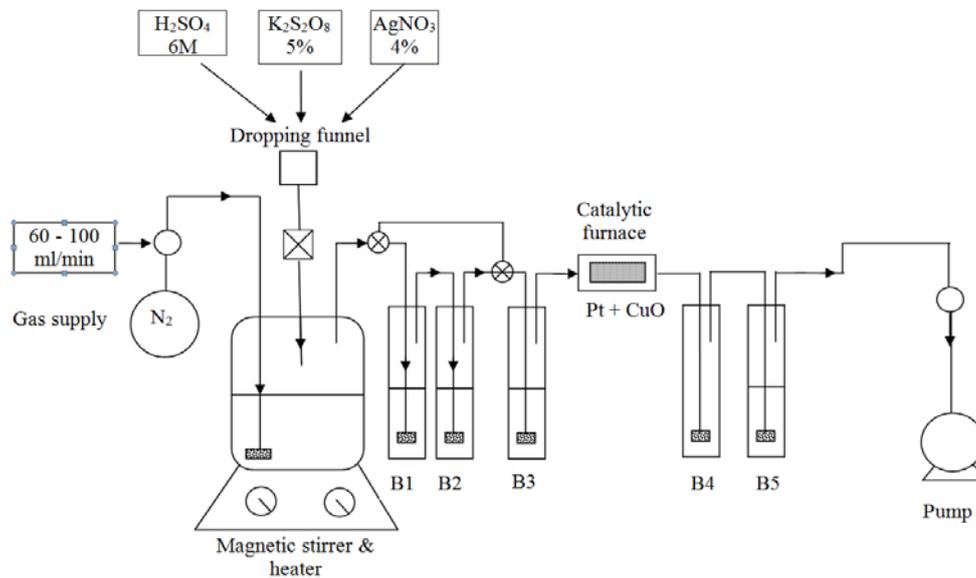


Figure 6. The experimental set-up used by RATEN to evaluate the ^{14}C released from the ^{14}C -labelled sodium acetate.

These tests showed that around 40% from the ^{14}C activity introduced in the reaction vessel was released as $^{14}\text{CO}_2$ in the acid stripping step and the rest after the wet oxidation.

A hypothesis that could explain the results of these tests is that the ^{14}C -labelled sodium acetate could be degraded and contains not only ^{14}C -labelled sodium acetate but also some ^{14}C -labelled carbonate. To test it, an acidification of a ^{14}C -labelled sodium acetate solution in fume hood was performed using both sulphuric acid and nitric acid to adjust the solution pH at 5 – assuming that the ^{14}C as sodium carbonate is released as $^{14}\text{CO}_2$ at pH around 5.4. By measuring the ^{14}C activity in the initial solution and after its acidification it was observed that indeed around 40% of the ^{14}C activity was released only by adjusting the pH to 5.

A further test was made using another organic labelled compound (a solution containing ^{14}C -labelled lauric acid). In these tests, good recoveries were obtained both for ^{14}C in inorganic form (as $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$) and organic form (as lauric acid) and no other radionuclides were identified. The recovery of ^{14}C -labelled lauric acid was around 98% and it was concluded that the proposed analytical method can be used to evaluate the inorganic and organic ^{14}C content in CANDU SIERS.

The experimental conditions chosen for the inorganic and organic ^{14}C measurement in CANDU SIERS were detailed in **Table 6**.

Table 6. Parameters for inorganic and organic ^{14}C measurement in CANDU SIERS

Resin mass	1 g
Mass of the carbon carrier	0.2 g
Carrier gas flow	60-80 ml/min
Stripping acid	20 ml of H_2SO_4 6M
Oxidation reagents	10 ml $\text{K}_2\text{S}_2\text{O}_8$ + 4 ml AgNO_3
Alkaline trapping solution	50 ml of NaOH
Gas flushing during acid stripping	1 hour
No. of wet oxidation cycles	3
Gas flushing during wet oxidation	1 hour / each cycle

CEA SET UP FOR SPECIATION

Similar tests have been performed by CEA, using the set up shown in **Figure 7**. A first step consists in introducing the sample in a glass reactor and mixing it with acidic solutions to provide the degassing of CO_2 and to trap 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 the ^{14}C was performed by a hot acidic dissolution with oxidizing reagent. Some experiments on virgin IERs spiked with ^{14}C as ^{14}C -carbonate or ^{14}C -glucose forms, or both, were done to optimize parameters of the dissolution to achieve the total recovery of ^{14}C and a good selectivity between mineral and organic form.

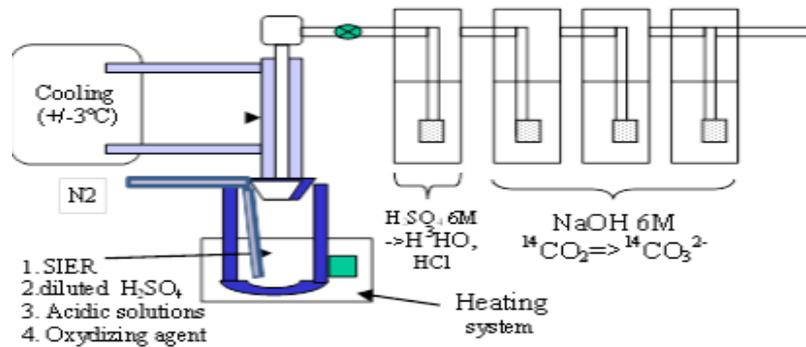


Figure 7 Set up of the CEA Carbon speciation system

All the parameters were optimized (**Table 7**) and the results showed that the recovery yield of ^{14}C was upper 95% for mineral form and upper 90% for organic without cross-contamination (**Table 8**)

Table 8.

Table 7 – Optimised parameters for the CEA Carbon speciation system

Mass of resin (g)	^{14}C	Solution	Carrier	Heating	Degasing
0.25	Mineral	5 mL H_2SO_4	Yes	NO	1 h
to					
0.5	Organic	30 mL $\text{H}_2\text{SO}_4/\text{HNO}_3 + \text{H}_2\text{O}_2$	No	3 h	3 h

Table 8. ^{14}C recovery and selectivity.

^{14}C recovery and selectivity	Identified as mineral	Identified as organic
Mineral origin	>95%	>3%
Organic origin	<6%	>90%

The results from CEA and RATEN-ICN show that in all the cases, mineral or organic or both forms, the recovery of ^{14}C is complete (100%).

ENEA SPECIATION SET-UP

ENEA has designed and implemented a targeted device (**Figure 8**), with a double chamber combustion cell, in order to run stepped combustion of ionic resins samples to obtain different volatile/non-volatile fractions.

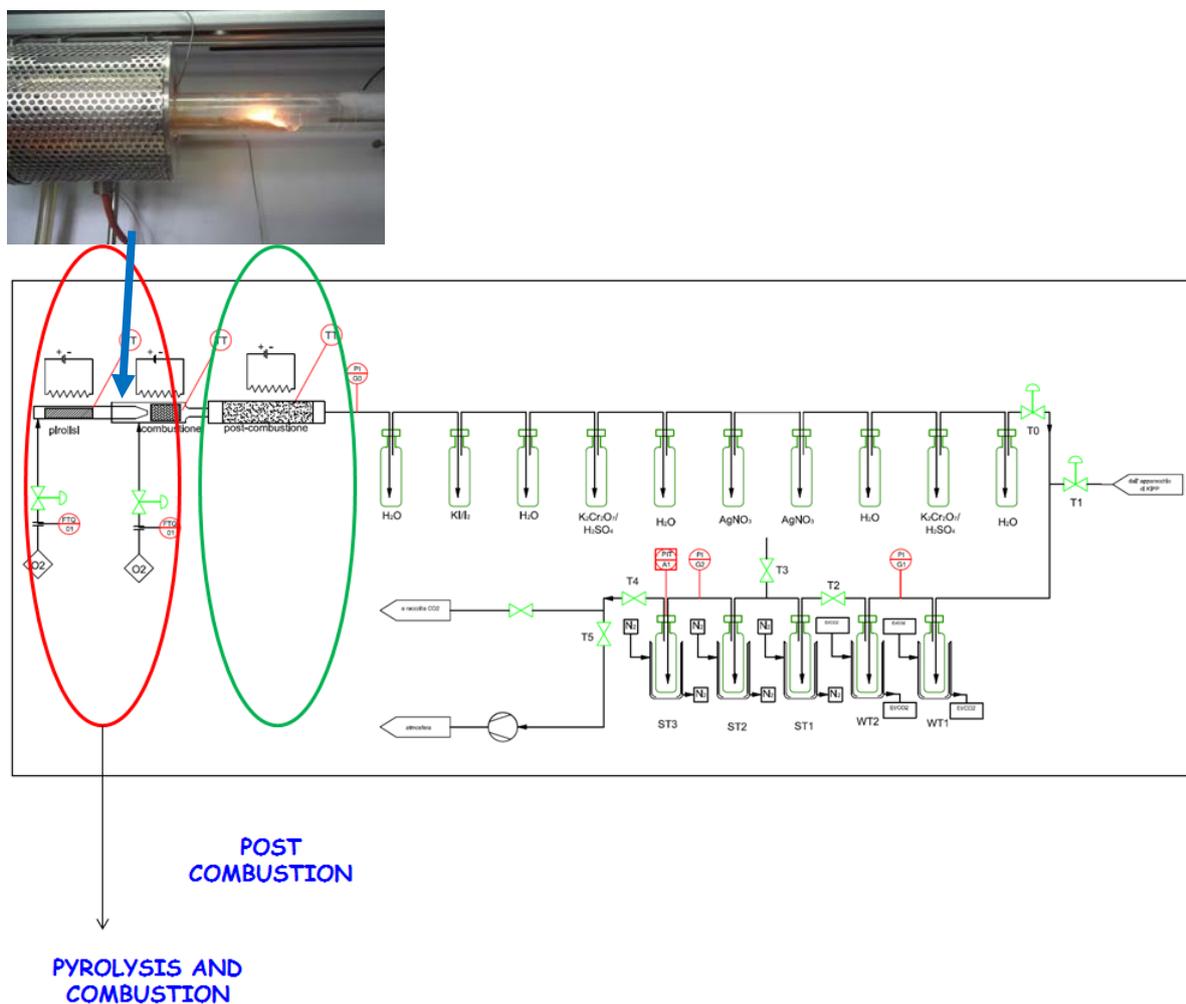


Figure 8. Equipment for stepped combustion of organic materials for benzene LSC analysis at ENEA ^{14}C laboratory.

The system has been tested with standard samples and has shown recovery of total carbon up to 80% (in terms of yield of benzene synthesis) and up to 98% (in terms of CO_2).

4. EXPERIMENTAL DATA OF ¹⁴C SPECIATION

The speciation experiment conducted by CAST partners has led the following results (Table 9). Available results seem to show that in the majority of the samples the ¹⁴C activity comes mainly from the inorganic part, with some discrepancies.

Table 9. ¹⁴C speciation between mineral and organic forms in SIERS.

Partners	ref	State	¹⁴ C form	¹⁴ C content (Bq/g)* (% of total)
CEA	EDF–A PWR	Wet sample	Mineral form	76.6 %
			Organic form	23.4 %
CEA	EDF–A PWR [†]	Dry sample	Mineral form	23.9 % ÷ 60.3 %
			Organic form	39.7 % ÷ 73.6 %
CEA	EDF–B PWR	Wet sample	Mineral form	2.8 %
			Organic form	97.2 %
RATEN-ICN	CANDU ^{‡2}	Wet samples	Mineral form	93.1 %
			Organic form	6.9 %
SKB [§]	CCU BWR	Wet samples	Mineral form	95-99 %
			Organic form	1-5 %
SKB ^{**}	CCU BWR	Dried samples	Mineral form	8%
			Organic form	92%
SKB	RWCU PWR	Wet samples	Mineral form	70 %
			Organic form	30 %
UJV	EDU-PWR	Wet samples	Mineral form	29.2 %
			Organic form	70.8 %
UJV	ETE-PWR	Wet samples	Mineral form	37.2 %
			Organic form	62.8 %
UJV	UJV-PWR	Wet samples	Mineral form	96.2 - 100%
			Organic form	3.8 – 0 %

* for EDF PWR samples the average values (over 3 samples) has been reported except for EDF-B, for CANDU samples the average value (over 5 samples) has been reported

[†] For the sample EDF –A (dry) the range of values has been reported as the different samples used for the tests exhibit different water content.

[§] For SKB samples the ¹⁴C was originally reported as Bq/MWth so, for simplicity, only the percentage has been reported

^{**} The release of ¹⁴C in the drying process has been measured in the exhaust air from the dryer. The release seems to be nearly 100 % for inorganic ¹⁴C, which the analyses of dried samples show. The sampling equipment was not designed to measure release of organic ¹⁴C

RATEN ICN CANDU samples

In CANDU reactors, the major part is retained as the inorganic form and this is in complete agreement with the literature data. Regarding the speciation between mineral and organic species, the results obtained show that the ^{14}C in the CANDU SIERS analysed is predominantly as inorganic form and only less than 7% from the measured ^{14}C is present as organic form.

Since the main source of the CANDU analysed spent resin is moderator purification system and in the CANDU moderator the major chemical form of ^{14}C is as bicarbonate, the chemical form of ^{14}C absorbed on the resin is also mostly probably bicarbonate ($\text{H}^{14}\text{CO}_3^-$).

EDF PWR samples

However, results on the partition of inorganic and organic molecules for PWRs and BWRs are contrasting. For EDF PWR samples the results obtained by the acidic dissolution methods have been compared with the total ^{14}C measurements and they show some discrepancies (**Table 10**). ^{14}C measurements showed that activities – mineral, organic, and total – are not similar. One reason for the discrepancy in the dry resin could be related with a possible loss of ^{14}C , mainly the mineral form, during the analytical process.

Table 10. Comparison of the method for the effect of drying for total ^{14}C determination. Experiment on EDF-A sample

Measure	Total ^{14}C	Total ^{14}C
	combustion with oxygen	Acidic dissolution
N°1		4060 ± 170 Bq.g ⁻¹ dry (H ₂ O = 19.6%) 3255 ± 139 Bq.g⁻¹ wet
N°2	10745 ± 680 Bq.g ⁻¹ dry (H ₂ O = 40%) 6470 ± 410 Bq.g⁻¹ wet	4860 ± 215 Bq.g ⁻¹ dry (H ₂ O = 47%) 2580 ± 115 Bq.g⁻¹ wet
N°3	10930 ± 760 Bq.g ⁻¹ dry (H ₂ O=57%) 4950 ± 300 Bq.g⁻¹ wet	2550 ± 120 Bq.g ⁻¹ dry (H ₂ O=58%) 1070 ± 50 Bq.g⁻¹ wet
Reference ^{14}C content	5630 ± 325 Bq.g⁻¹ wet	

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The entire tests were performed on EDF-A sample. The water content in the resin samples varies according to the tests from 40 % up to 58 %. This variation is probably due to the individual drying of each sub-sample before analyses. It seems difficult to have reproducible drying with such small samples. One experiment gave a very low content of water about 20 % which was not confirmed by the others sub-samples.

^{14}C activities after drying were corrected by taking into account the weight of water to compare the result without drying. This result shows that the method developed for the total carbon by combustion under oxygen gives individual results which are quite close of the reference ($\pm 15\%$). The variation between the two individual determinations could be due to the uncertainty in the water content. The accuracy of the water content can be improved by drying a larger amount of SIERS. However, the ‘wet’ mean ^{14}C activity for the two determinations is very close to the reference result, i.e. 5710 Bq.g^{-1} compared to the reference result of 5630 Bq.g^{-1} .

The results obtained by the acidic dissolution methods are different. ^{14}C measurements show that activities – mineral, organic, and total – are not similar for replicate determinations. This method does not seem to be adapted for “dry resin”, maybe because of a loss of ^{14}C , mainly the mineral form, during the analytical process. This result is not understood up to now because the same methodology was applied on wet or dry resin. The measurement of the chemical carrier (carbonate) gives a chemical yield around 100 % in all the case.

This indicates that the analytical methodology for determination of the ^{14}C mineral amount for this type of sample must be reviewed.

Similar test has been carried out on CANDU SIERS and no discrepancies were found: the total ^{14}C content in the analysed samples are quite closed with the value determined by combustion (around 92% from the value determined by combustion), demonstrating the good recovery of the acid stripping/wet oxidation method.

SKB BWR and PWR samples

SKB samples exhibit similar behavior. These results are based on fairly few samples, but they give a strong indication that the dried resins have released the main part of their ^{14}C activity to

air. This conclusion is supported by measurements of ^{14}C in the ventilation system – see Appendix 18 in ARONSSON *et al.* [2016]. In particular 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.

UVJ PWR samples

For UVJ samples (*Appendix IV*) the organic content were determined by difference between the amounts of total and inorganic ^{14}C in the material, measured by acidic dissolution and they also exhibit contrasting measurement.

SKB analysis of formic acid

A further test has been made by SKB to investigate the presence of formic acid in the SIERS. The experimental systems details are described in Appendix VI. The tests were performed on three BWR CCU and one sample from PWR BTRS (last column).

The results obtained were shown in **Table 11**.

Table 11 Analysis of organics forms (including formic acid) of ^{14}C in SKB BWR and PWR samples

Sample	O3-3			O12-33			Prov 3*			BTRS**
	Conc. Bq/kg	Std. Dev.	Det.Lim., Bq/kg	Conc. Bq/kg	Std. Dev.	Det.Lim., Bq/kg	Conc. Bq/kg	Std. Dev.	Det.Lim., Bq/kg	Conc. Bq/kg
Inorganic	1.37E+06	2.0%	7.92E+02	1.87E+05	2.1%	7.92E+02	7.66E+05	2.0%	7.68E+02	2.10E+04
Formic Acid (FA)	1.37E+04	4.2%	7.95E+02	7.66E+03	6.4%	7.95E+02	1.31E+04	4.3%	7.70E+02	2.99E+03
Other Organics	1.69E+03	22%	7.95E+02	6.48E+02	58%	7.95E+02	1.13E+04	4.7%	7.70E+02	1.98E+05
Total organic	1.54E+04	4.5%		8.31E+03	7.5%		2.44E+04	3.1%		1.99E+05
Total C-14	1.39E+06	1.9%		1.95E+05	2.0%		7.90E+05	1.9%		2.20E+05
Total org. fract.	1.1%			4.3%			3.1%			90%
FA fraction	1.0%			3.9%			1.7%			1.4%
FA/tot.org.	89%			92%			54%			1.5%
* Sample from F12; no more data available										
** Boron Thermal Regeneration System; from R3 and R4										

The BWR CCU samples gave a high fraction of formic acid, while the PWR BTRS sample gave a very low fraction of formic acid. A possible explanation for the low yield of formic acid may be the absence of iron oxides, since the BTRS resins have a position in the system

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where iron and iron oxides have already been separated. Another possible explanation may be that part of the ^{14}C in BTRS resins are present as elementary carbon.

These experiments show, on the one hand, that the samples are heterogeneous because they correspond to mixtures of different purification circuits and on the other hand that new analytical methodologies have to be developed. In conclusion, further measures are needed to allow a statistical approach and obtain significant results on the evaluation of the ^{14}C source term (inventory and speciation).

5. CONCLUSIONS

The wide range of ^{14}C inventory values shows that it's not possible to simply estimate the ^{14}C source term for ionic exchange resins but an accurate sampling and analysis programme has to be developed and executed.

Available results on the speciation of ^{14}C originated from SIERS – partition between inorganic (carbonate) and organic fractions – seem to show that the majority of the ^{14}C activity comes from the inorganic part. In particular, for CANDU reactors, the major part is retained in anionic exchange resins in an inorganic form. A minor fraction of ^{14}C -containing species were found in cation-exchange resins and were probably in the form of metal carbonates. However, results on the partition of inorganic and organic molecules are sometimes contrasting for PWRs, spanning between 30% up to 99% for the inorganic fraction. The BWR speciation seems to be more constant within a large amount of samples (SKB samples) ranging from 1% up to 5 % for the organic fraction, but it has been shown that the dryer procedure has strong influences on the speciation: its speciation ratio in the dried samples is completely reversed (92 % organic form) as if the mineral form was mainly lost during the drying for BWR samples.

Sampling a large number of samples over long time periods covered are factors favouring the final results and the understanding of the source term.

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