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CArbon-14 Source Term

CAST

Final report on the estimation of the source term and speciation of ^{14}C in spent ion-exchange resins (D 4.5)

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EURATOM

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.

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 Zircaloys and from the leaching of ion-exchange resins and irradiated graphites under geological disposal conditions, its speciation and how these relate to carbon-14 inventory and aqueous conditions. These results will be evaluated in the context of national safety assessments and disseminated to interested stakeholders. The new understanding should be of relevance to national safety assessment stakeholders and will also provide an opportunity for training for early career researchers.

For more information, please visit the CAST website at: http://www.projectcast.eu

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Final report on the estimation of the source term and speciation of 14C in spent ion-exchange resins (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 was found in cation-exchange resins and was probably in 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 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 amounts of IERs are used in water clean-up systems in the reactor coolant. Even if spent ion-exchange resins (SIERs) are not planned to be disposed in deep underground systems but in subsurface storage, the release of ^{14}C from 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 a 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 intends to collect all the available information, from the partners of WP4 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.

A 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 SIER 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 SIER types and locations within the reactor operating circuits;
- ^{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 ^{14}C speciation has been acquired determining its repartition between organic and organic form followed by more detailed speciation and content analysis, aimed at determining 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 report 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 also been conducted in order to set up the better procedure. The partners have chosen different analytical approaches for their samples, according to the typology of their samples.

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 others to fresh ones, so it was not possible to have very similar samples among the partners—as it had been considered desirable 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 with a view to 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;
- 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.

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

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[*] 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)	• SIERS from 5 different EDF nuclear reactors (PWR) • Non-irradiated IERs	Wet and dry beads (mixed anionic and cationic)
ENEA (Italy)	• IERS from PWR Trino NPP • non irradiated IERs stored for 10 years and of recent production	Wet beads (mixed anionic and cationic)
FZJ (Germany)	• SIERs from BWR (S)	Wet and dry beads, powder
ICN (Romania)	• SIERs from Cernavoda NPP storage tanks or non-fuel contact purification system	Wet and dry beads (mixed anionic and cationic)
SKB (Sweden)	• SIERS from Condensate Clean-up (BWR) • SIERS from Reactor Water Clean-up (PWR)	Wet and dry beads (mixed anionic and cationic)
UJV (Czech Republic)	• SIERs from PWR and	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.

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 have commissioned analyses of an important amount of data, consisting of 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 ^{14}C 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.

2.2.1. HIGH PRESSURE COMBUSTION (PARR BOMB)

The high pressure combustion (using the *Parr bomb* technique) was chosen by CEA: it was carried out under O_2 pressure (25 bars) in a closed system and the produced CO_2 was trapped in sodium hydroxide solution as carbonate by degassing the system under a venting station and letting the gases flush into sodium hydroxide bubblers (Figure 1).

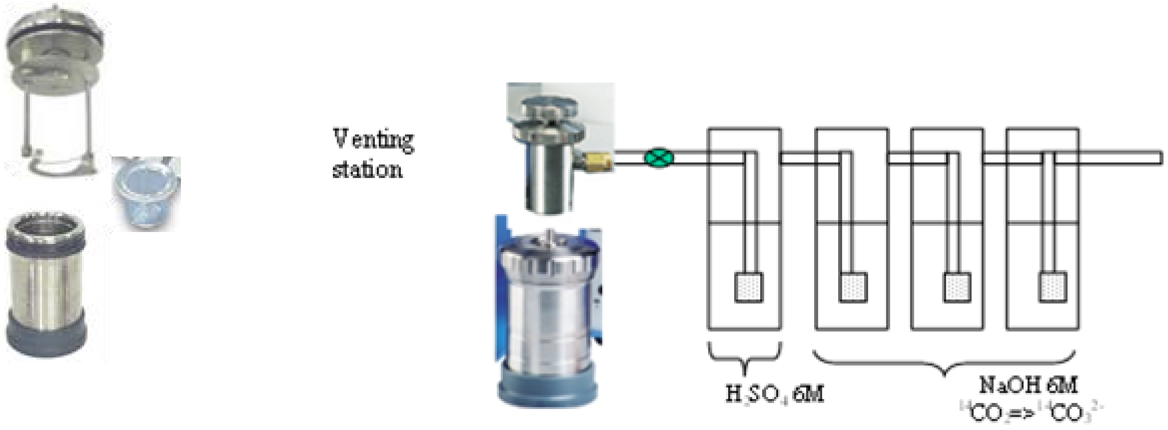


Figure 1. Parr bomb system at CEA

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 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

2.2.2. 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 carbammide 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*.

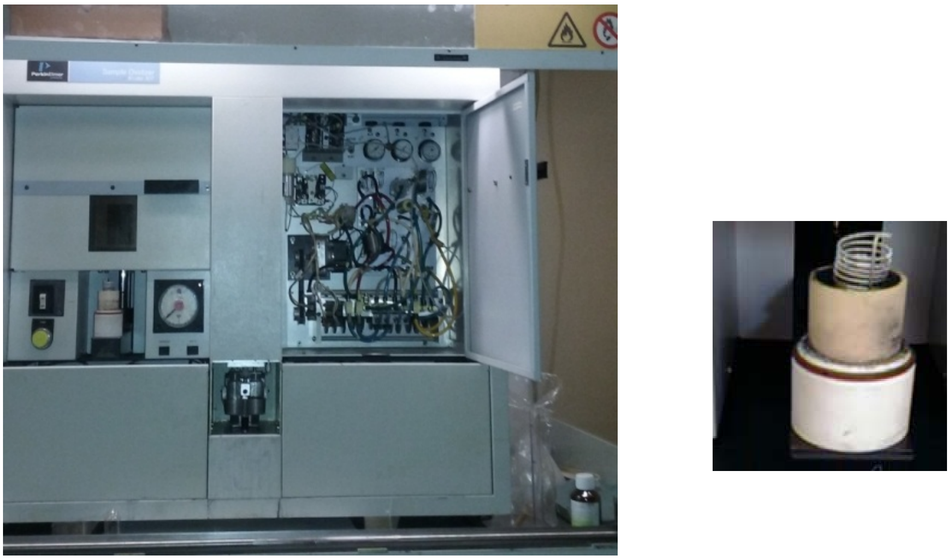


Figure 2. Non-catalytic oxidation and collection of carbon for total ^{14}C measurements in liquid samples

The Sample Oxider equipment also allowed the collection of the ^{3}H 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—, ^{3}H, ^{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 14C 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 ranged 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 either in the counting vial for ^{14}C measurement or in the ^{3}H 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 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].

2.2.3. ELEMENTAL COMBUSTION

Elemental combustion 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):

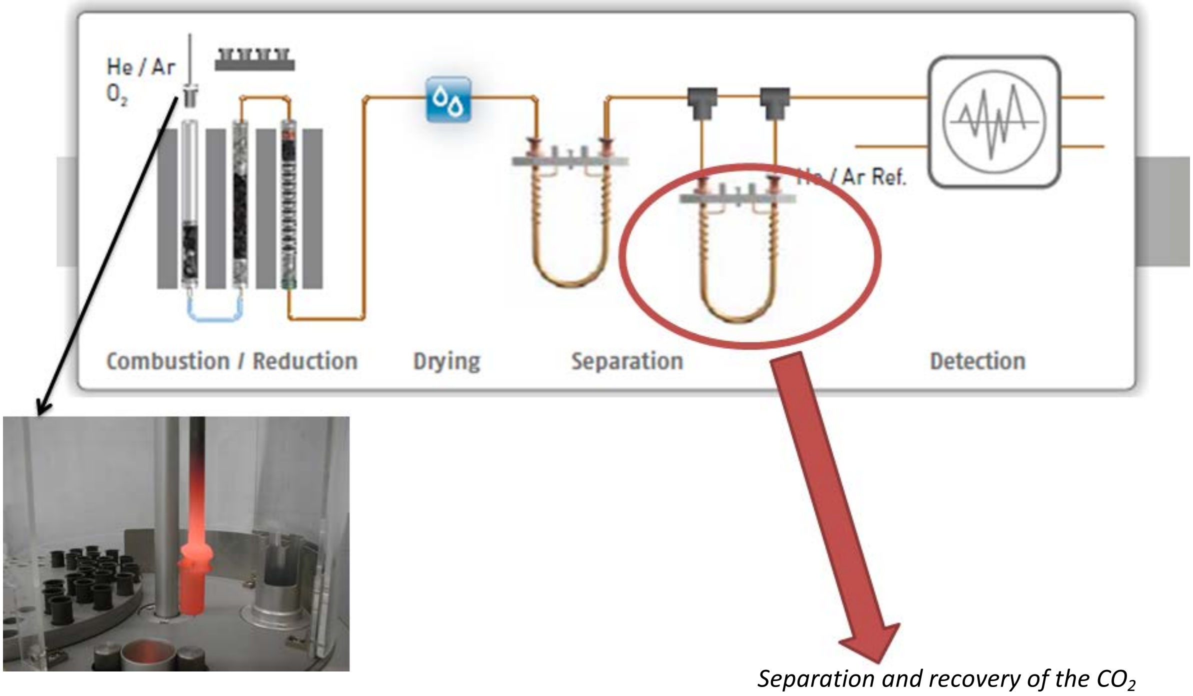
1) *Combustion*

- 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 CO_2 is then measured by a Thermal Conductivity Detector (TCD).



Separation and recovery of the CO_2

Figure 3. Total Carbon analyser at ENEA

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

3. EXPERIMENTAL DATA OF ^{14}C INVENTORY

The source term determinations by the measurement of the total ^{14}C content in the SIERs are evidently incomparable among the partners, because of the differences 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 ^{14}C

inventory for some common categories of SIERS; it will provide support for the evaluation of the safety cases and the performance assessment of a radioactive waste repository.

Table 4 summarizes the results obtained by the partners for their analysed SIERs. It is necessary to underline that some partners selected a batch of samples with very similar characteristic, so only the averages 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*, FZJ *Appendix III*). For all the studies, the complete reporting 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± 680 ÷ 10930 ±760 Bq/g (dry) (H_2O 40%) (H_2O 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 H_2O 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 only a few samples, but they give a strong indication that drying reduces the concentration of ^{14}C in the resins and that 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].

3.1. *WATER CONTENT IN EDF RESINS*

It has been observed that the water content in the EDF resin samples 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 mass of water to compare the result without drying. This result has shown that the method developed for the total carbon by combustion under oxygen gives results that are quite close to the reference (± 15%). This variation could be due to 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 introduces a modification in the original samples and the possible associated loss of ^{14}C should be taken into consideration.

3.2. *TOTAL CARBON CONTENT*

ENEA has conducted an 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.

4. ^{14}C SPECIATION

The results from MAGNUSSON AND STENSTRÖM [2005] and PARK *et al.* [2008] have showed that the majority of the ^{14}C activity in SIERS comes from the inorganic (ion exchangeable) compounds. Particularly, in CANDU reactors, most ^{14}C is retained in anion-exchange resins in inorganic form [PARK *et al.*, 2008]. A minor fraction of ^{14}C-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 the form of metal carbonate [MOIR *et al.*, 1994].

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

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

In order to clarify the form of ^{14}C, 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 ^{14}C fractions, a slight modification of the procedure could allow the location of the organic ^{14}C; 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 regarding whether ^{14}C 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 ^{14}C;
- the ^{14}C retained in the resins' backbone or in the particulate matter, however, cannot be distinguished with the currently applied techniques; the use 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.

4.1. *ANALYTICAL METHODOLOGY FOR ^{14}C SPECIATION*

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

The most used analytical method consists of 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.

4.1.1. “MAGNUSSON” SPECIATION SET UP

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

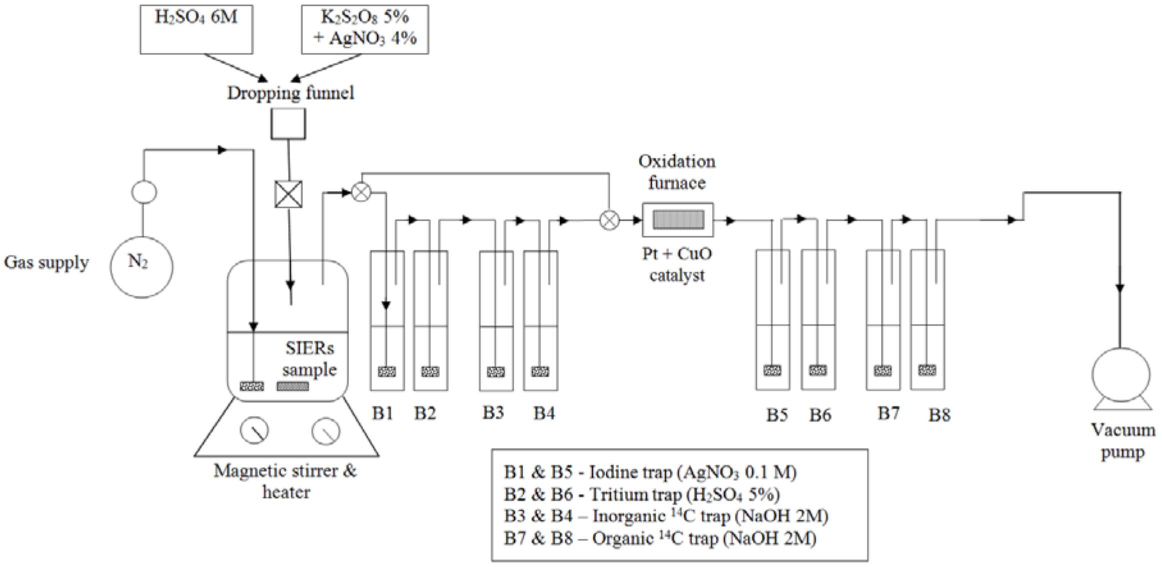


Figure 4. Scheme of experimental set-up for separation and purification of inorganic and organic ^{14}C compounds.

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 the acid stripping step of the analytical method mainly as $^{14}CO_2$ 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 CO_2 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-way 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 persulfate ($K_2S_2O_8$). The presence of a catalyser, such as silver nitrate ($AgNO_3$), 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 ^{14}C-labelled organic compounds decomposition is based on the $OH^{(*)}$ radicals [AHN *et al.*, 2013] and has been fully reported in *Appendix II*.

4.1.2. FZJ SPECIATION SET UP

During the CAST project FZJ partner has optimized the sequence of washing bottles for the radioanalytical analyses of ^{14}C released in the gas phase, allowing a lower dilution of the ^{14}C activity and an optimal volume for the ^{3}H and ^{14}C 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/Al_2O_3 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].

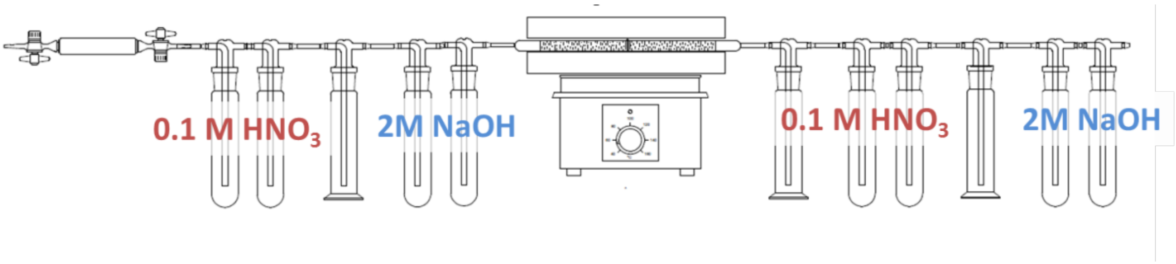


Figure 5. Experimental setup for the analysis of ^{14}C designed by FZJ, with a catalyser to convert HT to HTO, CO to CO_2 and organics to CO_2.

4.2. 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 $Na_2CO_3/NaHCO_3$), organic ^{14}C (sodium acetate and lauric acid), ^{3}H, 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 total activities 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 the ^{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 line after the acid stripping step, where we should expect to recover only the inorganic portion of the sample. It was inferred that the sulphuric acid used in the acid stripping step could reduce part of the ^{14}C-labelled sodium acetate, progressing at its release as $^{14}CO_2$ 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-way valves placed before and after them (Figure 6), after the acid stripping step of the analytical method.

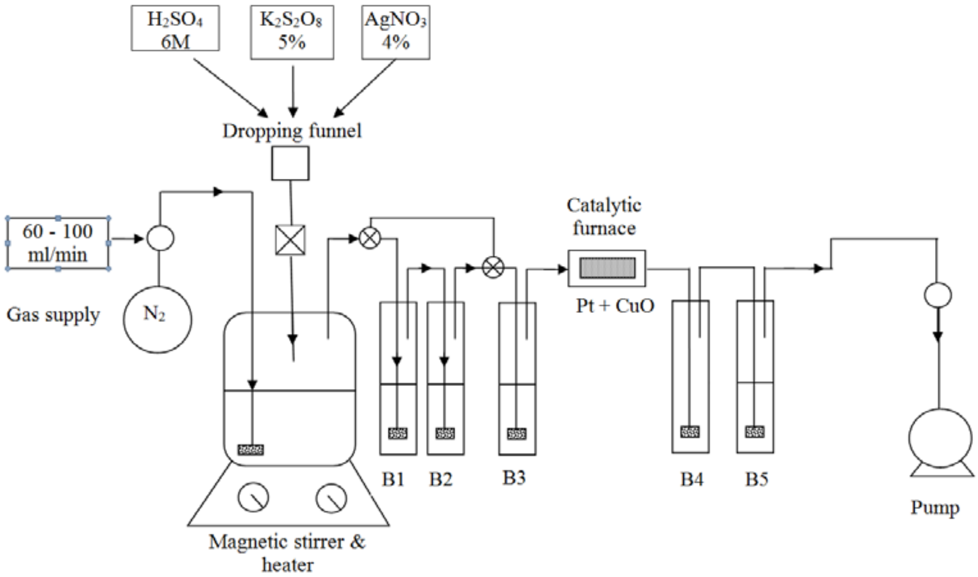


Figure 6. The experimental set-up used by RATEN to evaluate the ^{14}C released from the ^{14}C-labelled sodium acetate.

These tests showed that around 40% from the ^{14}C activity introduced in the reaction vessel was released as $^{14}CO_2$ in the acid stripping step and the rest after 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 this hypothesis, an acidification of a ^{14}C-labelled sodium acetate solution in a 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 $^{14}CO_2$ 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 $Na_2CO_3/NaHCO_3$) 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 are 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 $K_2S_2O_8$ + 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

4.2.1. CEA SET UP FOR SPECIATION

Similar tests have been performed by CEA, using the set up shown in Figure 7. A first step consists of 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.

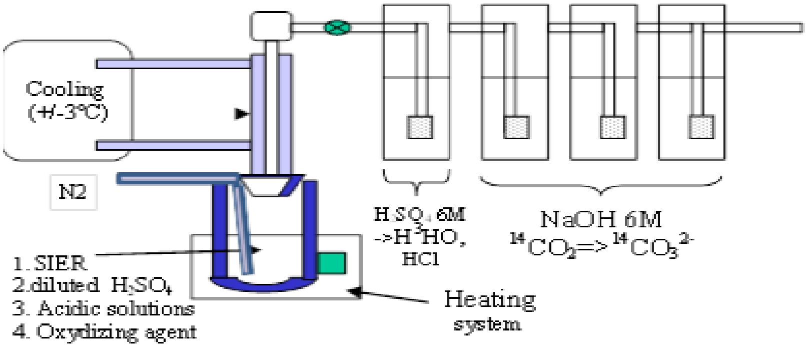


Figure 7 Set up of the CEA Carbon speciation system

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 to 0.5	Mineral	5 mL H_2SO_4	Yes	NO	1 h
	Organic	30 mL H_2SO_4/HNO_3 + H_2O_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%).

4.2.2. 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.

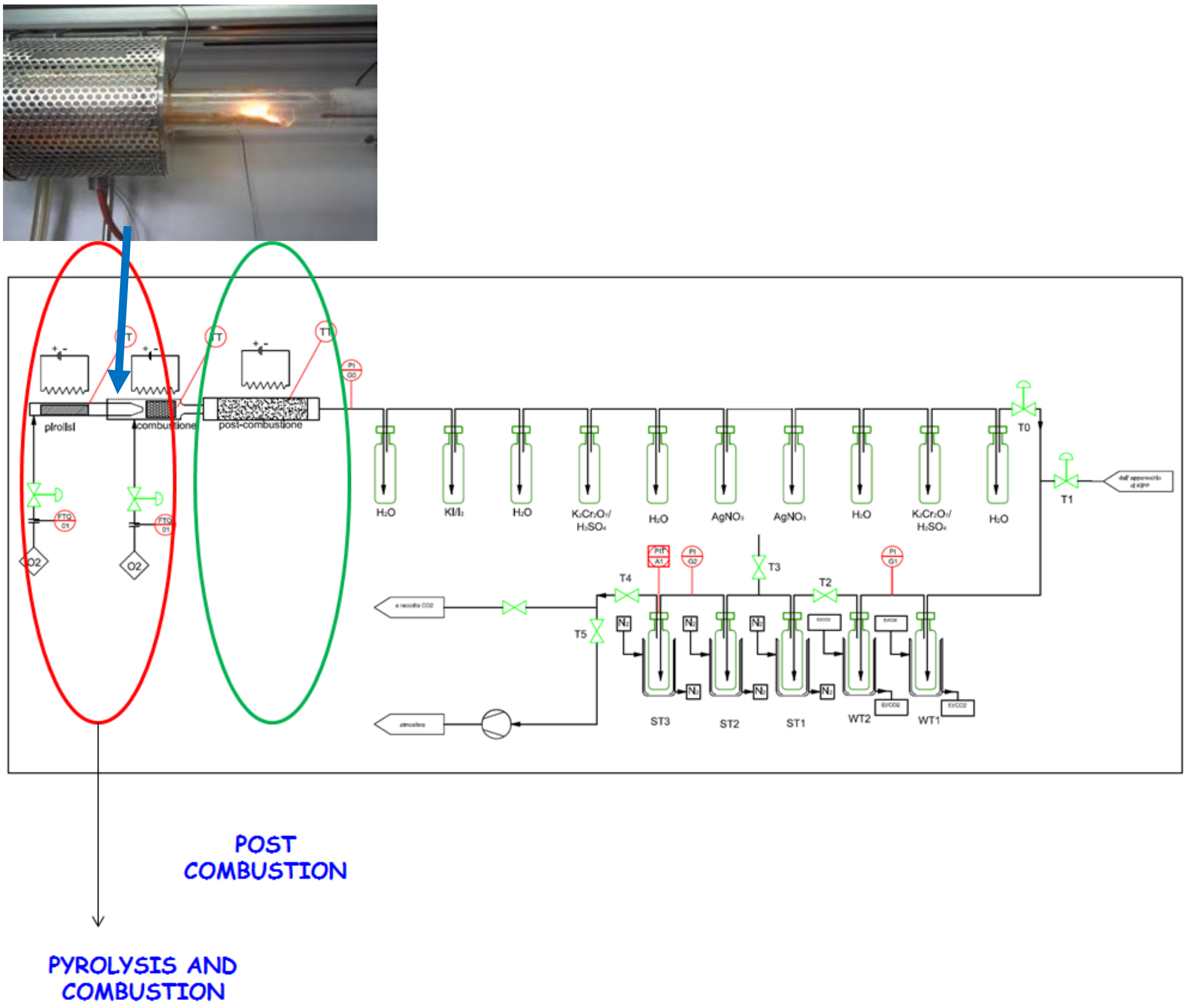


Figure 8. Equipment for stepped combustion of organic materials for benzene LSC analysis at ENEA ^{14}C laboratory.

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) ad up to 98% (in terms of CO_2).

5. EXPERIMENTAL DATA OF ^{14}C 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. ^{14}C 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[‡*]	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 %**

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[*] 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 ^{14}C was originally reported as Bq/MWhth so, for simplicity, only the percentage has been reported

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

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 %**

<u>RATEN ICN CANDU samples</u>

In CANDU reactors, the major part of ^{14}C 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 in 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 from 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 ($H^{14}CO_3^-$).

<u>EDF PWR samples</u>

However, results for 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** **combustion with oxygen**	**Total ^{14}C** **Acidic dissolution**
N°1		4060 ± 170 Bq.g^{-1} dry (H_2O = 19.6%) **3255 ± 139 Bq.g^{-1} wet**
N°2	10745± 680 Bq.g^{-1} dry (H_2O = 40%) **6470 ± 410 Bq.g^{-1} wet**	4860 ± 215 Bq.g^{-1} dry (H_2O = 47%) **2580 ± 115 Bq.g^{-1} wet**
N°3	10930 ± 760Bq.g^{-1} dry (H_2O=57%) **4950 ± 300 Bq.g^{-1} wet**	2550 ± 120 Bq.g^{-1} dry (H_2O=58%) **1070 ± 50 Bq.g^{-1} wet**
Reference ^{14}C content	**5630 ± 325 Bq.g^{-1} wet**	

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 other sub-samples.

^{14}C activities after drying were corrected by taking into account the mass of water to compare with the result obtained without drying. This result shows that method developed for the total carbon analysis by combustion under oxygen gives individual results which are quite close to the reference (± 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 as 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 close to 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 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.

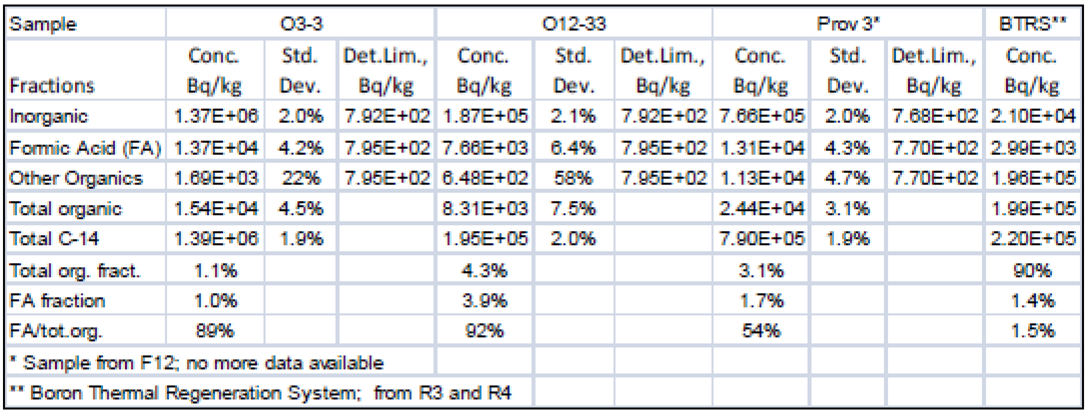
UVJ PWR samples

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

5.1. *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**
Fractions	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	1.96E+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 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).

6. 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 – partitioned 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 was found in cation-exchange resins and was probably under the form of metal carbonates. However, results on the partition of inorganic and organic molecules are sometimes contrasting for SIERs from PWRs, spanning between 30% up to 99% for the inorganic fraction. The BWR SIERs 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.

7. APPENDICES

In the Appendices (I-VI) the detailed and single reports of each partner are reported, for supplementary source of data and information.

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Final report on the estimation of the source term and speciation (D4.5) – Appendix I: CEA contribution

Author(s):

J. Comte (CEA –LARC) and S. Legand (CEA-LRMO)

D 4.5 APPENDIX I

Executive Summary

This document presents the methodologies and results of all the experiments carried out on the spent ion exchange resins (SIERS) from EDF PWR type nuclear reactors at the Commissariat à l'Énergie Atomique et aux Énergies Alternatives (CEA beneficiary N°4) within the framework of the European program CArbon Source Term (CAST). The studies concern both carbon-14 measurements and its speciation (inventory) and the measurement of organic molecules issues of extraction experiments in SIERS.

• For the measurement of total ^{14}C and / or its speciation, two different methods were developed during this project. These methods were applied on two samples from EDF PWR reactors. The results obtained show that these samples contain a total carbon-14 activity of the order of 2.1 $KBq.g^{-1}$ to 5.6 $KBq.g^{-1}$ of wet resin, with an organic fraction of ^{14}C which differs depending on the origin of the samples. Further studies on dried resins have led to the identification of an analytical bias that questions speciation values.
• For desorption studies, experiments were conducted on two sub-samples of one SIERS associated to a blank of reagent and two experiments on virgin resin. These experiments confirm that SIERs contain ^{14}C in organic form (38 % of the total ^{14}C). The observed Carbon mass balance is around 50 $mgC.L^{-1}$. Around 12% of carbon mass balance is identified. The only organic identified compound in resin desorption solutions, glycolate, is identified in very low concentration, around 1% of Total Organic carbon. No amine derivate is detected and ammonium is quantified in very low concentration by ionic chromatography. So these observations can confirm that no or very little chemical degradation coming from resin polymer or functional groups occurs in these conditions. However, an organic contamination in concentrated LiOH at 1M (solution used for resins desorption) makes difficult the characterization of organic molecules coming only from resins desorption.

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 carbon 14 source term (inventory and speciation).

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1 Introduction

This document presents the methodologies and results of all the experiments carried out by the Commissariat à l'Énergie Atomique et aux Énergies Alternatives (CEA) in the context of European program CArbon Source Term (CAST[1]) in the framework of WP4 (spent ion exchange resins). CEA labs participate to task 4.2 and 4.3.

The Laboratory of Radiochemical and Chemical Analyses (DEC/SA3C/LARC) in CEA Cadarache has proceeded to two types of experiments. First, the determination of the inventory of ^{14}C in spent ion exchange resins (SIERs) from nuclear power plants (EDF–PWR reactors), the objective of which is to determine the total activity of ^{14}C and the distribution among mineral and organic forms. Second, experimental desorption tests to release the organic and mineral forms of the ^{14}C, the objective of which is to obtain aqueous solutions for the determination of the hydrosoluble organic compounds. The desorption tests have been realized with virgin and spent ion exchange resins. Desorbed ^{14}C activities under organic or mineral forms have been measured. The solutions were transferred to the analytical laboratory in charge of organic compound measurement (Laboratory for the study of Radiolysis of Organic Matter, CEA Saclay)

This report presents the bibliography used for the development of the total carbon measurement and its distribution between mineral and organic forms. The methods developed were applied to two samples, especially provided by EDF, and the results obtained are detailed.
It also describes the experimental conditions of the carbon-14 desorption tests of ion-exchange resins for analytical purposes in order to identify the organic molecules. An analytical approach has been developed in CEA-LRMO to identify the organic compound speciation from resins desorption solution coming from CEA-LARC. The partition between organic/inorganic total carbon, the carboxylic acids and amines quantification (Ionic chromatography) and the detection of organic molecules with low or higher molecular mass (Gas chromatography or mass spectrometry) are presented.

This note is a synthesis of the work carried out by CEA in the CAST WP4 program, which began in 2013.

2 State of art, materials and methods

The main objective of the CEA work in Task 4.2 is to determine ^{14}C activity but also the speciation under which ^{14}C is present in SIERs. The State of the art presented below is limited to published studies on analytical methodologies compatible with the previous knowledge of the laboratory for the determination of ^{14}C and its speciation.

A more complete bibliography is presented in Åsa Magnusson's thesis[2] {Magnusson, 2007 #41} or in the "State of the Art Review on Sample Choice, Analytical Techniques and Current Knowledge of Release from Spent Ion-Exchange Resins (D4.1)"[3] {Rizzato, 2014 #72}. The origin of the samples supplied by EDF for this study is described (origin, method and date of sampling,...).

2.1 *Review of analytical methodology for ^{14}C determination in SIERS*

The first published works on the subject {Nott, 1982 #15} concern the determination of the mineral fraction of ^{14}C in spent ion exchange resins from heavy water reactors (CANDU). NOTT et al [4] {Nott, 1982 #15@@author-year} described the optimization of a treatment by acidification with hydrochloric acid, conversion of bicarbonate ions into CO_2, which is then trapped by bubbling into washing bottle containing soda solution. In 1993 Martin et Al [5] {Martin, 1993 #12@@author-year} used two methodologies for ^{14}C determination in SIERs: acid stripping consists in an acid-alkaline reaction between an added acid solution (HCl 6M) and the carbonate adsorbed in the SIER and a combustion method. The combustion method uses high temperatures (700°C) in oxidizing atmosphere for combustion and catalytic furnace (Pt and CuO as catalyst) in order to convert the carbon content in CO_2. Recovery yield was found to be 63 %.

In 1994, *Moir et Al* [6] {Moir, 1994 #13@@author-year} have performed a complete study on SIERs coming from CANDU reactor type with the analytical scheme of the figure below.

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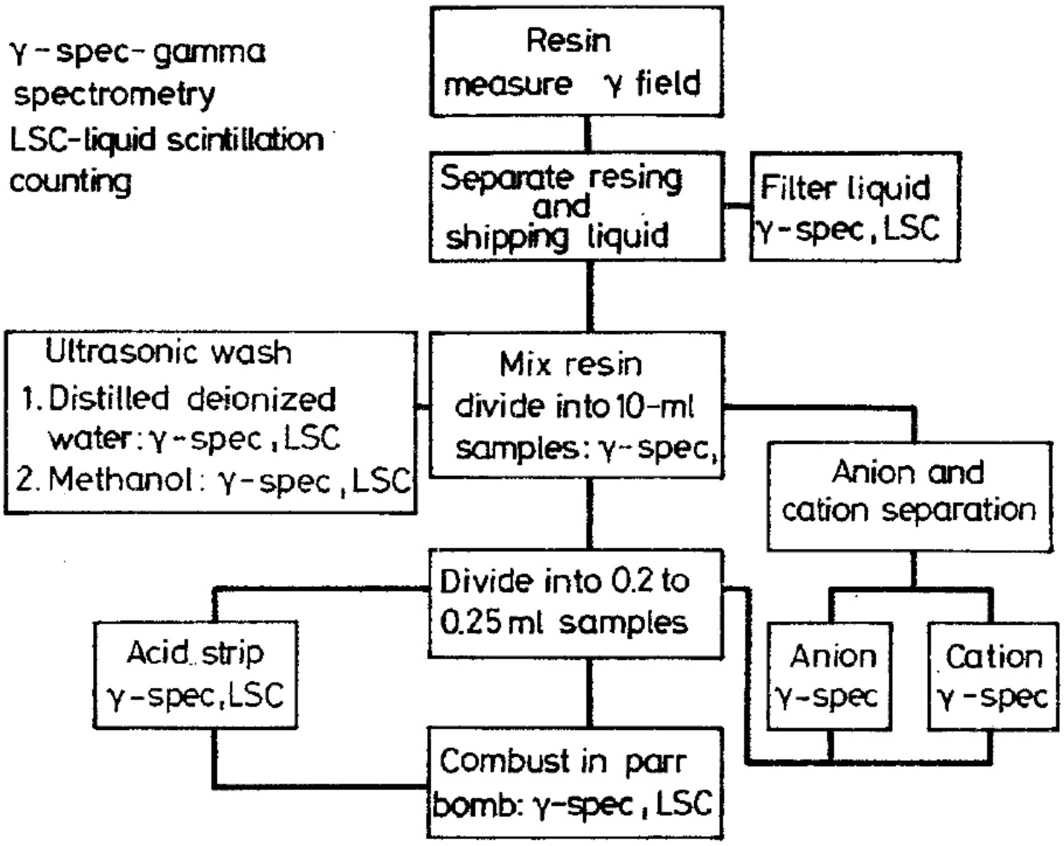

Fig. 1. Simplified resin analysis protocol

Figure 1. Simplified resin analysis protocol (*Moir et Al)*{Moir, 1994 #13}

The ^{14}C was measured after Parr bomb mineralization, where the samples is inserted in a pressurized vessel with oxygen (2.5 MPa) and let it combusted. The gaseous products are released using a carrier gas (N_2) and then trapped into NaOH solution. The measurement of ^{14}C is then carried out directly by mixing the basic solution (NaOH) with a scintillation cocktail (Hionic fluor[*]). The authors show that the anionic resins contain the majority of the ^{14}C (lower activities are measured in the cationic resins). The authors attribute this activity to the presence of ^{14}C in organic forms or carbonate-metal complexes. This hypothesis is partially validated by measurements of the resins after desorption in an acid medium, which still contain a low ^{14}C activity.

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[*] Hionic fluor, https://www.perkinelmer.com/Content/MSDSDatabase/MSDS_6013319_Hionic-Fluor_(GB).pdf

For samples of unseparated spent ion exchange resins, the results of the two methods for determining ^{14}C showed differences, in particular that the activities measured by Parr bomb combustion are lower than those determined by acid desorption. The authors conclude that this is probably related to sub-sampling operations, heterogeneity of resins and the very large difference in the distribution of ^{14}C activity between anionic and cationic resins.

PARK et al [7] {Park, 2006 #24@@author-year} developed a method for measuring ^{14}C speciation in spent ion exchange resins. After having extracted the inorganic carbon fraction of a sample by acid stripping with the addition of sulfuric acid (H_2SO_4), the remaining organic fraction is extracted by a strong oxidation reaction (wet oxidation) with the addition of potassium peroxodisulphate ($K_2S_2O_8$) and silver nitrate ($AgNO_3$) with simultaneous heating. The CO_2 evolving is absorbed in gas washing bottles containing a liquid scintillation cocktail specific for ^{14}C (Carbosorb[*] from Perkin Elmer). A duplicate analysis of the ^{14}C content of the same SIERs samples was performed by wet oxidation-acid stripping and by the Sample Oxidizer (combustion of SIERs). Their results were compared and were relatively in good agreement or without higher difference. Their methodologies for total and speciation measurement of ^{14}C are applied in 2008 on SIERS coming from CANDU reactors [8] {Park, 2008 #45}. The results obtained show that there is a considerable variability in the activities of ^{14}C among the analyzed spent ion resin samples. The waste sources of the spent resins are the demineralizers which are used in the various water purification systems. All kinds of the spent resins are being stored in the same storage tank located in each reactor unit site without classifying them from their production streams.

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[*] *Carbosorb E® fournisseur Perkin-Elmer*
h*ttp://www.perkinelmer.com/Content/MSDSDatabase/MSDS_6013729_CarboSorb_E_(GB).pdf*

Table 1. Result of the ^{14}C and ^{3}H activity concentration in CANDU – SIERs (PARK 2008)

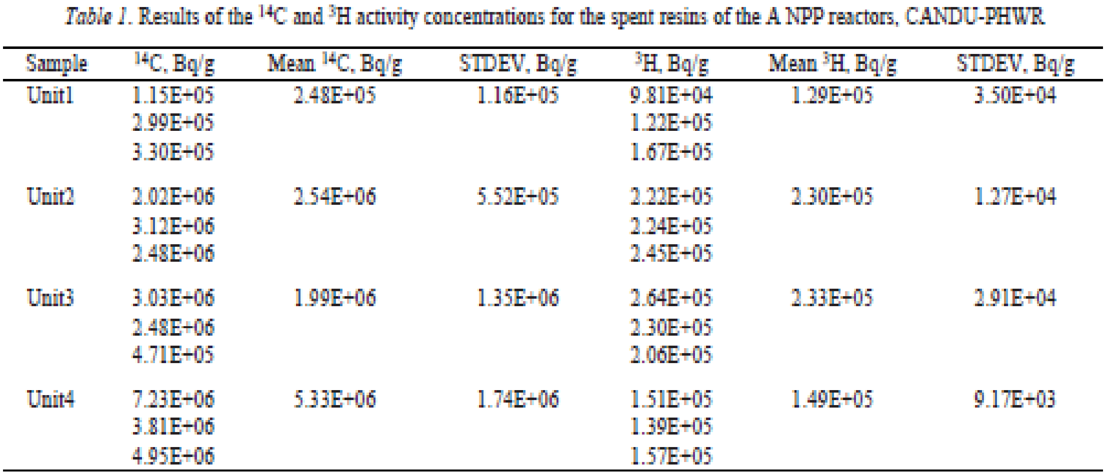


Table 1. Results of the ^{14}C and ^{3}H activity concentrations for the spent resins of the A NPP reactors, CANDU-PHWR

Sample	^{14}C, Bq/g	Mean ^{14}C, Bq/g	STDEV, Bq/g	^{3}H, Bq/g	Mean ^{3}H, Bq/g	STDEV, Bq/g
Unit1	1.15E+05	2.48E+05	1.16E+05	9.81E+04	1.29E+05	3.50E+04
	2.99E+05			1.22E+05		
	3.30E+05			1.67E+05		
Unit2	2.02E+06	2.54E+06	5.52E+05	2.22E+05	2.30E+05	1.27E+04
	3.12E+06			2.24E+05		
	2.48E+06			2.45E+05		
Unit3	3.03E+06	1.99E+06	1.35E+06	2.64E+05	2.33E+05	2.91E+04
	2.48E+06			2.30E+05		
	4.71E+05			2.06E+05		
Unit4	7.23E+06	5.33E+06	1.74E+06	1.51E+05	1.49E+05	9.17E+03
	3.81E+06			1.39E+05		
	4.95E+06			1.57E+05		

However, in order to exclude an analytical problem and to confirm the analytical dispersion, which varies from 22 % to 68 % (see Table 1), the authors compared the results of measurements between the two methodologies developed for ^{14}C determination. The duplicate analysis results for the 4 spent resin samples by the wet oxidation stripping process and the sample oxidizer combustion shows that except for the Unit 2 sample, the results of total ^{14}C by the sample oxidizer combustion method for the other 3 samples (Unit 1, 3 and 4) were higher, between 1%–34 %, than those obtained by the wet oxidation stripping process. Based on these results, the authors considered that these differences of ^{14}C activities for the same samples between the wet oxidation and the sample oxidizer combustion resulted from different anionic and cationic resin fraction of the analyzed samples. The authors recommend, when considering the sample homogeneity of the mixed spent resin, the anion and cation fractions, it is required to use as large sample as possible to acquire more representative analysis results. To complete this study experiments on the separation of the cationic and anionic resin by a 40 % sugar solution have been conducted. More than 90 % of ^{14}C was retained on the anionic resin fraction and inorganic ^{14}C was the predominant species.

More recent and complete works has been done by Swedish Nuclear Fuel and Waste Management (SKB) and in Magnuson studies {Magnusson, 2005 #33}{Magnusson, 2008 #11} [9-10-11]. The analytical method used is briefly described below. After having extracted the inorganic carbon fraction of a sample by acid stripping with the addition of sulfuric acid (H_2SO_4), the remaining organic fraction is extracted by a strong oxidation reaction (wet oxidation) with the addition of potassium peroxodisulphate ($K_2S_2O_8$) and silver nitrate ($AgNO_3$) with simultaneous heating. The CO_2 evolving is absorbed in gas washing bottles. This process is repeated several times (2-3) in order to achieve efficient extraction of the organic compounds. A catalytic furnace, located between the two sets of washing bottles, ensures oxidation of reduced compounds (as example CO-CO_2). The carrier gas is nitrogen so the catalytic furnace should have good performance in oxidizing carbon compounds even in absence of oxygen. A water trap could be utilized to avoid interfering radionuclides (e.g. ^{3}H) from reaching the absorbers. The combination of acid stripping and wet oxidation allows the separation of inorganic and organic fraction and the independent ^{14}C determination in both fractions. The obtained recoveries vary from 94 to 97 %.

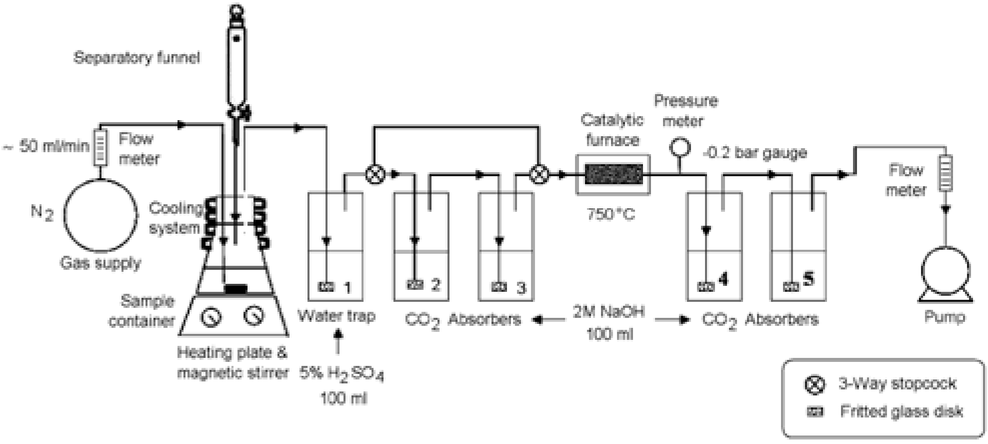
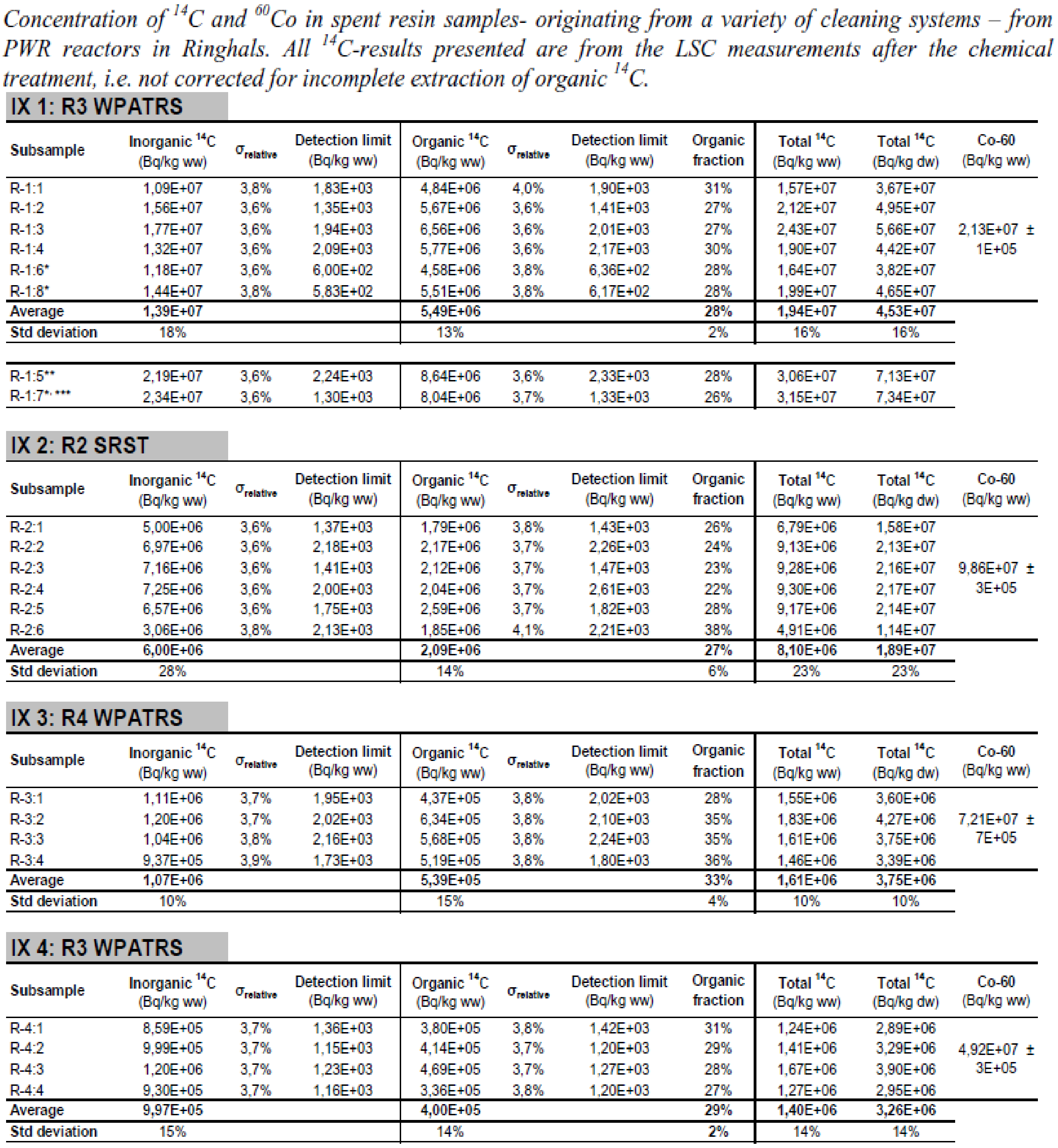


Figure 2. Representation of separation equipment (MAGNUSSON [2]).

For sample coming from pressurized reactors (Ringhals plant, R2, R3 and R4), the results of the different measurements, with four to eight measurements per sample, are presented in the Figure 3. The table also shows the dispersions of measurements between the test samples, which range from 10 to 28 % for carbon in mineral form and 13 to 15 % for carbon in organic form.

D 4.5 APPENDIX I



Concentration of ^{14}C and ^{60}Co in spent resin samples- originating from a variety of cleaning systems – from PWR reactors in Ringhals. All ^{14}C-results presented are from the LSC measurements after the chemical treatment, i.e. not corrected for incomplete extraction of organic ^{14}C.

IX 1: R3 WPATRS

Subsample	Inorganic ^{14}C (Bq/kg ww)	$\sigma_{relative}$	Detection limit (Bq/kg ww)	Organic ^{14}C (Bq/kg ww)	$\sigma_{relative}$	Detection limit (Bq/kg ww)	Organic fraction	Total ^{14}C (Bq/kg ww)	Total ^{14}C (Bq/kg dw)	Co-60 (Bq/kg ww)
R-1:1	1,09E+07	3,8%	1,83E+03	4,84E+06	4,0%	1,90E+03	31%	1,57E+07	3,67E+07	2,13E+07 ± 1E+05
R-1:2	1,56E+07	3,6%	1,35E+03	5,67E+06	3,6%	1,41E+03	27%	2,12E+07	4,95E+07	
R-1:3	1,77E+07	3,6%	1,94E+03	6,56E+06	3,6%	2,01E+03	27%	2,43E+07	5,66E+07	
R-1:4	1,32E+07	3,6%	2,09E+03	5,77E+06	3,6%	2,17E+03	30%	1,90E+07	4,42E+07	
R-1:6*	1,18E+07	3,6%	6,00E+02	4,58E+06	3,8%	6,36E+02	28%	1,64E+07	3,82E+07	
R-1:8*	1,44E+07	3,8%	5,83E+02	5,51E+06	3,8%	6,17E+02	28%	1,99E+07	4,65E+07	
Average	**1,39E+07**			**5,49E+06**			**28%**	**1,94E+07**	**4,53E+07**	
Std deviation	18%			13%			2%	16%	16%	
R-1:5**	2,19E+07	3,6%	2,24E+03	8,64E+06	3,6%	2,33E+03	28%	3,06E+07	7,13E+07	
R-1:7*, ***	2,34E+07	3,6%	1,30E+03	8,04E+06	3,7%	1,33E+03	26%	3,15E+07	7,34E+07	

IX 2: R2 SRST

Subsample	Inorganic ^{14}C (Bq/kg ww)	$\sigma_{relative}$	Detection limit (Bq/kg ww)	Organic ^{14}C (Bq/kg ww)	$\sigma_{relative}$	Detection limit (Bq/kg ww)	Organic fraction	Total ^{14}C (Bq/kg ww)	Total ^{14}C (Bq/kg dw)	Co-60 (Bq/kg ww)
R-2:1	5,00E+06	3,6%	1,37E+03	1,79E+06	3,8%	1,43E+03	26%	6,79E+06	1,58E+07	9,86E+07 ± 3E+05
R-2:2	6,97E+06	3,6%	2,18E+03	2,17E+06	3,7%	2,26E+03	24%	9,13E+06	2,13E+07	
R-2:3	7,16E+06	3,6%	1,41E+03	2,12E+06	3,7%	1,47E+03	23%	9,28E+06	2,16E+07	
R-2:4	7,25E+06	3,6%	2,00E+03	2,04E+06	3,7%	2,61E+03	22%	9,30E+06	2,17E+07	
R-2:5	6,57E+06	3,6%	1,75E+03	2,59E+06	3,7%	1,82E+03	28%	9,17E+06	2,14E+07	
R-2:6	3,06E+06	3,8%	2,13E+03	1,85E+06	4,1%	2,21E+03	38%	4,91E+06	1,14E+07	
Average	**6,00E+06**			**2,09E+06**			**27%**	**8,10E+06**	**1,89E+07**	
Std deviation	28%			14%			6%	23%	23%	

IX 3: R4 WPATRS

Subsample	Inorganic ^{14}C (Bq/kg ww)	$\sigma_{relative}$	Detection limit (Bq/kg ww)	Organic ^{14}C (Bq/kg ww)	$\sigma_{relative}$	Detection limit (Bq/kg ww)	Organic fraction	Total ^{14}C (Bq/kg ww)	Total ^{14}C (Bq/kg dw)	Co-60 (Bq/kg ww)
R-3:1	1,11E+06	3,7%	1,95E+03	4,37E+05	3,8%	2,02E+03	28%	1,55E+06	3,60E+06	7,21E+07 ± 7E+05
R-3:2	1,20E+06	3,7%	2,02E+03	6,34E+05	3,8%	2,10E+03	35%	1,83E+06	4,27E+06	
R-3:3	1,04E+06	3,8%	2,16E+03	5,68E+05	3,8%	2,24E+03	35%	1,61E+06	3,75E+06	
R-3:4	9,37E+05	3,9%	1,73E+03	5,19E+05	3,8%	1,80E+03	36%	1,46E+06	3,39E+06	
Average	**1,07E+06**			**5,39E+05**			**33%**	**1,61E+06**	**3,75E+06**	
Std deviation	10%			15%			4%	10%	10%	

IX 4: R3 WPATRS

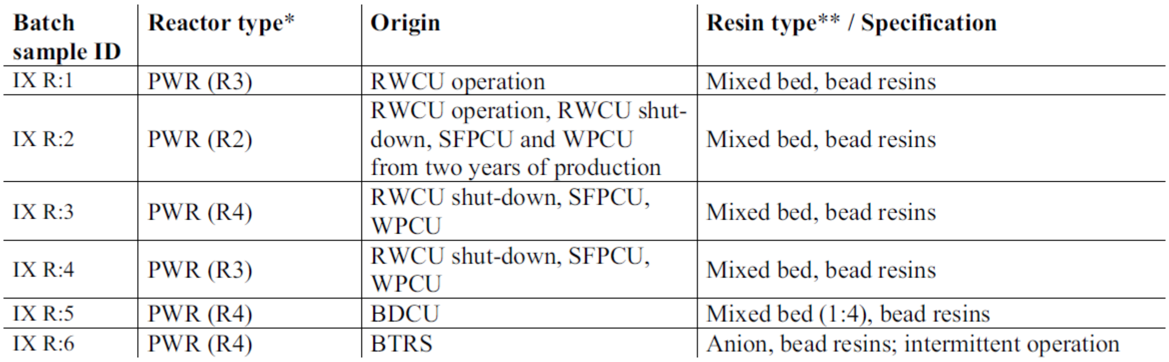
Subsample	Inorganic ^{14}C (Bq/kg ww)	$\sigma_{relative}$	Detection limit (Bq/kg ww)	Organic ^{14}C (Bq/kg ww)	$\sigma_{relative}$	Detection limit (Bq/kg ww)	Organic fraction	Total ^{14}C (Bq/kg ww)	Total ^{14}C (Bq/kg dw)	Co-60 (Bq/kg ww)
R-4:1	8,59E+05	3,7%	1,36E+03	3,80E+05	3,8%	1,42E+03	31%	1,24E+06	2,89E+06	4,92E+07 ± 3E+05
R-4:2	9,99E+05	3,7%	1,15E+03	4,14E+05	3,7%	1,20E+03	29%	1,41E+06	3,29E+06	
R-4:3	1,20E+06	3,7%	1,23E+03	4,69E+05	3,7%	1,27E+03	28%	1,67E+06	3,90E+06	
R-4:4	9,30E+05	3,7%	1,16E+03	3,36E+05	3,8%	1,20E+03	27%	1,27E+06	2,95E+06	
Average	**9,97E+05**			**4,00E+05**			**29%**	**1,40E+06**	**3,26E+06**	
Std deviation	15%			14%			2%	14%	14%	

* Subsample processed half a year later than the others
** Subsample contained approximately 50 % transparent beads, 25 % anionic beads (white) and 25 % cationic beads (dark)
*** Subsample contained nearly 100 % transparent beads

Figure 3. Measurement of ^{14}C and ^{60}Co in PWR SIERS (MAGNUSSON [9])

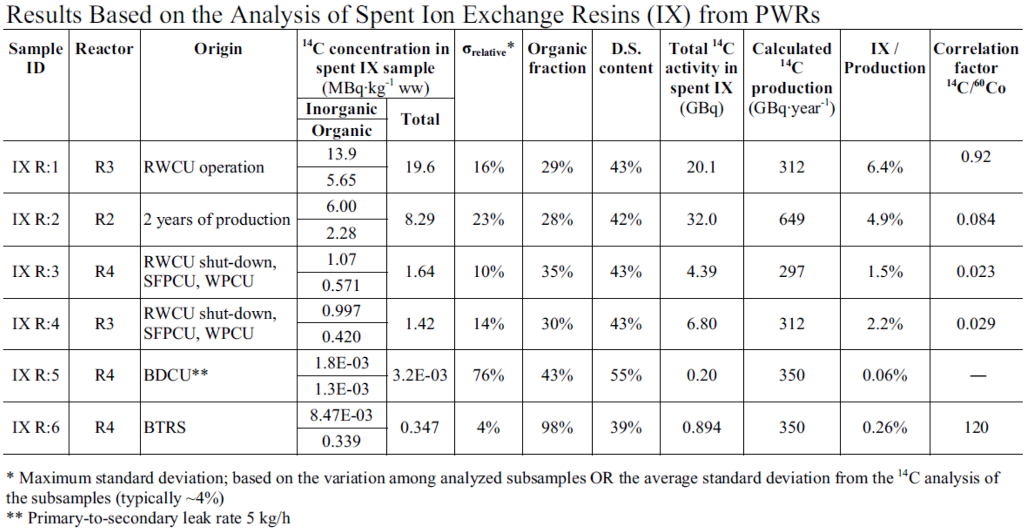
These spent resins, sampled between 2004 and 2006, come from different purification circuits or different reactor operating phases (start, cycle, shutdown, oxygenation, etc. see Figure 4). More precisely in mixed-bed from primary circuit (IX: R: 1), the total ^{14}C activity is the highest, around 20 KBq.g^{-1}, with 29 % on organic form. For SIERs coming from the different circuits (IX R: 2, R: 3, R: 4) the total ^{14}C activity is lower, from 1.4 up to 8.3 KBq.g^{-1}, but still with a proportion of 30 % in organic form. In the case of SIERS coming from the secondary circuit (IX R:5), the ^{14}C activity is much lower, around 3 Bq.g^{-1}, with

43% under organic form. For Sample IX R: 6 composed only by anionic resin, a total ^{14}C activity of 347 Bq.g^{-1} is measured almost exclusively in organic form (98%). We can conclude that the speciation of ^{14}C thus seems to be dependent on the type of purification circuit.



Batch sample ID	Reactor type*	Origin	Resin type** / Specification
IX R:1	PWR (R3)	RWCU operation	Mixed bed, bead resins
IX R:2	PWR (R2)	RWCU operation, RWCU shut-down, SFPCU and WPCU from two years of production	Mixed bed, bead resins
IX R:3	PWR (R4)	RWCU shut-down, SFPCU, WPCU	Mixed bed, bead resins
IX R:4	PWR (R3)	RWCU shut-down, SFPCU, WPCU	Mixed bed, bead resins
IX R:5	PWR (R4)	BDCU	Mixed bed (1:4), bead resins
IX R:6	PWR (R4)	BTRS	Anion, bead resins; intermittent operation

Figure 4. Origin of the sample PWR SIERs (MAGNUSSON [2])



Results Based on the Analysis of Spent Ion Exchange Resins (IX) from PWRs

Sample ID	Reactor	Origin	^{14}C concentration in spent IX sample (MBq·kg^{-1} ww)			$\sigma_{relative}$*	Organic fraction	D.S. content	Total ^{14}C activity in spent IX (GBq)	Calculated ^{14}C production (GBq·year^{-1})	IX / Production	Correlation factor $^{14}C/^{60}Co$
			Inorganic	Organic	Total							
IX R:1	R3	RWCU operation	13.9	5.65	19.6	16%	29%	43%	20.1	312	6.4%	0.92
IX R:2	R2	2 years of production	6.00	2.28	8.29	23%	28%	42%	32.0	649	4.9%	0.084
IX R:3	R4	RWCU shut-down, SFPCU, WPCU	1.07	0.571	1.64	10%	35%	43%	4.39	297	1.5%	0.023
IX R:4	R3	RWCU shut-down, SFPCU, WPCU	0.997	0.420	1.42	14%	30%	43%	6.80	312	2.2%	0.029
IX R:5	R4	BDCU**	1.8E-03	1.3E-03	3.2E-03	76%	43%	55%	0.20	350	0.06%	—
IX R:6	R4	BTRS	8.47E-03	0.339	0.347	4%	98%	39%	0.894	350	0.26%	120

* Maximum standard deviation; based on the variation among analyzed subsamples OR the average standard deviation from the ^{14}C analysis of the subsamples (typically ~4%)
** Primary-to-secondary leak rate 5 kg/h

Figure 5. Measurement of ^{14}C in PWR SIERs (MAGNUSSON [2])

In conclusion the state of the art shows that:

- **At least, two analytical methods must be developed to determine ^{14}C activity in SIERs. These methods must be applied on significant masses (> 0.1 g) to minimize the sampling deviations because by definition the samples are heterogeneous (resins of various origins, mixture of cationic and anionic resins) and replicated to acquire more representative analysis results;**

- **For the measurement of the ^{14}C speciation, all the analytical methods developed are based on the same principle, first a wet-acidification/stripping of the mineral fraction and recovery of the CO_2 gas produced into bubblers filled with hydroxide solutions, followed, in a second step, by a total/partial oxidation of the organic matter and recovery of the CO_2 produced in new bubblers,**

- **The ^{14}C activity varies according to the origin of the SIERs (CANDU, BWR, PWR reactor), but the measurements performed on samples from all the purification circuits of PWR reactor are between 1.4 to 8.3 $kBq.g^{-1}$ of ^{14}C with a fraction of 30 % under organic form.**

All there points were taken into account for the development of the analytical methodology for ^{14}C quantification and its speciation in SERS during the CAST project.

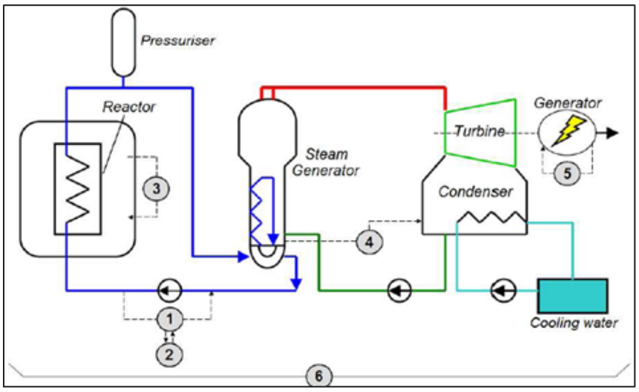
2.2 *Ions exchange resins*

EDF operates 58 PWR type nuclear reactors in France. IERs are widely used in these nuclear facilities for the purification of water coolant. Important applications include primary circuit, secondary circuit and effluent treatment, which require high quality nuclear grade IERs 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.

2.2.1 EDF SIERs specifications

Generally, purification of the various circuits is ensured by a chain of filters and demineralizers using IERs. A combination of cationic, anionic and/or mixed bed resins are used depending on the circuits' physicochemical conditions and on their specific needs. These circuits are presented in Figure 6.

Indeed, the choice of IERs for EDF facilities depends on numerous criteria. Because of the possibly harsh nature of the fluids to be treated (temperature, chemistry, radiation) the IERs need to be of a high grade in order to reduce the degradation and the release of potentially harmful substances into the circuits, and therefore the loss of reactor performance. Based on literature knowledge and on EDF industrial experience it has been specified that all IERs used in EDF nuclear facilities must be of polystyrene divinylbenzene (DVB) copolymer type. Cation exchange resins must be of the strong acid sulphonated type, in hydrogen or lithium form depending on the application. All anion exchange resins must be of the strong base quaternary trimethylamine type, in hydroxide form.



	Cation resins	**Anion resins**
Polymer	polystyrene DVB	polystyrene DVB
Functional group	Sulphonic acid	Trimethylammonium
Ionic shipped	$^{7}Li^{+}$ (primary circuit) H+ (others circuit)	OH^{-}
Impurity	Nuclear grade	Nuclear grade

(1) The Chemical and Volume Control System
(2) The Primary Effluent Treatment System
(3) The Reactor Pool and Spent Fuel Pool Cooling and Treatment System
(4) The Steam Generator Blowdown System
(5) The Stator Water Purification System
(6) The Liquid Waste Treatment System

Figure 6. General location of the key purification systems on an EDF PWR and the mains characteristics of IERs.

Another important property of an IER is the total exchange capacity. Fortunately, this property can be measured practically with decent accuracy and therefore are fully listed in EDF specifications. Type I anion exchange resins are required since they completely dissociate, have a greater selectivity towards the range of ions to be removed and are more resistant to temperature degradation.

Thus, depending on the function of the IER, it can be of different nature. At the end, the SIERs produced in EDF nuclear facilities 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;
- 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 thanks to the radioactive decay of the very short-lived radionuclides. Then the SIERs are conditioned onsite with the “Mercure” process and sent to Andra disposal facility.

2.2.2 SIERs management in France

SIERs are classified as Low- and Intermediate-level Short-Lived waste (LILW-SL) in France. They contain short-lived radionuclides, such as ^{60}Co, and may also contain strictly limited amounts of long-lived radionuclides such as ^{14}C. They are disposed of at the Andra

CSFMA[*] waste disposal facility (located in the Aube district). Waste is disposed of at surface in reinforced concrete cells, 25 meters square and 8 meters high (see Figure 7). Once filled, these cells are closed with a concrete slab and then sealed with an impermeable coat. Finally, the cell will be capped with a several meters thick layer of clay, to ensure the long-term confinement of the waste.

Figure 7. Andra CSFMA disposal facility – Aerial view of the site (left) and a reinforced concrete cell in operation (right – ref ANDRA web site).

By 2030, around 45,000 m^3 of conditioned SIERs will be disposed of at CSFMA[†] (Table 2). The waste packages sent by the waste producer must fulfill Andra's technical specifications.

Table 2. Quantities of conditioned SIERs (in concrete packages) in CSFMA.

	Quantities	Forecast (added values)	
Date	2010	2020	2030
Volume (m^3)	18,928	31,608	45,108

2.2.3 On-site conditioning of EDF spent ion exchange resins

EDF's SIERs are encapsulated in a non-leachable epoxy matrix inside shielded cylindrical concrete shells in compliance with ANDRA technical specifications on the encapsulation of

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[*] http://www.andra.fr/international/pages/en/menu21/waste-management/waste-classification/short-lived-low--and-intermediate-level-waste-1609.html

[†] http://www.andra.fr/inventaire2012/02_pdf_dechets/03-FMA-VC/F3-2-03.pdf

waste intended for CSFMA. The shells are manufactured by CDB[*] and the encapsulation process (called Mercure) is implemented onsite by SOCODEI[†] (Figure 8).

SOCODEI carries out on-site packaging campaigns thanks to a mobile device (Figure 9) including the following modules:

- the Mercure encapsulation tunnel itself (UME), a self-propelled unit carried on a special road trailer;
- a double tank unit for process reactants (epoxy resin and hardener);
- a control station integrated in a 20-feet ISO container;
- a workshop truck containing tools and spare parts composed of 2 IP2 containers for conditioning contaminated equipment;
- two office bungalows;
- a cold container.

Before conditioning, SIERs are spin-dried up to 40 to 50 % remaining water. Around 280 to 360 kg of wet SIERs are embedded for a total mass of embedded waste (SIERs + epoxy matrix) of 400 to 680 kg.

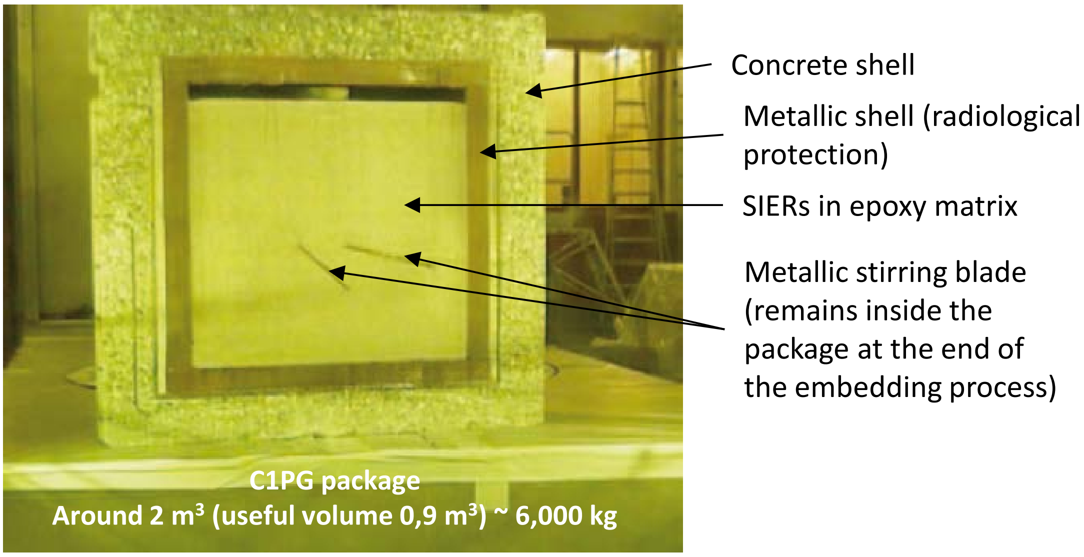

Figure 8. Cutting of a SIERs package during a random quality check and expertise control performed on request of Andra.

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[*] http://www.socodei.fr/en/cdb/

[†] http://www.socodei.fr/en/

Figure 9. Mobile unit used for SIERs conditioning on-site.

2.2.4 Samples choice

As previously explained, it is not possible to define an “average” and representative EDF-SIER. In fact, the embedded EDF-SIERs for storage surface is a mix of SIERs from different circuits whose radiological characteristics depend on numerous parameters, closely linked to the nuclear reactor cycle (nuclear fuel operational life). Moreover, it is very important to take into account that these samples will not be representative of the final waste intended for surface storage: the final waste is a mixture of SIERs embedded into a non-leachable epoxy matrix, contained in a metallic shield protected by a durable concrete shell.

EDF have provided 5 samples to CEA in the framework of the CAST project as described in Table 3. The sampling is made in the storage tanks without any possibility to know the exact SIERs origin (it is a mixture) and thus their detailed history. These samples have been chosen for their different origins (power reactor units, nature of the fuels). The amount of each sample is defined onsite in compliance with the ADR regulation rules [12] {ADR, 2013 #50}, and the Chicade facility (CEA Cadarache Centre, France) acceptance criteria.

The characteristics of these samples are summarized in Table 3.

Table 3. Characteristics of the EDF samples.

Name of the sample	Power reactor unit (MWe)	Type of fuel	Sampling date	Received	Mass (g)	Dose rate (mass) at reception
EDF-A	1450	UOX	02/14	06/14	10	15 µSv/h (10 g)
EDF-B	1300	UOX	11/14	02/15	4*~10	300 µSv/h (10 g)
EDF-C	900	UOX	02/15	06/15	4*~10	950 µSv/h (10 g)
EDF-D	900	MOX	11/14	02/15	~1,7	530 µSv/h (1 g)
EDF-E	1300	UOX	02/15	05/15	4*~10	900 µSv/h (10 g)

The huge heterogeneity of dose rates is due to the fact as mentioned above that the SIERs come from different circuits and are sampled after different storage delays (radioactive decay of short life radionuclides).

All the SIERS samples received at CEA are stored in the dark at room temperature.

2.2.5 Sample used

For methodologies for total and speciation measurement of ^{14}C development, virgin sample provided by EDF is used. For application on SIERs, the choice of samples was made according to their availability at the date of the tests (date of reception and mass available see Table 3). The developed methodologies for total and speciation measurement of ^{14}C are applied on:

- wet irradiated ion exchange resin samples (Sample EDF-A and EDF-B);
- dry irradiated ion exchange resin sample (Sample EDF-A).

The experiment for desorption and measurement of organic compound is applied on:

- Virgin sample;
- wet irradiated ion exchange resin samples (EDF-B).

Figure 10 shows the differences in the aspects of the samples.

Non active resins Sample EDF-A Sample EDF-B

Figure 10. Photographs of the EDF-A and EDF-B SIERs samples compared to the non-active IER sample.

2.3 *Analytical methodologies*

2.3.1 Liquid scintillation measurements of ^{14}C

^{14}C is a weak β-emitter (Qmax = 156 keV) of 5700 years of half live, which disintegrates 100% to the ground state of the stable nuclide ^{14}N. It is measured by liquid scintillation counting (LSC). LSC is an analytical technique, which is defined by the incorporation of the nuclide into uniform distribution with a liquid chemical medium capable of converting the kinetic energy of nuclear emissions into light energy. A β-particle, passing through a scintillation cocktail, leaves a trail of energized solvent molecules. These excited solvent molecules transfer their energy to scintillator molecules, which give off light. Each scintillator molecule gives off only one photon on activation, and the wavelength of that photon is characteristic of the scintillator, not the β-particle. The number of photons generated is directly proportional to the path length of the β-particle, which is in turn determined by its emission energy – the β-particle rebounds from solvent molecule to solvent molecule, until its incident energy is exhausted. The intensity of each light pulse corresponds to the emission energy and the number of pulses per second corresponds to the number of radioactive emissions.

This technique has the disadvantage of being non-selective of the radionuclide to be measured. The measurements of each transmitter β^-, and therefore of the ^{14}C in our case, must be done after isolating the radionuclide.

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To take into account the counting efficiency and quenching a calibration curve is established as a function of a quench index parameter (SQPE). Quenching is a reduction in the scintillation intensity seen by the photomultiplier tubes quenching due to absorption of the scintillation light by materials present in the scintillation solution or anything which interferes with the conversion of decay energy emitted by the radionuclide into light. The quenching curve is performed by adding increasing amounts of quenching agent to seven vials containing the same activity of the ^{14}C standard.

For the measurement of all the solutions provided by the methodology for total ^{14}C or its speciation's the same analytic procedure is applied. An aliquot of basic solution is acidified and ^{14}C as carbonate is transformed in CO_2 gas and then it is trapped into a carbon-14-specific scintillating liquid (solution containing 3-methoxypropylamine which reacts with CO_2 to form carbamates).The ^{14}C activity measurements are performed at LARC on ultra-low level spectrometer from PerkinElmer, Quantulus 1220.

^{14}C Standard : C14 - ELSB 30 758015/9, CERCA LEA

Apparatus *:* Quantulus liquid scintillator 1220, *Perkin Elmer N°2200277*

Counting time: 3600 secondes

Scintillating liquid: Oxysolve C400- Zinsser Analytical.

2.3.2 ^{14}C standard solutions

The ^{14}C solutions used for optimization of the methodologies are the following:

- ^{14}C standard solution in the form of glucose reference C14 - ELSB 30 7037/7 from CERCA LEA, which will serve as tracer of the organic forms of ^{14}C;
- ^{14}C solution, purified in the form of carbonate in 2 M sodium hydroxide solution, qualified by measurement in the laboratory, which will serve as tracer of the mineral forms of ^{14}C.

2.3.3 Principle of methodology for ^{14}C analyses

2.3.3.1 Total ^{14}C

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 (call “Parr bomb”, IKA AOD 1[*]). The combustion of the ions exchange resin produced CO_2 which is trapped in sodium hydroxide solution as carbonate inside de device. To achieve the recovery of ^{14}C, the mineralization system is degassing under a venting station and the gases are flushed into sodium hydroxide bubblers (Figure 11).

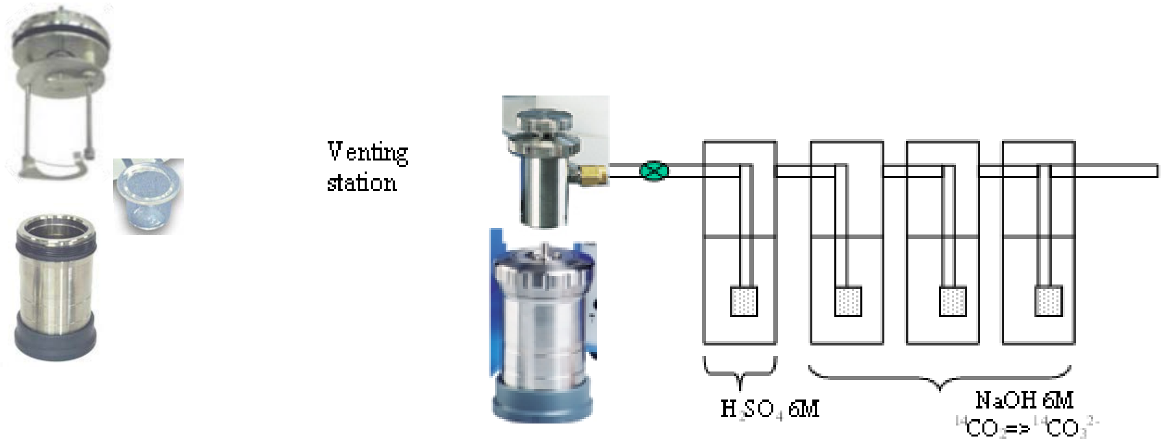

Figure 11. System for total ^{14}C measurement using mineralization under O_2 in closed system.

Tests on virgin IERs spiked with ^{14}C (carbonate, or glucose forms, or both) were operated to optimize combustion and the concentration of the sodium hydroxide solutions in the mineralization system or in the bubblers to trap CO_2. The main points optimized are the mass of the stable carbon carrier and SIERS and the concentration of sodium hydroxide solution.

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[*] http://www.ika.com/ika/product_art/manual/ika_aod_1.pdf

2.3.3.2 Speciation of ^{14}C

The study of inorganic and organic forms distribution was carried out by acidic dissolution of the ion exchange resin (Figure 12). 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 catch CO_2 into bubblers with sodium hydroxide solution (mineral form). During a second step, a total oxidation of the ion exchange resin and the organic forms of the ^{14}C was performed by a hot acidic dissolution with oxidant reagent. Some experiments on virgin IERs spiked with ^{14}C as carbonate or glucose forms, or both, were operated to optimize parameters of the dissolution to achieve the total recovery of ^{14}C and a good selectivity between mineral and organic forms.

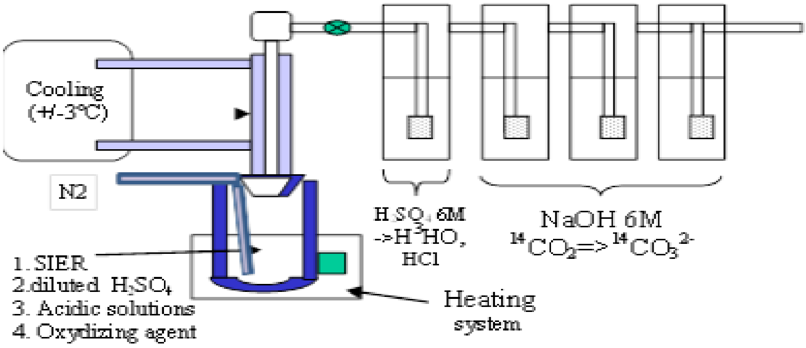

Figure 12. Schematic representation of dissolution process.

3 Results

All the result (activities) are given with an uncertainty at k = 2.

3.1 *Development of the analytical methodology*

3.1.1 Methodology for total ^{14}C

In order to stabilize the carbon produced during the oxygen combustion of the SIERs, different medium are tested with the objective of having the highest recovery efficiency in the solution in decomposition vessel. As a precaution, solutions coming from the gas trapping system (bubblers filled with basic solutions) were also analyzed.

For this purpose wet resins sample are impregnated with ^{14}C standard solution (organic form) without addition of a “stable carbon” tracer. The recovery efficiency was not total whereas the mineralization leads visually to the complete destruction of the resin.

Table 4. Experimental conditions for optimization of the concentration of the trapping solution.

Mass of IER (g)	Solution (10 mL)	Washing (50 mL)	Recovery in aqueous phase	Recovery in gaseous phase	Total Recovery	pH
0.4135	NaOH 1M	Eau	33 ± 3 %	32 ± 3 %	65 ± 7 %	<8
0.2045	NaOH 2M	Eau	65 ± 7 %	12 ± 1 %	77 ± 8 %	9-10
0.4015	NaOH 2M	Eau	65 ± 7 %	<10 %	65 ± 7 %	9-10

The result shows that a minimal concentration of 2M of hydroxide solution is necessary to minimize the carbon into the gas phase.

To complete this study, experiments have been undertaken by adding and mixing a stable carbon trainer (graphite powder) at the IERs which facilitates the exchange and minimizes losses of carbon. The results obtained are presented in the Table 5.

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Table 5. Experimental conditions for optimization of the mass of IERs and carbon carrier

Mass of IERs (g))	Mass of Carrier (g)	^{14}C #1 Spike (Bq)	Solution (10 mL)	pH	Recovery in aqueous phase	Recovery in gaseous phase	Total Recovery
0.40	no	10 Bq	NaOH 2M	9-10	65 ± 7 %	<10 %	65 ± 7 %
0.39	0.10	10 Bq	NaOH 2M	9-10	67 ± 7 %	<10 %	67 ± 7 %
0.40	0.19	10 Bq	NaOH 2M	9-10	85 ± 8 %	<10 %	85 ± 8 %
0.28	0.21	50 Bq	NaOH 2M	9-10	95 ± 9 %	4.9 ± 0.5 %	100 ± 10 %
0.31	0.29	50 Bq	NaOH 2M	<8	65 ± 5 %	42 ± 4 %	107 ± 10 %

#1 organic form

The addition of carbon-carrier increases the recovery of total ^{14}C but its excess modifies the distribution between aqueous trapping in the device and trapping in flasks of the gas phase in equilibrium. However, this has no consequence for the determination of the total ^{14}C because the experiments will systematically include the measurement of solutions from trapping device and solution from decomposition vessel.

Table 6. Parameters for total dissolution of spent ion exchange resins and ^{14}C total measurement

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

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

3.1.2 Speciation of ^{14}C

The 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 catch CO_2 into traps filled with sodium hydroxide solution (6 M NaOH).

All the parameters (mass of carrier and IERS, acidic solution, duration of degassing) of the first step were optimized with a ^{14}C standard solutions as mineral form and the yield of recovery allow us the chose the best conditions.

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Table 7. Experimental conditions for the optimization of the measurement of mineral form of ^{14}C

Mass of IER (g)	Mass of Na_2CO_3 (mg)	^{14}C [#1] Spike (Bq)	Solution	rate ($mL.H^{-1}$)	Duration of degassing	Recovery ^{14}C
0.25	No	50 Bq	30 mL H_2SO_4 4,5M	10	15 min	65 ± 6 %
0.25	400	50 Bq	30 mL H_2SO_4 4,5M	10	60 min	>85 %
0.25	400	500 Bq	30 mL H_2SO_4 4,5M	10	60 min	>92 %
0.25	400	500 Bq	5 mL H_2SO_4 9M	10	60 min	>86 %
0.30	400	500 Bq	5 mL H_2SO_4 9M	10	60 min	>89 %
0.50	400	500 Bq	5 mL H_2SO_4 9M	10	60 min	>86 %

#1 mineral form

The first parameter tested is the addition of carbonate ions as chemical carrier, to allow better recovery in the trapping bottles. To this, 50 Bq or 500 Bq of ^{14}C in the form of carbonate ions and around 400 mg carbonate ions (2 mL of 200 $g.L^{-1}$ solution) are introduced into the device. The results obtained show that, in the presence of carbonate carrier, the recovery efficiency is increased and quasi-total (included in the measurement uncertainties). The increase of the activity makes it possible to have a better estimation in regard with the estimated values in SIERs. The influence of the molarity of sulfuric acid was also studied to avoid excessive dilution of the sample. The results are identical for the two concentration tested to acidify the carbonate ions into CO_2. The optimization of the mass of IERs was also carried out. There is no limiting effect for the mass of EIRs for the determination of the mineral form of ^{14}C.

The second step consists in a total oxidation and dissolution of the ion exchange resin and the organic forms of the ^{14}C. It is performed by a hot acidic dissolution with oxidant reagent. The ^{14}C as organic form is oxidized into CO_2 and trapped into new bubblers with sodium hydroxide solution (mineral form). To validate the dissolution and recovery methodologies, virgin resins were spiked with a ^{14}C standard solution in organic form (glucose). Two parameters were more particularly optimized during this phase: the sample mass and the nature of the oxidizing medium (Table 8). The oxidizing solution is added via a dropping funnel at a flow rate of 60 $mL.h^{-1}$. The stable carbon present in the polymers of the resins is used as chemical carrier.

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Table 8. Experimental conditions for the optimization of the measurement of organic form of ^{14}C

Mass of IER (g)	^{14}C #1 Spike (Bq)	Solution	Duration of Heating /Degassing#3	Recovery ^{14}C	Dissolution
0.25 g	50 Bq	30 mL H_2SO_4 9M+ 5 mL H_2O_2	3 h	33 ± 3 %	Total
0.25 g	50 Bq	30 mL H_2SO_4 9M+ 5 mL H_2O_2	3 h	51 ± 4 %	Total
0.25 g	500 Bq	30 mL H_2SO_4 /HNO_3 #2+ 5 mL H_2O_2	3 h	>87 %	Total
0.31 g	500 Bq	30 mL H_2SO_4/HNO_3#2 +5 mL H_2O_2	3 h	91 ± 9 %	Total
0.50 g	250 Bq	30 mL H_2SO_4/HNO_3#2 + 5 mL H_2O_2	3 h	85 ± 7 %	Total

#1 as organic form (glucose)
#2 Acid mixture H_2SO_4 18M 3/4 + HNO_3 14M 1/4 in volume
#3 from the boiling of the solution

Addition of nitric acid to the oxidation medium increases the recovery efficiency of ^{14}C. For more than 0.5 g of resin an addition of oxidation solution will be required. The minimal heating time is 3 hours from the boiling of the solution.

The best parameters for each step are summarized in Table 9.

Table 9. Parameters for total dissolution of spent ion exchange resins and ^{14}C speciation measurement

Mass of resin (g)	^{14}C	Solution	Carrier	Heating#2	Degassing
0.25 to 0.5	Mineral	5 mL H_2SO_4 9M	400 mg (carbonate)	No	Yes (1 h)
	Organic	30 mL H_2SO_4/HNO_3#1 + 5 mL H_2O_2	no	Yes (3 h)	Yes (3 h)

#1Acid mixture H_2SO_4 18M 3/4 + HNO_3 14M 1/4 in volume #2 from the boiling of the solution

The selectivity of the separation between the organic and inorganic forms was checked. Measurements on virgin resins spiked only with ^{14}C in mineral form or organic form have been mineralized with complete protocol. A final validation test was carried with mixture of mineral and organic forms of ^{14}C. The results show that the yield of recovery of ^{14}C was above 95 % for mineral form and above 90 % for organic without cross-contamination (Table 10).

Table 10. ^{14}C recovery and selectivity

^{14}C recovery and selectivity	^{14}C mineral	^{14}C organic
^{14}C mineral	> 95 %	< 3 %
^{14}C organic	< 6 %	> 90 %

3.2 ^{14}C measurements on SIERs

The methodologies for total quantification and speciation measurement of ^{14}C developed were applied on:

1. Wet irradiated ion exchange resin samples (Sample EDF-A and EDF-B);
2. Dry irradiated ion exchange resin sample (Sample EDF-A).

3.2.1 Total ^{14}C

The results obtained on dry and wet samples in Bq.g^{-1} are indicated in Table 11.

Table 11. ^{14}C total determination in SIERs

Ref	State	Wet sample N°1 Bq.g^{-1}	Wet sample N°2 Bq.g^{-1}	**Average** Bq.g^{-1}
EDF-A	Wet	5500 ± 290	5630 ± 325	***5570 ± 430***
EDF-A	Dry	10745 ± 680 (H_2O = 40 %)	10930 ± 760 (H_2O=57 %)	≠ H_2O content
EDF-B	Wet	2130 ± 135	2120 ± 145	2125 ± 200

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3.2.2 ^{14}C repartition between mineral and organic forms

The results obtained in Bq.g^{-1} on dry and wet same samples are presented in Table 12.

Table 12. ^{14}C determination for the repartition between mineral and organic forms in SIERs

ref	**State**	**^{14}C**	**N°1 Bq.g^{-1}**	**N°2 Bq.g^{-1}**	**N°3 Bq.g^{-1}**	**Average Bq.g^{-1}**
EDF–A	Wet sample	Mineral form	4480 ± 260	4110 ± 210	/	4300 ± 620
		Organic form	1220 ± 70	1410 ± 80	/	1315 ± 290
		Total	5700 ± 270	5520 ± 226	/	5610 ± 430
EDF–A	Dry sample	Water content	*H_2O = 19.6 %*	*H_2O = 47 %*	*H_2O = 58 %*	≠ H_2O content
		Mineral form	2450 ± 150	1280 ± 80	610 ± 40	
		Organic form	1610 ± 90	3580 ± 200	1945 ± 115	
		Total	4060 ± 170	4860 ± 215	2550 ± 120	
EDF–B	Wet sample	Mineral form	*48 ± 4*	*44 ± 4*	/	*46 ± 8*
		Organic form	1560 ± 94	1570 ± 120	/	1565 ± 150
		Total	1610 ± 94	1615 ± 120	/	1612 ± 150

4 Interpretations

4.1 *^{14}C inventory and speciation in SIERs (Task 4.2)*

4.1.1 Results on wet samples

The results show that in the case of sample EDF-A, the total ^{14}C deduced from measurement by combustion or by summation of the mineral and organic form give similar results. In case of sample EDF-B the results are significantly different.

Table 13. Comparison of methodologies.

Sample	**Type**	**Total ^{14}C Combustion with oxygen Bq.g^{-1}**	**Total ^{14}C Acidic dissolution Bq.g^{-1}**	**Difference Bq.g^{-1}**
EDF-A	Wet sample	5630 ± 325	5610 ± 430	20 (0.3 %)
EDF-B	Wet sample	2125 ± 200	1612 ± 150	513 (24 %)

Both tests were carried out with the same method and by the same operator. In the case of EDF-B sample, difference obtained in total activity is not explained yet. EDF-B sample contains less ^{14}C than EDF-A sample.

EDF-B sample presents a very low ^{14}C activity in mineral form (Table 12) which lead to an underestimation of 24 % of the total ^{14}C activity. The speciation in this sample therefore requires additional tests to be validated. It should be noted that the total carbon-14 activity is around 2 kBq.g^{-1} wet.

EDF-A sample is the only one with consistent results in terms of reproducibility between the sub sample analysis and total ^{14}C and for the two methods used (Parr bomb and acidic speciation protocol). The two methods of measurement allow confirming a total activity of 5.6 kBq.g^{-1} wet.

4.1.2 Result on dry sample

The entire tests were performed on EDF-A sample (Table 11 and Table 12). 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 (Table 17). 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 (± 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, '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 must be reviewed.

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

Measure	**Total ^{14}C combustion with oxygen**	**Total ^{14}C 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	**5630 ± 325 Bq.g^{-1} wet**	

4.1.3 Conclusion on analytical developments and measurements at CEA

Developments of two methods were made and validated using ^{14}C standard in organic (glucose) and mineral (carbonate) forms. The application of this analytical method was performed on dry and wet SIERs. An analytical problem for the ^{14}C measurement by acidic dissolution was identified in the case of dried samples (EDF A) and maybe also in the case of one wet sample (EDF B). This problem has been identified by using two methodologies for ^{14}C measurement inventory in SIERs. Only the results obtained on the wet EDF-A sample are consistent and reproducible between the different sub-samples and methods. A total carbon content of the order of 5.6 kBq g^{-1} is measured with a distribution between organic carbon and mineral carbon of 23 % / 77 %, which is globally consistent with the few results available in the literature. Table 18 gives the main results for the EDF-A sample.

Table 15. Main results for EDF-A samples.

Sample	**Method**		**Activity ^{14}C (Bq g^{-1})**	**Repartition**
EDF-A WET	Combustion with oxygen	Total	5630 ± 325	
	Acidic dissolution	Mineral form	4300 ± 620	~77 %
		Organic form	1315 ± 290	~23 %
		Total (sum)	5610 ± 430	
	Difference between the two methods (balance)		20 Bq	

The tests carried out on dried samples in order to allow a comparison between different SIERs did not produce conclusive results. The water contents, measured with the single selected drying protocol, provide variable values for different sub-samples of the same sample. Moreover, drying does not allow in the majority of cases to obtain the speciation and total ^{14}C activity measured beforehand on wet SIERs. A systematic underestimation of ^{14}C activity in mineral form is observed. The origin of this problem remains to be identified.

It can be concluded that the assessment of ^{14}C speciation in SIERs cannot be achieved through such a limited number of samples and measurements. More measurements are needed to allow a statistical approach in order to obtain reliable results on the determination of ^{14}C inventory and speciation in the EDF SIERs. Moreover, more work is needed to understand the analytical problems evidenced in the comparison of wet and dried samples. Because of timescale and cost limitations, it is not possible to carry out theses complementary studies in the framework of the CAST project.

5 Conclusion

In the framework of Task 4.2, two analytical procedures for the measurement of the total ^{14}C, and the distribution between organic and mineral form on real samples, dry or wet, were optimized and tested on SIERs. The use of this two methods has permitted to check the accuracy and the consistency of the results obtained for each tested resin. The application of these analytical methods was performed on dry and wet SIERs. An analytical problem for the ^{14}C measurement by acidic dissolution was identified in the case of dried samples (EDF A) and maybe also in the case of one wet sample (EDF B). However, the results obtained on the wet EDF-A sample are consistent and reproducible between the different sub-samples and methods. A total carbon content of the order of 5.6 kBq g^{-1}wet is measured with a distribution between organic carbon and mineral carbon of 23/77%, which is globally consistent with the few results available in the literature.

In the framework of Task 4.3, desorption tests were performed with 10^{-3} and 1 M LiOH aqueous solutions. A 1 M LiOH solution is needed to achieve a nearly complete desorption of ^{14}C. In that case, an apparent loss of ^{14}C is evidenced. The solutions have been transferred for analyses by LRMO to have a first identification of the nature of the organic molecules.
The observed Carbon mass balance is around 50 mgC.L^{-1}. Around 12% of carbon mass balance is identified. The only organic identified compound in resin desorption solutions, glycolate, is identified in very low concentration, around 1 % of Total Organic carbon. No amine derivate is detected and ammonium is quantified in very low concentration by ionic chromatography. So these observations can confirm that no or very little chemical degradation coming from resin polymer or functional groups occurs in these conditions. However, an organic contamination in concentrated LiOH at 1 M (solution used for resins desorption) makes difficult the characterization of organic molecules coming only from resins desorption.

To conclude, the representativeness of the sampling but also the conservation over time – including time between discharge from reactor and sampling, shipment, and storage time before analyses – is although questioned. The SIERs coming from different circuits were sampled and analysed after different storage delays – radioactive decay of short life radionuclides, time for transport and analyses. More measurements are needed to allow a statistical approach to obtain significant results on the assessment of ^{14}C in SIERs. All these elements show that further studies should be done.

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CArbon-14 Source Term

CAST

Final report on the estimation of the source term and speciation (D4.5): Appendix II: RATEN ICN contribution

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Executive Summary

The total ^{14}C content and its partition between inorganic and organic species as well as inventories of^{3}H, ^{137}Cs, ^{134}Cs, ^{60}Co, and ^{54}Mn were determined in spent ion exchange resins (SIERs) received from Cernavoda NPP.

The method used for total ^{14}C measurement consists of combustion in oxygen reach atmosphere, while for the measurement of inorganic and organic fraction an analytical method based on acid stripping and wet oxidation was applied.

The ^{14}C measurement were carried out by liquid scintillation counting (LSC) using a Tri-Carb® analyser Model 3110 TR.

The experimental results obtained by combustion for total ^{14}C were in good agreement with those obtained by acid stripping/wet oxidation. The total ^{14}C inventory in SIERs sample analysed is 3.37E+04 Bq/g, predominantly as inorganic ^{14}C (around 97% of inorganic ^{14}C and 7% of organic^{14}C).

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1 Introduction

Two CANDU (Canadian Deuterium Uranium Pressurized Heavy Water Reactor) units are currently in operation at Cernavoda NPP (Unit U1 in operation since December 1996 and U2 since November 2007). Two more CANDU units are foreseen to be commenced on Cernavoda site. Each CANDU unit is designed for an operational time of 30 years, but for all four Cernavoda units a refurbishment after 25 years of operation is expected to extend their operational time to 50 years. Around 6.65 m^3 of spent ion exchange resins (SIERs) are generated per year at each CANDU reactor, from which around 3.6 m^3 are non-fuel resins. Due to the high ^{14}C inventory, the non-fuel contact resins shall be disposed of in the future geological repository (foreseen to be operational in 2065). Around 720 m^3 of non-fuel contact SIERs will be generated from the four CANDU units for an operational period of 50 years. These resins could contain around 210^{15}Bq of ^{14}C [SEDOR, 2012].As ^{14}C is a pure β-emitter, it belongs to the category of difficult to measure radionuclides. Up to CAST project, no real measurements on Cernavoda SIERs were performed.

RATEN ICN objective in CAST WP4 was to measure the total ^{14}C content in CANDU spent ion exchange resins as well as its partition between inorganic and organic species (Task 4.2). To evaluate the ^{14}C release from CANDU SIERs in alkaline environment, desorption tests in NaOH 0.1 M solution and degradation tests have been proposed to be carried out.

2 Materials and Methods

Currently, at Cernavoda NPP the SIERs are stored Cernavoda SIERs are stored in three reinforced concrete vaults, lined with epoxy resin, with capacity of 200 m^3 each segregated as fuel contact and non-fuel contact resins.

No SIERs sampling from the Cernavoda storage tanks were performed but during maintenance operation spent resins are collected from the strainers of the purification systems and stored in Cernavoda storage facility. A sample of SIERs originating from purification systems of moderator (MOD) and of Primary Heat Transport System (PHTS) from Unit 1 of Cernavoda NPP was transferred to RATEN ICN in 2015 to be used in the experimental programme developed under CAST WP4.

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The systems from where SIERs were collected contain heavy water that after almost 19 years of operation has a high ^{3}H activity. To decrease the tritium activity and also to get a D_2O content less than 10%, a volume of distilled water were added over the 100 g of SIERs and the container was put in a gas tight vessel and transferred to RATEN ICN.

Mixed resin type Amberlite IRN-150 is used in MOD and PHTS purification systems. Amberlite IRN-150 is a nominal 1:1 chemical equivalent (same anion and cation exchange capacity) mixture of IRN 77 (a strong acid cation-exchange resins) and IRN 78 (a strong base anion-exchange resin).

2.1 *Methods used for ^{14}C measurement in CANDU SIERs*

For total ^{14}C measurement in CANDU SIERs, non-catalytic combustion by flame oxidation method was used. For inorganic and organic ^{14}C measurement the analytical method adapted after the method developed by Magnusson [Magnusson et al., 2008] for ^{14}C measurement in spent ion exchange resins and process waters was used. This method distinguishes between $^{14}CO_2$ released during acid stripping and $^{14}CO_2$ released by wet oxidation of hydrocarbons allowing determination of the inorganic and organic fractions of ^{14}C in SIERs.

2.1.1 Method for total ^{14}C measurement

For total ^{14}C measurement in SIERs, non-catalytic combustion by flame oxidation method was used. By his method, the resins samples are combusted in an oxygen-enriched atmosphere with a continuous flow of oxygen using Sample Oxidizer, Model 307 PerkinElmer® (Figure 1).By this combustion any hydrogen is oxidized to H_2O and any carbon is oxidized to CO_2.

The Sample Oxidizer consists of the following major functional areas: combustion system, tritium collection system, and ^{14}C and ^{3}H collection systems, water injection system, nitrogen system and programmer.

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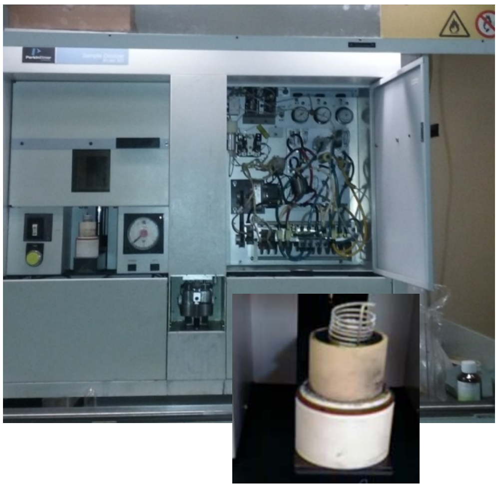

Figure 1. The experimental device used for total ^{14}C measurements in liquid samples

Since the carbon dioxide readily reacts with compounds containing amines, the Carbo-Sorb® E was chosen to absorb the $^{14}CO_2$ released during combustion process. The absorption reaction of carbon dioxide can be described as follows [Ahn at al., 2013]:

$$^{14}CO_2 + RNH_2 \rightarrow RNH_2^{+\,14}COO^- \qquad \text{(eq. 1)}$$

$$RNH_2^{+\,14}COO^- + \begin{bmatrix} RNH_2 \rightarrow RNH^{14}COO^- + RNH_3^+ \\ H_2O \rightarrow RNH^{14}COO^- + H_3O^+ \\ OH^- \rightarrow RNH^{14}COO^- + H_2O \end{bmatrix} \qquad \text{(eq. 2)}$$

$$RNH^{14}COO^- + H_2O \rightarrow RNH_2 + H^{14}CO_3^- \qquad \text{(eq. 3)}$$

As shown in eq. 2, the amine contained by the Carbo-sorb E solution reacts with ^{14}C-labelled carbon dioxide to form a zwitterion, which reacts with H_2O to form a stable carbonate compound (eq. 3). This resulted carbonate compound is mixed with the LSC cocktail (Perma-fluor® E+) directly in the counting vial.

The ^3H_2O resulted in the combustion process is condensed in a cooled coil, washed into a counting vial where it is mixed with LSC cocktail (Monophase®S).

At the end of combustion process, two separate samples, one for ^{14}C measurement and one for ^{3}Hmeasurement, are trapped at ambient temperature minimizing the cross-contamination.

The ^{14}C and ^{3}Hradioactivityin the samples resulted from SIERs combustion was measured by liquid scintillation counting (LSC) using a Tri-Carb® analyser Model 3110 TR. This analyser allows for ultra-low level counting mode with typical count rate in the range of 1-20 CPM (counts per minute) above background.

2.1.2 Analytical method for inorganic and organic ^{14}C measurement

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

The experimental set-up used for release and separation of inorganic and organic ^{14}C is schematically presented in Figure 2. 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.

An Erlenmayer flask (300 ml) with a three-hole rubber stopper (two for gas and separatory funnel inlets and one for gas outlet) was used as reaction vessel and a tap-water cooling loop, made of copper tubing that fit the outer side of the Erlenmeyer flask (Figure 2) ensured the vapour condensation. The reaction vessel was placed on a heater with magnetic stirring.

To ensure that no gases are released from the system, all dissolution and wet oxidation experiments were carried out under vacuum (0.2 bar below atmospheric pressure) and the carrier gas (N_2) was introduced into the system with a flow rate between 60 and 80 ml/min (controlled by a flow meter).

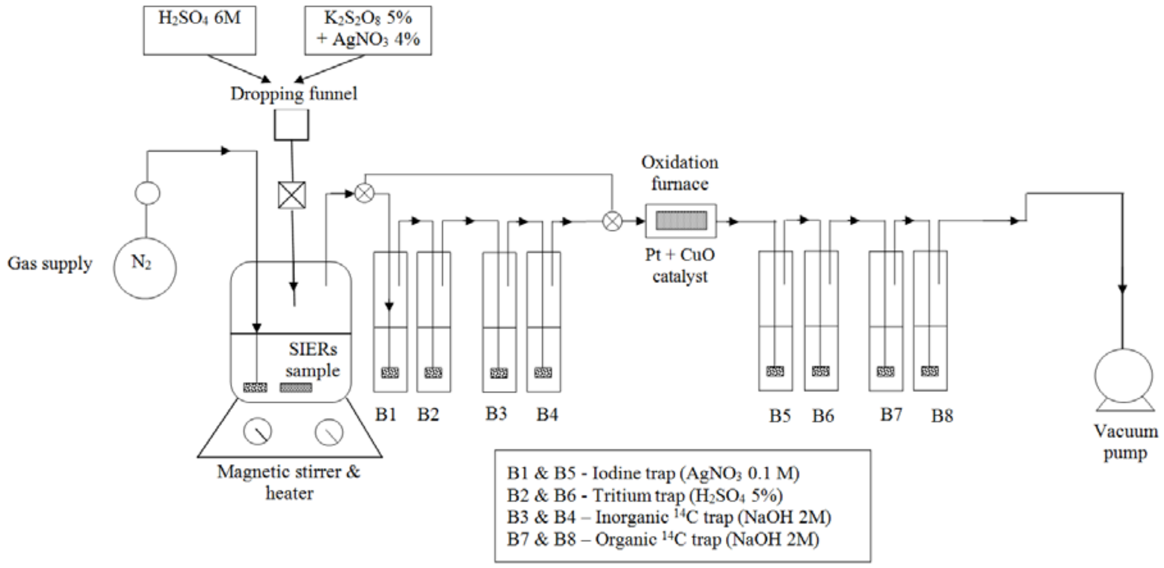

Figure 2. The experimental set-up for separation and purification of inorganic and organic ^{14}C.

Since SIERs could contain beside ^{14}C also tritium, iodine and other beta emitters that interfere with ^{14}C measurement by LSC the gas washing lines consists in iodine traps (both before and after the catalytic furnace) with silver nitrate ($AgNO_3$), slightly acidic trap with sulphuric acid (5% H_2SO_4) for absorption of the tritium and other potential interfering radionuclides and four alkaline traps (two placed before the catalytic furnace and two after it) with 2M sodium hydroxide (NaOH) [COMTE et al., 2017].

Since the inorganic ^{14}Ccompounds (i.e. carbonates and bicarbonates) are easily decomposed by week acids to carbon dioxide, the inorganic ^{14}C is released during acid stripping step of the analytical method mainly as $^{14}CO_2$ and the gases released are carried by the carrier gas through the first gas washing line (Figure 2).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 CO_2 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 forth one.

Because the organic compounds have high bounding energies between atoms they are decomposed by strong oxidants such as potassium persulphate ($K_2S_2O_8$). Presence of a catalyser such as silver nitrate ($AgNO_3$) 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 ^{14}C-labelled organic compounds decomposition is based on the OH$^{(*)}$ radicals and can be expressed by the following equations [AHNet al., 2013]:

$$K_2S_2O_8 \xrightarrow{H_2O} 2K^+ + S_2O_8^{2-} \quad \text{(eq. 4)}$$

$$S_2O_8^{2-} + 4H_2O \underset{Ag}{\rightarrow} 2SO_4^{2-} + 2H^+ + 2OH^* \quad \text{(eq. 5)}$$

$$^{14}C_nH_m + (4n+m)OH^* \rightarrow n^{14}CO_2 + (2n+m)H_2O \quad \text{(eq. 6)}$$

The ^{14}C released during wet oxidation step of the analytical procedure (both as CO_2, but also as CO or CH_4) is carried by the carrier gas through a catalytic furnace that ensures oxidation of any reduced compounds to CO_2that is after that absorbed in the scrubbing bottles of the second gas washing line (Figure 2).

Three wet oxidation steps were carried out in order to ensure the complete decomposition of the organic ^{14}C-labelled compounds, and the carrier gas was purged into the system for 1 hour in each wet oxidation steps.

The ^{14}C activity in the alkaline traps as well as and ^{3}H activity in solutions sampled from the acid scrubbing bottles were measured by liquid scintillation counting (LSC), using a Tri-Carb® analyser Model 3110 TR.

Hionic Fluor liquid scintillation cocktail was used for ^{14}C measurement by LCS, and Ultima Gold AB liquid scintillation cocktail for tritium measurement. The ratio between sample and scintillation cocktail was 1 to 10. All samples were kept in darkness over night before their counting.

Aliquots from the reaction vessel solution, as well as from all scrubbing bottles were sampled for gamma measurements. The system used for the gamma spectrometry comprises of the following components: HPGe ORTEC detector, digiDart analyser and GammaVision software. The spectrometer was calibrated in energy and efficiency using a standard liquid source containing ^{60}Co, ^{137}Cs, ^{241}Am, ^{152}Eu in 20 ml glass vials. The same geometry was used for gamma measurements on the sampled aliquots solutions from the acid stripping/wet oxidation experiments. Each sample was counted for more than 4 hours.

3 Results and discussion

3.1 *Tests to assess the ^{14}C recovery and the memory effect of the analytical methods used for ^{14}C measurement*

3.1.1 Recovery and memory effect of the combustion

Preliminary combustion tests were carried out using ion exchange resin samples spiked with the interest radionuclides (^{14}C – as sodium carbonate/bicarbonate and sodium acetate, ^{3}H, ^{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 combusto-cone together with different volumes (between 0.1 and 0.5 ml) of combustaide (an agent that enhance the combustion process) and the combusto-cone with sample was placed into the platinum ignition basket.

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

- resin mass: 0.15 g;
- volume of combustaide:0.5 ml;
- combustion time: 3 minutes.

The ^{14}C recovery obtained in these combustion tests was ranging between 93.8% and99.9%, with an average of 97.5%and standard deviation of1.24.

The memory effect was less than 0.04% and no gamma emitters were identified either in the counting vial for ^{14}C measurement or in the ^{3}H one.

3.1.2 Recovery and memory effect of the acid stripping/wet oxidation method

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

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Before starting the recovery tests, the stock solution for inorganic ^{14}C was obtained by stripping the ^{14}C content of a barium carbonate standard with activity of 1 mCi (37 MBq) and subsequent $^{14}CO_2$ absorption in scrubbing bottles with 100 ml of NaOH 2M. By this approach a solution containing ^{14}C in form of sodium carbonates/bicarbonates with activity of 37.06E+03 Bq/mL was obtained to be used in the recovery tests. The scrubbing bottles and silicon tubing used to prepare inorganic ^{14}C stock solution were not further used in the recovery tests.

In first set of recovery tests only inorganic ^{14}C, ^{3}H, and gamma emitters were used. Five acid stripping tests were carried out to assess the radionuclides recoveries and the reproducibility of the experimental results.

In the reaction vessel, beside the radioactive solutions 100 mg of non-radioactive sodium carbonate and 100 mg of non-radioactive sodium acetate were added as carrier. Also few drops of methyl orange were added as pH indicator.

After a low vacuum (0.2 bars below the atmospheric pressure) was achieved the nitrogen gas was introduced in the system with a flow rate between 60 and 80 mL/min. The stripping acid (20 ml of H_2SO_4 6M) was dropped into reaction vessel through the separation funnel and the carrier gas was purged into the system for 1 hour.

Since iodine was not used in these tests, first scrubbing bottle was used for tritium absorption and the following three was filled with alkaline solution for $^{14}CO_2$ absorption. The ^{14}C recovery was between 94.79 and 98.32%. The average recovery was 96.97% with a standard deviation of 1.46%. From the recovered ^{14}C around 99% was found in the gas washing bottle #2, and around 0.8% in the third gas washing bottle. No $^{14}C$was found in the fourth scrubbing bottle and it was decided to use only two alkaline gas washing bottles in the following tests. No gamma emitters were identified in any of the scrubbing bottles and 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%). Also the solutions sampled from the alkaline gas washing bottles were counted for tritium (using double labelled mode) but tritium was not detected above the background in these samples. All tritium added in the reaction vessel was found in the acid scrubbing bottle.

An average memory effect of less than 1% was observed. No washing step was performed between the recovery step and the memory one.

In the second set of recovery tests beside the radionuclides used in the previous tests organic ^{14}C in form of sodium acetate was also added in the reaction vessel. The experimental results obtained for ^{14}C recovery from these tests are reported in Table 1.

From these tests it was observed that the recovery of the ^{14}C-labelled sodium acetate was quite low but in the content of ^{14}C in the gas washing bottles designated to absorb $^{14}CO_2$released in the acid stripping step was higher that the ^{14}C introduced in the reaction vessel as^{14}C-labelled sodium carbonate/bicarbonate. Since no other radionuclides were identified in the solutions sampled from the alkaline scrubbing bottles demonstrating that the ^{14}C measurement by LSC was not affected by interferences, the total ^{14}C recovery was computed and it was close to 100%. To confirm these results a second test was carried out in the same conditions with similar results. 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$^{14}CO_2$ in the acid stripping step.

In the next test the amount of sulphuric acid used as stripping reagent was decreased to 10 ml, but the experimental results were similar with those obtained by using 20 ml. Similar results were also obtained using as stripping reagent nitric acid.

The next test was performed using as stripping acid chloric acid but in this test the chlorine ions destroyed the catalyser and very low ^{14}C was measured in the alkaline gas washing bottles designed to absorbed the $^{14}CO_2$released during wet oxidation step.

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Table 1. The experimental results obtained in the recovery tests

Test #	^{14}Ctype	Bq in reaction vessel	Bq recovered in scrubbing bottles	η %
Test 1 20 ml H_2SO_4 6M	^{14}C-labelled sodium carbonate/bicarbonate	5.10 10^3	8.50 10^3	166.66
	^{14}C-labelled sodium acetate	1.64 10^4	1.37 10^4	83.22
	total ^{14}C	2.15 10^4	2.22 10^4	102.99
Test 2 20 ml H_2SO_4 6M	^{14}C-labelled sodium carbonate/bicarbonate	6.06 10^4	9.92 10^4	163.75
	^{14}C-labelled sodium acetate	1.64 10^5	1.17 10^5	71.11
	total ^{14}C	2.25 10^5	2.16 10^5	96.07
Test 3 10 ml H_2SO_4 6M	^{14}C-labelled sodium carbonate/bicarbonate	9.41 10^3	1.27 10^4	134.75
	^{14}C-labelled sodium acetate	1.05 10^4	7.18 10^3	68.69
	total ^{14}C	1.99 10^4	1.99 10^4	99.99
Test 4 20 ml HCl6M	^{14}C-labelled sodium carbonate/bicarbonate	3.03 10^4	5.19 10^4	171.36
	^{14}C-labelled sodium acetate	8.21 10^4	8.54 10^2	1.04
	total ^{14}C	1.12 10^5	5.27 10^4	46.92

To assess how much from the ^{14}C in 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 3) after the acid stripping step of the analytical method.

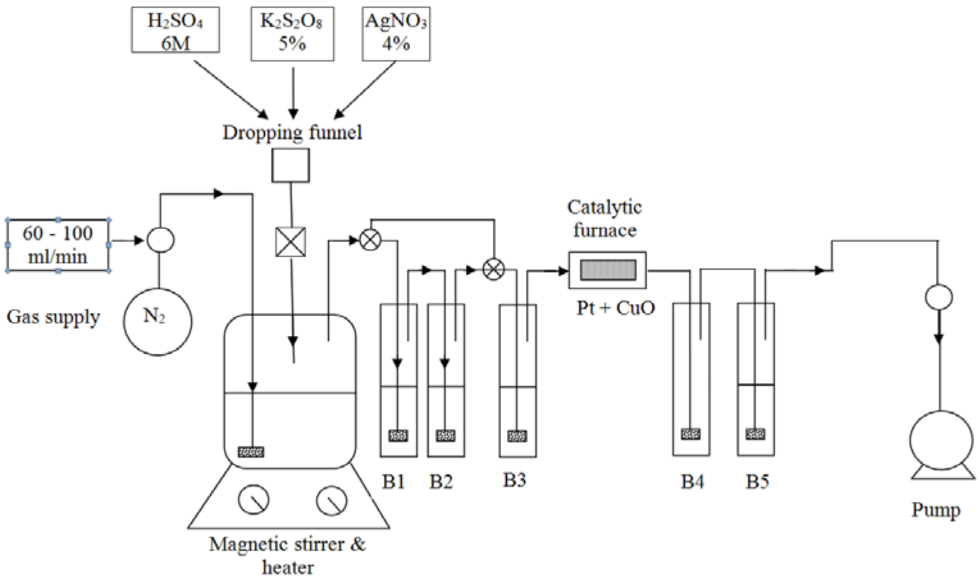

Figure 3. The experimental set-up used to evaluate the ^{14}C released from the ^{14}C-labelled sodium acetate

These tests showed that around 40% from the ^{14}C activity introduced in the reaction vessel was released as $^{14}CO_2$ in the acid stripping step and the rest after the wet oxidation.

A hypothesis that could explain the results of these tests was 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 $^{14}CO_2$ 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.

To have no doubt on the good selectivity between inorganic and organic form of the proposed analytical method a solution containing ^{14}C-labelled lauric acid (even this chemical form is less probable to be present in the SIERs and more in the liquid waste generated by NPP operation as it is present mainly in soaps and other solutions) was used in another set of acid stripping/wet oxidation experiments.

In these tests, good recoveries were obtained both for ^{14}C in inorganic form (as sodium carbonate/bicarbonate) and organic form (as lauric acid) and no other radionuclides were identified by gamma spectrometry in the solutions sampled from the alkaline scrubbing bottles.

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 following experimental conditions were chosen for the inorganic and organic ^{14}C measurement in CANDU SIERs.

Table 2. 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 $K_2S_2O_8$ + 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

To account for the uncertainty associated to this analytical method, 6 identical tests were carried out using virgin ion exchange resin (IRN 150) spiked both with inorganic and organic ^{14}C solutions, as well as with tritium and gamma emitters. The standard deviation of the results of these tests was less than15%.

3.2 *Total ^{14}C content in CANDU SIERs*

Before analysed the spent resins by combustion, a mass of resin was filtered to remove the excess of water and the water content of the resin sample after filtering was measured using a thermo balance. The water content measured was 60.10% (calculated based on mass loss at 105°C).From this sample, 5 sub-samples of around 0.15 g were prepared for combustion.

These sub-samples were analysed by combustion using experimental conditions described in Chapter 3.1.1.

Permafluor E+ was used as LSC scintillation cocktail, with a ratio sample/scintillator of 1/19. After the combustion process, the ^{14}C vials were kept in dark and cold place for at least 4 hour before their counting by LSC.

The activity of ^{14}C in the SIERs samples analyzed is reported in Table 3, as Bq of ^{14}C per gram of wet resin.

Table 3. The total ^{14}C content in CANDU SIERs transferred from Cernavoda NPP

# SIERs	**SIERs mass, g***	**^{14}C activity, Bq/g**
CANDU 1	0.149	3.82 10^{4}
CANDU 2	0.149	3.38 10^{4}
CANDU 3	0.154	3.91 10^{4}
CANDU 4	0.153	3.65 10^{4}
CANDU 5	0.152	3.48 10^{4}
	Average	**(3.65 ± 0.22) 10^{4}**

*wet mass

After combustion no other beta-gamma emitters were identified neither in the ^{14}C vials. The experimental results obtained for these samples indicate that the SIERs transferred from Cernavoda NPP contain around 3.6 Bq/g of ^{14}C.

3.3 *Inorganic and organic ^{14}C in CANDU SIERs*

From the same filtered resin prepared for total ^{14}C measurement by combustion, five sub-samples of 1 g each were used to measure the inorganic and organic ^{14}C content in experimental conditions resumed in Table 2.

Both filtered spent resin samples and the excess water were analysed. For spent resins, in the reaction vessel beside 1 g of resin and 0.2 g of carbon carrier (0.2 g of carrier (Na_2CO_3 and CH_3COONa), also 20 ml of NaOH 2 M was added, while for the excess water samples, 10 ml of water and 10 ml of NaOH 2M were added in the reaction vessel together with the carbon carrier.

The experimental results obtained for inorganic and organic ^{14}C in five CANDU SIER subsamples are presented in Table 4.

Table 4. Inorganic and organic ^{14}C contentin CANDU SIERs transferred from Cernavoda NPP.

SIERs #	Bq/g in wet SIERs (ω = 60.10%)			% from the total ^{14}C	
	Inorganic ^{14}C	Organic ^{14}C	Total ^{14}C	Inorganic ^{14}C	Organic ^{14}C
CANDU 1	$(2.99\pm 0.59)\cdot 10^4$	$(3.44\pm 0.69)\cdot 10^3$	$(3.33\pm 0.66)\cdot 10^4$	89.68±17.94	10.32±2.06
CANDU 2	$(3.04\pm 0.61)\cdot 10^4$	$(1.88\pm 0.37)\cdot 10^3$	$(3.23\pm 0.65)\cdot 10^4$	94.18±18.84	5.82±1.16
CANDU 3	$(3.27\pm 0.65)\cdot 10^4$	$(2.04\pm 0.41)\cdot 10^3$	$(3.47\pm 0.69)\cdot 10^4$	94.12±18.82	5.88±1.18
CANDU 4	$(3.25\pm 0.65)\cdot 10^4$	$(2.00\pm 0.44)\cdot 10^3$	$(3.45\pm 0.69)\cdot 10^4$	94.19±18.84	5.81±1.16
CANDU 5	$(3.17\pm 0.63)\cdot 10^4$	$(2.18\pm 0.46)\cdot 10^3$	$(3.39\pm 0.68)\cdot 10^4$	93.56±18.71	6.44±1.29
Weighed average	$\mathbf{(3.14 \pm 0.13)\cdot 10^4}$	$\mathbf{(2.13 \pm 0.50)\cdot 10^3}$	$\mathbf{(3.37 \pm 0.10)\cdot 10^4}$	**93.08 ± 2.01**	**6.30 ± 1.46**

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.

The analysis of the excess water shows that it contains no inorganic ^{14}C and only a small amount of organic ^{14}C (around 4.42 Bq/ml).

Regarding the partition 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.

Even these results were not obtained on a representative SIERs sample from the SIERs that will have to be geological disposed, them are similar with those reported by PARK, who obtained for CANDU SIERs only an average of 5% of organic ^{15}C [PARK*et al.*, 2008].

Since the main source of the 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 bicarbonate ($H^{14}CO_3^-$).

Since the analytical method used measuring from the same SIER sample also tritium content and gamma emitters, the concentration activities of these radionuclides were also measured. These data are reported in Table 5.

Table 5. The concentration activity of tritium and gamma emitters content in CANDU SIERs transferred from Cernavoda NPP

SIERs #	Bq/g of wet resin				
	^{3}H	**^{137}Cs**	**^{60}Co**	**^{134}Cs**	**^{54}Mn**
CANDU 1	$1.70\ 10^{5}$	$1.62\ 10^{4}$	$1.04\ 10^{3}$	$3.27\ 10^{2}$	$1.60\ 10^{1}$
CANDU 2	$8.25\ 10^{4}$	$1.69\ 10^{4}$	$1.34\ 10^{3}$	$3.34\ 10^{2}$	< SLD
CANDU 3	$1.65\ 10^{5}$	$1.75\ 10^{4}$	$9.07\ 10^{2}$	$3.60\ 10^{2}$	$3.15\ 10^{1}$
CANDU 4	$1.05\ 10^{5}$	$1.78\ 10^{4}$	$7.83\ 10^{2}$	$3.62\ 10^{2}$	$2.24\ 10^{1}$
CANDU 5	$1.92\ 10^{5}$	$1.78\ 10^{4}$	$8.22\ 10^{2}$	$3.58\ 10^{2}$	$2.22\ 10^{1}$
average	**$1.43\ 10^{5}$**	**$1.72\ 10^{4}$**	**$9.78\ 10^{2}$**	**$3.48\ 10^{2}$**	**$1.84\ 10^{1}$**
stdev	**$4.91\ 10^{4}$**	**$6.88\ 10^{2}$**	**$2.25\ 10^{2}$**	**$1.64\ 10^{1}$**	**$1.17\ 10^{1}$**

3.4 *Uncertainties*

The uncertainty of ^{14}C measurement by LSC was around 7%. To evaluate the uncertainty associated to the analytical procedure for measuring the inorganic and organic ^{14}C, six identical tests were carried out and the standard deviation of the results were below15% and consequently, a covering uncertainty of 20% was considered for the values reported for the inorganic and organic in Table 4.

Conclusions

The ^{14}C inventory and its partition between inorganic and organic species in CANDU SIERs were determined by RATEN ICN on a SIERs transferred from the Cernavoda unit 1.

Since currently the SIERs are stored at Cernavoda on site under water (in concrete vaults lined with epoxy) and up to now no SIERs sampling was performed, in the experimental programme carried out under CAST WP4 a SIERs sample collected during maintenance operation from MOD and PHTS purification circuits were used.

The experiments performed show that this sample contains around $3.37\ 10^{4}$Bq/g of ^{14}C, mostly as inorganic form (only less than 7% from the measured ^{14}C was found to be in organic form).

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D 4.5   APPENDIX III

CArbon-14 Source Term

FZJ contribution to

Final report on the estimation of the source term and speciation (D4.5)

Author(s):

C. Rizzato, N. Shcherbina

D 4.5 APPENDIX III

Executive Summary

Forschungszentrum Juelich (FZJ) is involved in all tasks of WP4, in particular on ^{14}C on SIERs and in the fractions released from (S)IERs used in BWR. Quantitative evaluations of the total, organic and inorganic ^{14}C on and released by the resins have been performed for the BWR SIERs, similarly to earlier works [MAGNUSSON et al., 2008]. The effect of different conditions, *e.g.* pH, radiolysis, degradation, rehydration, on ^{14}C speciation has been studied.

In a first step, the state of the art is drawn from the reported data, which is anticipated to constitute the basis for optimization of further investigations on ^{14}C release. This is considered to be a necessary input for the safe assessment of a repository, going beyond the total activity and partitioning of ^{14}C.

It has to be noted that the work at FZJ, related to WP4, is part of an on-going PhD thesis, which is scheduled to be submitted in 2016. Authorisation by the PhD candidate is necessary prior to publication or quotation of any results.

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1. Progress in Task 4.1

FZJ contributed to the “Current status review of ^{14}C and its release from SIERs”. FZJ is also involved in other relevant R&D activities to establish and deepen the understanding of ^{14}C forms and leaching behaviour. Accordingly, this will allow for predictions on the source term with lower uncertainties than in the past and, in parallel, for the development of appropriate treatment and conditioning methods to ensure the safe disposal of this specific waste.

In the following, a short summary is reported together with the updated list of samples (Table 13) and criteria for the sample choice.

1.1. *Sample choice*

Sample selection criteria have been reported in D4.1 [RIZZATO et al., 2014].

The SIERs samples selected and received by FZJ are summarized in Table 13. Samples FZJ-C and FZJ-E were not delivered after internal decision at the Nuclear Power Plants – see D4.3 [BUCUR et al., 2015] for details.

Table 1. Summary of the different samples received by FZJ.

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

(n/a=not available; x=received; y=yes)

1.2. *Analytical techniques*

FZJ focused on the speciation of the released ^{14}C, both in solution and in the gas phase. The total ^{14}C released in the liquid and gas phase must be quantified and linked to the operational/storage conditions, *e.g.* temperature, dry or wet storage, pH, etc. In case of a detectable amount with radio-analytical methods (Liquid Scintillation Counting), and a direct speciation of ^{14}C in the gas phase could be determined by R-GC/GC-MS. Correspondingly LSC, HPLC are being used for analysis of the liquid phase.

Analytical development to lower the detection limits for the ^{14}C-speciation/quantification in solution and in the gas phase has been performed in FZJ. Particular effort was put in the validation of the equipment implied for the gas phase analyses. In detail, the conversion efficiency of organic compounds in the catalyser has been investigated with reference gases (CO, H_2, CH_4) at different gas flows. The experimental set-up is reported in Figure 17. A sample of calibration gases (extra pure and certified) has been loaded in a gas mouse at a well-defined pressure. After the background stabilization of the quadrupole mass-spectrometer under argon, a by-pass allows the flowing of the sample through the catalyser. The resulting gas composition was analysed by MS and the conversion efficiency has been calculated. The experiments have been performed with the catalyser at room temperature and at 750°C, in order to have a reliable comparison of the results.

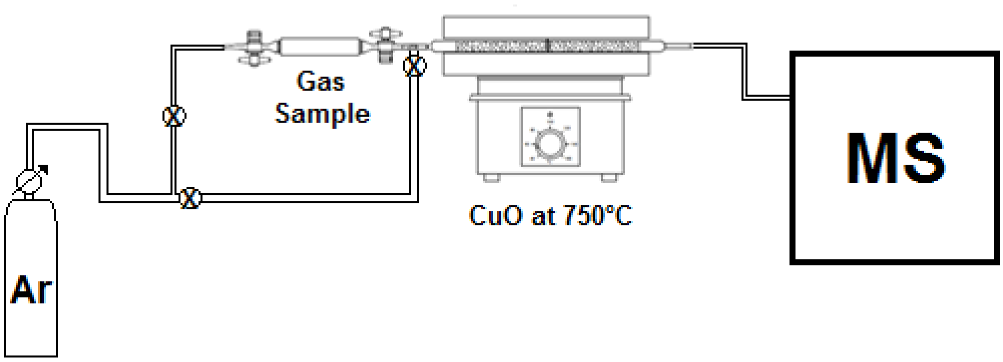

Figure 1: Experimental set-up for testing the conversion efficiency of the CuO catalyser.

Pressures of 50, 100, 200, and 350 mbar have been employed for the gas sample preparation in the gas mouse. A flow-rate of about 6 ml/min with 50 g of catalyser resulted in a successful conversion of all the gases. This value has been chosen accordingly to the average flow-rate of the developed washing bottles – see CAST D.4.3 [BUCUR *et al.*, 2015]. In all cases, a total conversion of H_2 has taken place. The conversion efficiency for CO resulted higher than 99%. At last, the conversion of methane resulted higher than 99% as well. In conclusion, the chosen parameters (*i.e.* temperature of the catalyser, gas flow, amount of catalyser) showed an efficient conversion of the gases at different partial pressures (concentrations).

The sequence of washing bottles for the radioanalytical analyses of ^{14}C released in the gas phase has been successfully optimized, allowing a lower dilution of the ^{14}C activity and an optimal volume for the ^{3}H and ^{14}C 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/Al_2O_3, initially considered, has been abandoned due to the activity retention (memory effect) experienced during leaching tests on graphite. Only CuO has been employed for the catalyser. The washing bottles, positioned after the catalyser, are absorbing the new-formed HTO and $^{14}CO_2$. However, gaseous releases from SIERs could be more complex and variegated as the ones from i-graphite. Therefore, GC-MS has been used for the measurement of the compounds in the gas phase.

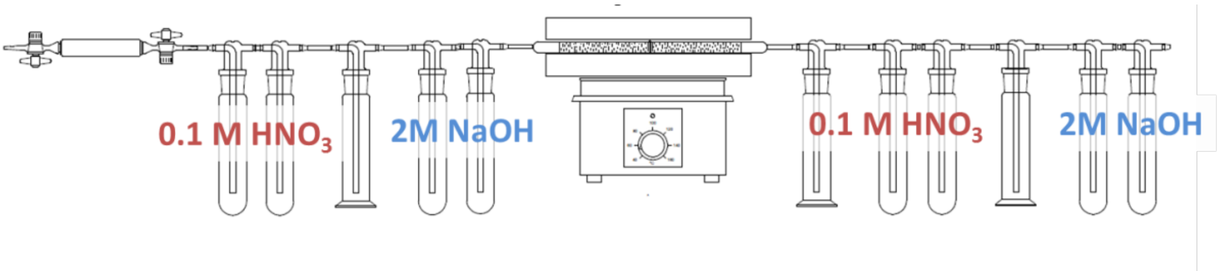

Figure 2. Experimental setup for the analysis of ^{14}C in FZJ, with a catalyser to convert HT to HTO, CO to CO_2 and organics to CO_2.

Morphological investigations of (S)IERs are performed with Scanning Electron Microscopy (SEM) and the activity distribution is analysed with Autoradiography (see § 2.3.2, page 6).

It is anticipated that methods like IC, SS-NMR, ^{1}H-NMR and ^{13}C-NMR have been applied for the investigation of model SIERs in order to simulate radiation-induced effects altering the speciation of ^{14}C (see § 2.3.3, page **Error! Bookmark not defined.**).

2. Progress in Task 4.2

The results from MAGNUSSON AND STENSTRÖM [2005] and PARK *et al.* [2008] show that the majority of the ^{14}C activity comes from the inorganic (ion exchangeable) compounds. Particularly, in CANDU reactors, most ^{14}C is retained in anion-exchange resins in inorganic form PARK *et al.* [2008]. A minor fraction of ^{14}C-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 in form of metal carbonate [MOIR *et al.*, 1994].

Analyses performed at FZJ, aimed at the determination of the total and organic/inorganic ^{14}C fractions, are still in progress. First results confirm the findings reported by MAGNUSSON AND STENSTRÖM [2005] and PARK et al. [2008], *i.e.* most of the ^{14}C is retained in the resins in inorganic form – most probably as hydrogeno-carbonate. A small fraction, up to few % of the total ^{14}C, was found to be under organic form.

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

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

In order to clarify the form of ^{14}C, different approaches have been adopted:

- direct measurement of the species released into solution after regeneration of the resins by HPLC (quantification and qualification); formate ions have been detected in small amounts ($\mu g/g_{resin}$). However, interference of other compounds, e.g. amines, cannot be excluded;
- in reference to the method reported in MAGNUSSON AND STENSTRÖM [2005] and PARK et al. [2008], related to the determination of the organic/inorganic ^{14}C fractions, a slight modification of the procedure could allow the location of the organic ^{14}C; 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 to understand whether ^{14}C is in ionic or non-ionic from; this approach is going to be tested in the next future;
- indirect measurement by combustion of fully regenerated resins did not result in any detectable activity; this result demonstrates that the fraction of organic non-exchangeable ^{14}C is negligible; however, only a preliminary test has been performed, with low amounts of resins, *ca.* 0.3 g, in order to avoid saturation of the solution in the washing bottles due to the high amounts of CO_2 produced;
- the ^{14}C 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.

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2.1. *Separation of mixed-bed resins*

Experiments on the separation of the cation- from the anion-exchange fraction by NaCl in solution have been conducted in FZJ with fresh IERs, in order to test the method (Figure 19). Taking advantage of the different density of bead resins in different ionic forms, a successful separation of the two fractions has been achieved, with efficiencies up to 90-95%, depending on the sample amount.

The separation process, related to the SIERs aims to investigate:

- only the organic non-exchangeable ^{14}C, since a stripping (or regeneration) of the resins is necessary during the process (by means of NaCl in solution);
- the residual ion-exchange capacity (anion/cation fraction), which could be an important indicator to understand the degradation status of the SIERs.

The process is working properly only for resins in bead form, due to the broad particle size distribution of the powder resins that is hindering an efficient separation. After first unsuccessful experiments, an optimization of the equipment resulted in the separation of mixed-bed powder resins. However, the separation is time-consuming (in the order of several days per single sample). Additionally, powder resins are mixed with a flocculation media (acrylic fibres) and contain particulate matter. The separation efficiency is going to be evaluated in the near future.

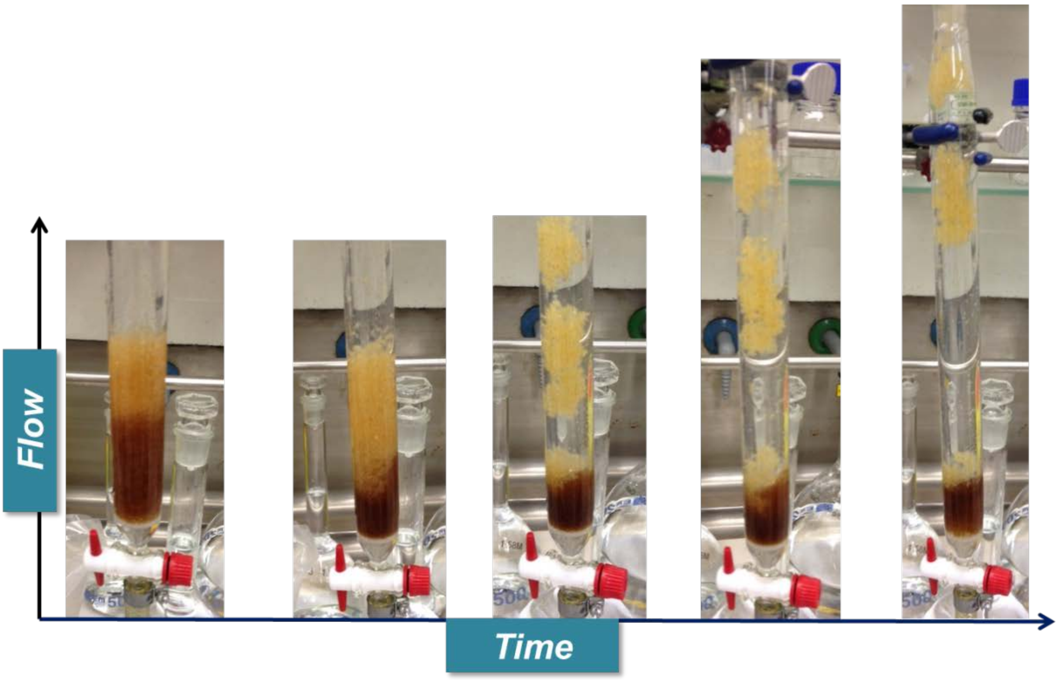

Figure 3. Separation of mixed bed resins in bead form

2.2. *Morphology of powder resins*

The morphology of SIERs could highlight degradation of different nature, which could be significant for what concerns the releases of ^{14}C. SEM investigations on the morphology of resins in powder form have been performed using reference material, i.e. flocculation media and fresh SIERs – see CAST D.4.3 [Bucur et al., 2015].

Spectroscopic analyses of SIERs (samples FZJA-FZJB) are reporter in Figure 20. It can be noticed that SIERs are mixed (anion and cation-exchange), together with a flocculation media. The inert material, used in the past to flocculate the powder resins in-situ, shows a characteristic fibre-like shape (Figure 20). The size distribution of the powder resins seems quite broad, with particles ranging from few to some hundred micrometres.

The presence of particulate matter, earlier hypothesized, has been confirmed in both cases and it can be identified as bright agglomerates, *i.e.* higher atomic number, in Figure 20. In fact, powder IERs implied in BWR are acting also as a mechanical filter. The agglomerates (particulate matter) were analysed by EDX and revealed the presence of several metals, like Co and Fe.

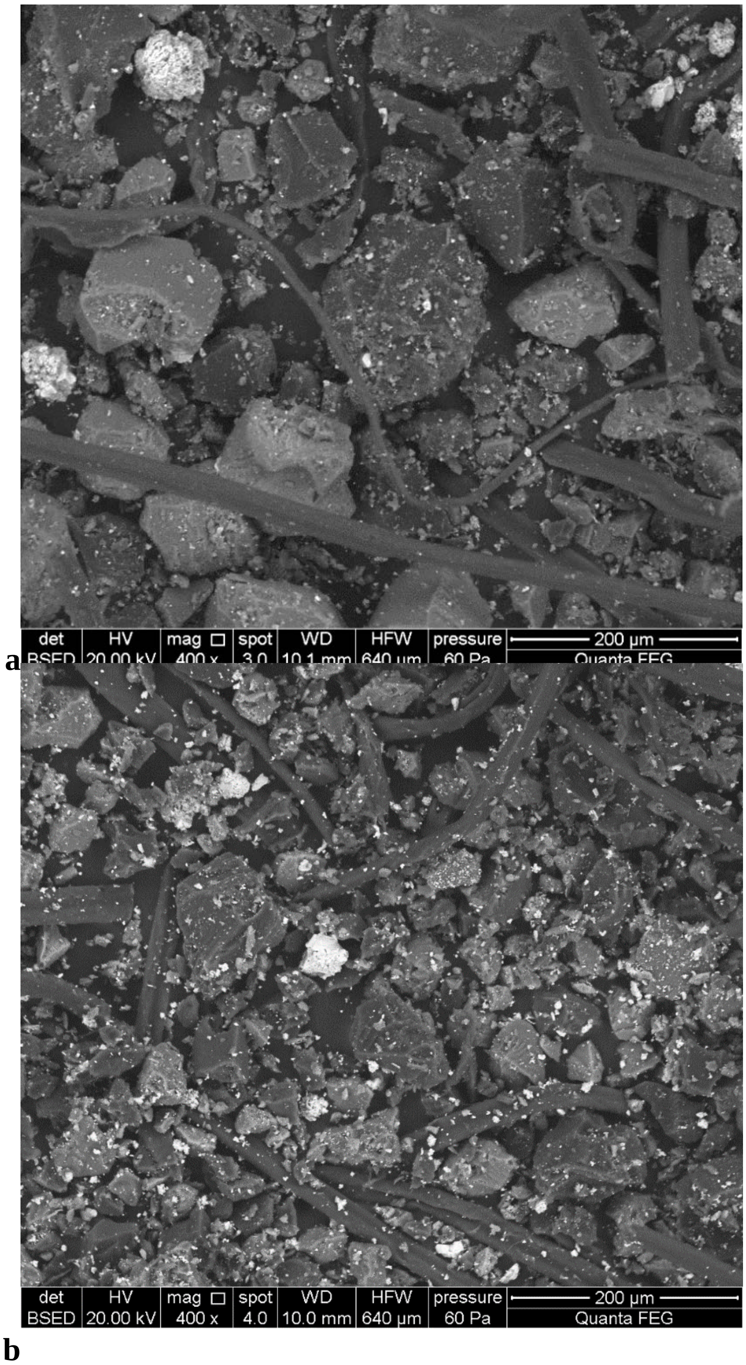

Figure 4. Powder SIERs from FZJA (a) and FZJB (b) (with particulate matter and acrylic fibers)

Autoradiographic analyses on powder SIERs were performed in order investigate a possible activity concentration on such agglomerates (hot-spots). The presence of “hot-spots” in the SIERs, probably arising from the particulate matter, has been confirmed. In order to better understand the nature of the hot-spots, autoradiography and SEM were planned on the same samples. The aim was to perform a “mapping” of the samples in order to localize and identify the activity distribution and its sources. SEM analyses with powder materials require, however, an immobilization of the sample. Therefore, autoradiography has been performed on powder SIERs samples, immobilized with a carbon-based tape, but the small amount of material (few mg) did not contain sufficient activity to overcome the background. In a second step, an immobilization of powder SIERs with epoxy resins has been attempted. However, a strong shielding effect, together with many artefacts, resulted in unsatisfactory autoradiographies. In conclusion, the presence of metals in the agglomerates could represent an inhomogeneous source of γ/β-activity and it cannot be excluded that a fraction of ^{14}C is retained in the particulate matter.

APPENDIX IV

CArbon-14 Source Term

CAST

UJV contribution to

Final report on the estimation of the source term and speciation (D4.5)

Author(s):

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APPENDIX IV

Executive Summary

Three types of spent ion exchange resins were used for desorption/leaching test. Two of the SIERs were from nuclear power plant operation and the third one was from research reactor operation. In following text all of these samples are commonly denoted as "real" ion exchange resins samples. All of these samples had some join characteristics, mainly the storing conditions and history.

Experimental work in ÚJV laboratory was mainly focused on desorption/leaching studies of inorganic form of carbon (using hydrogeno-carbonates) fixed on ion exchange resins from reactor operation and testing of resins fixation into the cement matrix.

1. ANALYTICAL TECHNIQUE FOR 14C INVENTORY AND SPECIATION

1.1. *Determination of inorganic 14C content*

Defined amount of analysed material is weighed into the round-bottom flask together with NaOH solution, and also 0.5 of Na_2CO_3 is added. The distillation apparatus is assembled as shown in Fig. 1. Erlenmeyer flask and ending flask are filled with NaOH solution. By the funnel on the top of the apparatus the concentrated H_2SO_4 is added to dissolve inorganic material. The heater is switched on to start distillation process. After the distillation of approx. 40 ml of water, the distillation is stopped. Solutions from Erlenmeyer flask and ending flask are mixed with solution of $BaCl_2$ and $BaCO_3$ is precipitated. The precipitate is filtered and analysed for ^{14}C content.

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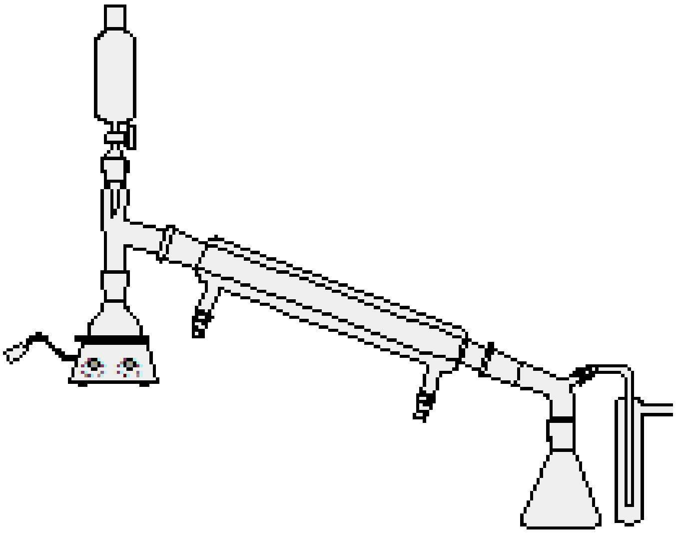

Figure 1: Apparatus for total or inorganic 14C content determination.

1.2. *Determination of total 14C content*

The process is almost similar to inorganic 14C determination. Defined amount of analysed material is weighed into the round-bottom flask together with NaOH solution, and also 0.5 of Na_2CO_3 is added. The distillation apparatus is assembled as shown in Fig. 1. Erlenmeyer flask and ending flask are filled with NaOH solution. By the funnel on the top of the apparatus the chromic acid (a mixture of concentrated sulphuric acid and dichromate) is added to dissolve/digest all analysed material. The heater is switched on to start distillation process. After the distillation of approx. 40 ml of water, the distillation is stopped. Solutions from Erlenmeyer flask and ending flask are mixed with solution of $BaCl_2$ and $BaCO_3$ is precipitated. The precipitate is filtered and analysed for ^{14}C content.

1.3. *Determination of organic ^{14}C content*

The amount of organic ^{14}C content is calculated as a difference between the amounts of total and inorganic ^{14}C in the material.

APPENDIX IV

2. Resins from nuclear reactor operation

Three types of spent ion exchange resins were used for desorption/leaching test. Two of the SIERs were from nuclear power plant operation and the third one was from research reactor operation. In following text all of these samples are commonly denoted as "real" ion exchange resins samples. All of these samples had some join characteristics, mainly the storing conditions and history. Spent real resins samples from each reactor operation are collected in storing tanks. Because resins are collected in the tank for all time of reactor operation, it is not possible to determine the age of the sample.

2.1. *EDU SIER*

Spent ion exchange resins from Dukovany Nuclear Power Plant (EDU) operation were sampled in 1998. Unfortunately there is no more detailed information about the sample – date, place, procedure of sampling, conditions etc. Stored sample was wet and contained impurities, sediments and mud (see Figure 2). Therefore it was necessary to separate resins beads from impurities and mud by rinsing and decantation. Separated resins were then used for desorption/leaching experiments.

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 EDU spent resin during this process. EDU resin was analysed to obtain activities of ^{14}C in total and as organic and inorganic species and also of other major radionuclides (see Table 1). As other major radionuclides ^{60}Co and ^{137}Cs were observed.

Figure 2. SIER from Dukovany Nuclear Power Plant operation

Table 1. ^{14}C and other major radionuclides activity in EDU SIER

Nuclide	Activity (Bq/g)
^{14}C (total)	48 ± 5.9
^{14}C (inorg.)	14 ± 2.2
^{14}C (org.)	34 ± 5.5
^{60}Co	140 ± 8.3
^{137}Cs	22 ± 2.8

2.2. *ETE SIER*

Spent ion exchange resins from Temelín Nuclear Power Plant (ETE) operation were sampled in 2013. Unfortunately there is no more detailed information about the sample (date, place, procedure of sampling, conditions etc.). Stored sample was wet and contained some impurities (see Figure 3) that were removed before using resin in experiments.

ETE resin was analysed to obtain activities of ^{14}C in total and as organic and inorganic species and also of other major radionuclides (see Table 2). As other major radionuclides ^{125}Sb, ^{137}Cs, ^{125}I, ^{134}Cs, ^{51}Cr, ^{40}K and ^{60}Co were observed.

Figure 3. SIER from Temelín Nuclear Power Plant operation

Table 2. ^{14}C and other major radionuclides activity in ETE SIER

Nuclide	Activity (Bq/g)
^{14}C (total)	43 ± 4
^{14}C (inorg.)	16 ± 2
^{14}C (org.)	27 ± 4
^{137}Cs	2077 ± 65
^{134}Cs	388 ± 12
^{125}Sb	2245 ± 70
^{125}I	1858 ± 62
^{60}Co	23 ± 0.9
^{51}Cr	89 ± 4.8
^{40}K	24 ± 2.1

2.3. *ÚJV SIER*

Spent ion exchange resins from research reactor of ÚJV Group (UJV), which is placed in Řež. There is no detailed information about sampling of this SIER (date, place, procedure of sampling, conditions etc.). Stored sample was wet and without impurities (see Figure 4).

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Figure 4. SIER from ÚJV Group research reactor operation

ÚJV resin was analysed to obtain activities of ^{14}C in total and as organic and inorganic species and also of other major radionuclides (see Table 3). As other major radionuclides ^{60}Co and ^{108m}Ag were observed.

Table 3. ^{14}C and other major radionuclides activity in ÚJV SIER

nuclide	activity (Bq/g)
^{14}C (total)	2000 ± 280
^{14}C (inorg.)	2000 ± 280
^{14}C (org.)	77 ± 11
^{60}Co	590 ± 34
^{108m}Ag	860 ± 64

APPENDIX V

CArbon-14 Source Term

CAST

ENEA contribution to

Final report on the estimation of the source term and speciation (D4.5)

Author(s):

A. Rizzo, S. Bruni, A. Gessi, G. Marghella, C. Telloli,

APPENDIX V

Executive Summary

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.

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List of contents

1. ^{14}C Inventory and speciation in SIERs

ENEA has received nine wet samples (3.5-10.0 g for each sample) from Italian WMO (Figure 1). They have been operated in the Trino Vercellese NPP and they are more than 10 years old. Some samples were taken and processed with traditional wet oxidation for the measurement of ^{14}C content, but phenomena of flocculation and partial digestion were observed. The partial digestion jeopardised the accurate measurement of ^{14}C content, so further investigation has been planned in order to completely dissolve the ionic resin matrix. The used procedure was the same as other partners applied to their samples so we were studying what type of ageing effect could have affected the solubility of the resins.

Figure 1. Spent ionic resins received by the Italian WMO SOGIN

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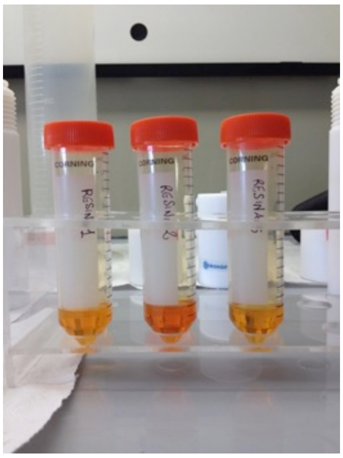

Figure 2. Residual solutions after wet oxidation of the aged ionic exchange resins

1.1. *Speciation experiment*

As regard the speciation, the re-location of the radiocarbon laboratory has been completed and the prototype of the newly designed combustion system [BUCUR *et al.*, 2015] has been installed. A double chamber combustion cell is now directly connected within the pipeline of the existing combustion system so it is possible to run a stepped pyrolysis and/or complete oxidation directly in the combustion system – Figure 3, see scheme in the circle.

A further post combustion furnace – highlighted in green in Figure 7 – has been added to the original design in order to have a complete oxidation of the sample and to get rid of the chemical oxidation trap with bichromate solution – in agreement with green chemistry principle.

The characterisation of the pipeline has started and the synthesis of benzene exhibit a good recovery yield (70-80 %). The speciation experiments will be carried out on the new and old inactivated resins.

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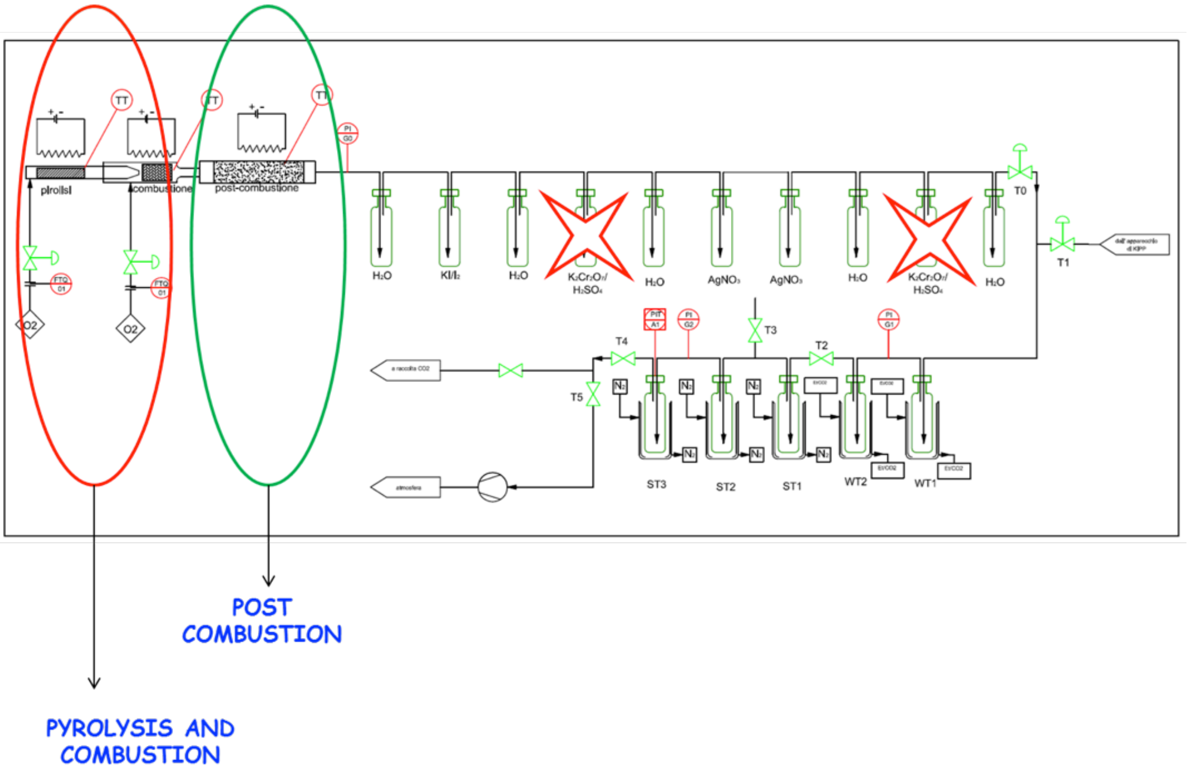

Figure 3. Scheme of the stepped combustion/pyrolysis system integrated with post combustion chamber, designed and implemented by ENEA

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

1.2. *Ageing effect*

We are investigating if the ageing of the resins has some effect on the degradation of the 3D polymeric structure and on the release of carbon. In order to achieve this objective we have planned to measure the total carbon content and to analyze the morphology of different resins of different age. The outcome will represent a valuable knowledge about the possible release of ^{14}C from the stored resins and the mechanism of release. The study has been carried out on inactive resins and could be extended to the spent ones.

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Two type of resins were selected:

- LEWATIT ® MonoPlus S200KR, which is a monodisperse, strong acidic gel type resin, nuclear grade designed. The functional group for H^+ exchange is sulphonic on cross type polystyrene beads. The bead size is specified at (0.6 ± 0.05) mm. Formerly known named as LEWATIT® S100 KR-H (Cl frei);
- LEWATIT ® MonoPlus M500KR, which is a monodisperse, strongly basic, gelular anion exchange resin, nuclear grade. The functional group of OH^- exchange is a quaternary amine, on cross type polystyrene beads. The bead size is specified at (0.64 ± 0.05) mm.

We further collected two categories among these two types: “new” and “aged” samples:

- the aged resins (both cationic and anionic) were provided by Italian WMO SOGIN and they were stored for about 15 years in a temporary repository;
- the freshly produced resins were provided by the company Lanxess S.r.l.

The choice to use “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.

1.2.1. Ageing effect on the morphology of the IERs

The morphology of the resin beads was studied by means of a SEM electronic microscope, a FEI Inspect S. Some preliminary investigation, done at the very beginning of CAST project [REILLER *et al.*, 2014] had shown that there is the evidence of degradation features in the aged ionic exchange resins provided by SOGIN. In order to investigate if the morphological degradation is pre-existent and caused by the process or it is due to the decommission operations, storage and ageing of the resins, we run a dedicated series of measures on the same samples that were analysed for the carbon content.

The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the sample surface, and a 2-dimensional image is generated that displays spatial variations in these properties. The diameters of the beads were also assessed by means of the digital imaging analysis tool “Macnification”.

One of the key parameters for the efficiency assessment of ion exchange resins, especially as far as the ^{14}C containment is concerned, is the preservation of their spherical shape in time. “Sphericity” is defined as the measure of the amount of ion exchange resin beads that are unbroken. The assessment of the sphericity reservation along time is a purely qualitative index, but could give some understanding of the general behaviour.

By means of the image analysis software Macnification®, SEM micrographies were imported, manually analysed and statistics on diameter variations and beds status were then summarized graphically.

The Figure 4a shows the typical appearance of an anionicbeads specimen. Large-scale images such the one depicted have been used for the diameters assessment.

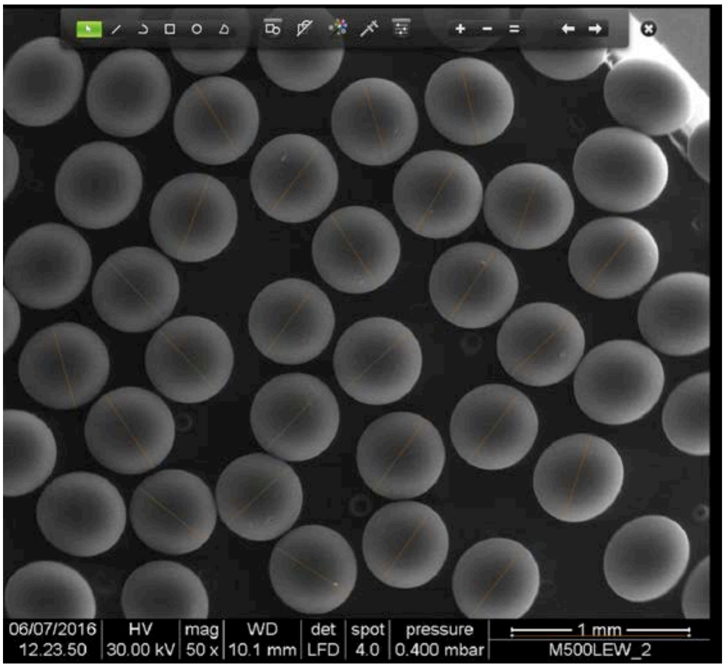

Figure 4a. 1mm scale image of anionic resin beads

Figure 4b represents an aged specimen of the same anionic resin, appearing heavily damaged.

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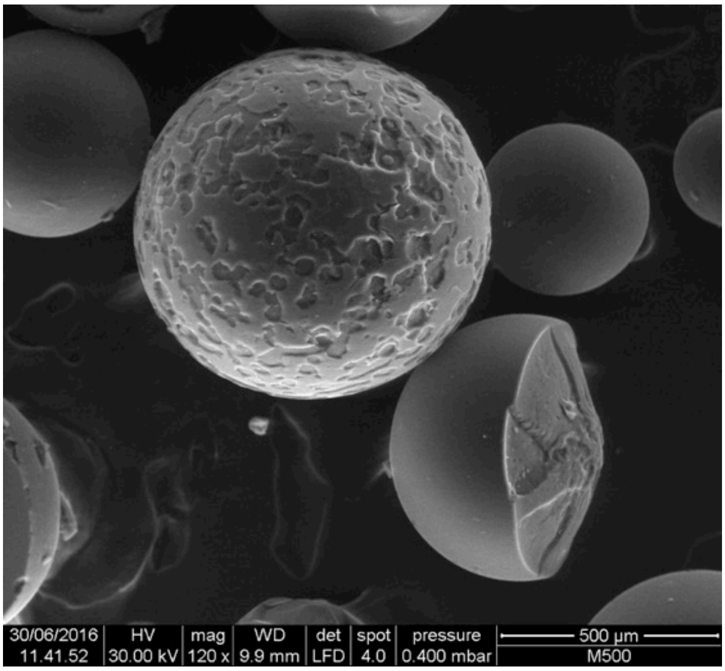

Figure 4b. 500µm scale SEM micrography of anionic resin

In Figure 4b the three degrees of sphericity degradation are apparent: some spheres are still intact, the foreground one is still spherical but with a clear surface corrosion, the right one shows a large material loss, ending in a shape loss. The aged samples appear, macroscopically, as full of random dimensions debris, hardly contained by storage filters, designed for the original beads diameters.

Figure 5a shows an aged sample of the cationic resin, which appears less damaged when compared to the anionic one.

APPENDIX V

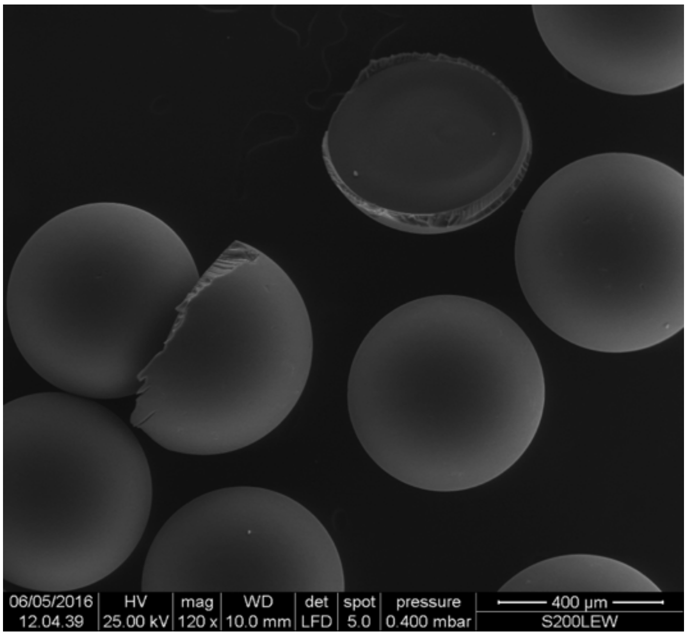

Figure 5a. Aged cationic beads

Very few spheres are damaged, mainly because of a “half” rupture. No corroded layers were determined, as well as partial or main material loss. The sample appears with less debris. From a purely qualitative point of view, it can be stated that the main difference between S200 and M500 resin beads is that the degradation in the first appears as a half sphere break, while in the latter as a random corrosion rate.

In order to classify the features of the beads, three definitions have been proposed:

- **as new**: the beads appear as supplied, both for shape and diameter;
- **degraded**: the surface of the beads appears corroded and ruined, but the global spherical shape is preserved;
- **damaged**: a heavy loss of material took place and the beads appear fragmented, without spherical shape.

We associated a colour code to each definition (Figure 5b).

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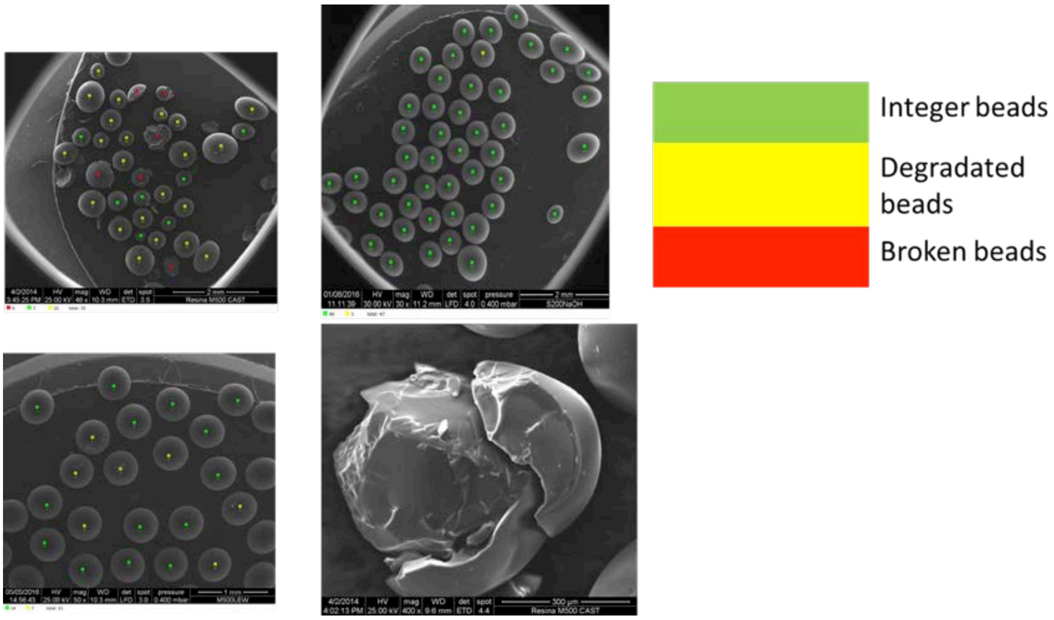

Figure 5b. Colour table classification of the beads according to their morphology

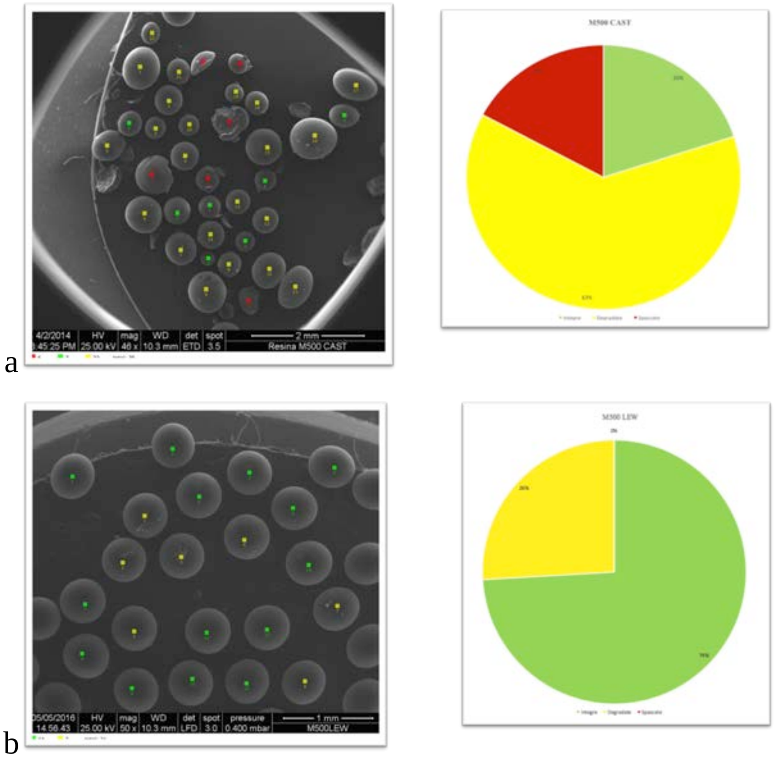

Figure 5. Classification of anionic aged (a) and new (b) resins M500

APPENDIX V

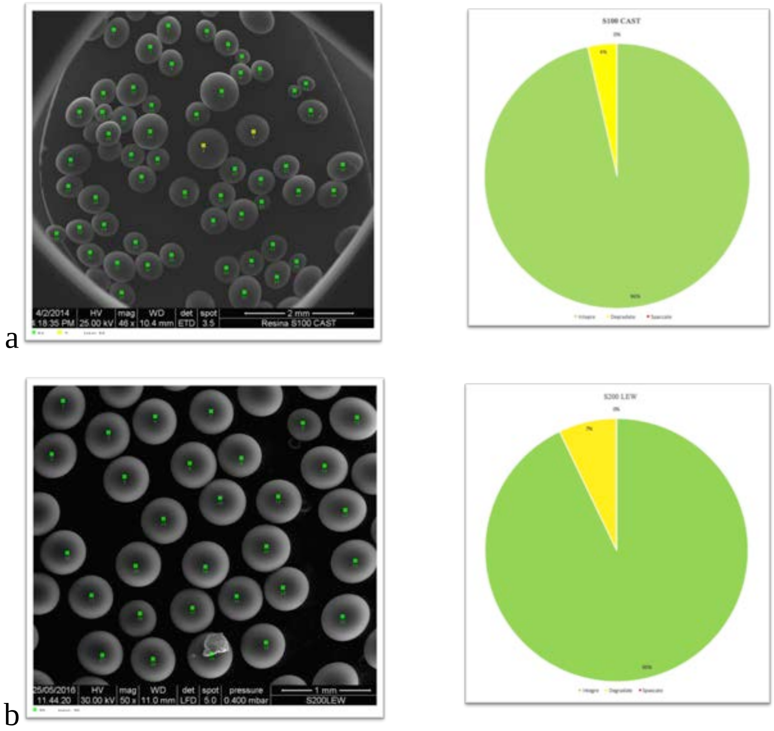

Figure 6. Classification of cationic aged (a) and new (b) resins S200

Figure 5 and Figure 6 show the classification of cationic and anionic beads, both new and aged, according to their structure, It’s evident that the anionic aged beads show more structure degradation if compared with the cationic ones.

Figure 7 summarizes the diameters evolution in time of the two resins. The sheets’ specified diameters are confirmed, with small variations from sample to sample: diameters are globally preserved in time, with small variations.

APPENDIX V

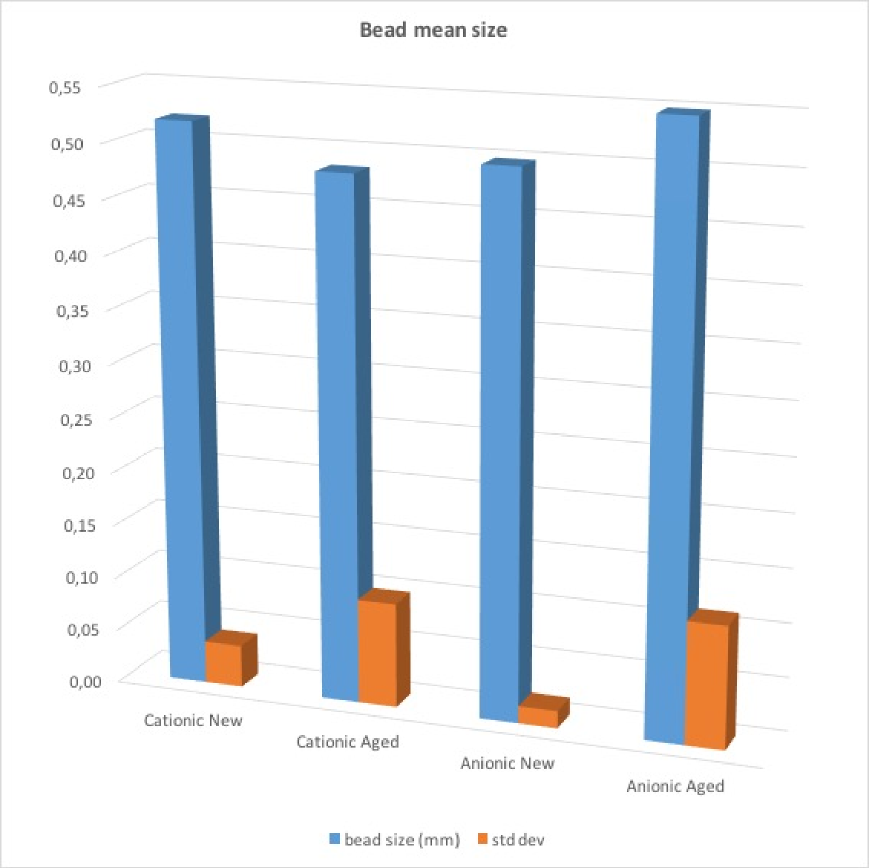

Figure 7. Comparison of bead mean diameters for new and aged resins

Analysing the full set of images, it shows up that new cationic resin are more homogeneous in size and show less defect in the spherical structure,. The amount of damaged beads reaches the 21% of the total in the anionic, whilst only the 8% in the cationic one.

After 15 years of ageing, the resin beads depict a very different feature: the cationic shows that only the 25% of the amount of beads suffered damage, while the anionic resin appeared with a 19% of the total number of beads damaged and up to the 29% with heavy random material loss. The SEM images clearly showed that the two resin behaved differently, as far as the sphericity preservation in time is concerned. The anionic beads (M500) showed a stronger degradation in time, with randomly distributed behaviours. Several beads appeared with great material losses, complete cleavage, and heavy damages over the spherical surface.

On the other hand, the cationic resin (S200), even though the original quality in terms of statistic distribution of the beads' diameters is equal to the cationic one, showed only a 20% ca. of damaged beads after ageing. This suggests that the anionic resin beads show a lower overall quality, in terms of average sphericity.

If we combine the latter outcomes with the observation of the "apparent" uptake of carbon content shown by the aged anionic resins (Figure 9), it could be hypothesised that degradation mechanism could cause some preferential exchange of elements in the terminal functional groups of the resins. It will be interesting to verify this hypothesis with the measurement of ionic exchange capacity of the new and aged resins. The possibility that the change in the composition of the terminal groups could also exhibit isotopic fractionation mechanism should be also verified or modelled in order to better understand the release phenomena.

1.3. *TOTAL CARBON CONTENT*

The total carbon content of the resins was measured for both the freshly produced resins and the aged ones. The resins were combusted at 900°C in a mixture of oxygen/helium by an elemental combustor system, recently acquired [BUCUR *et al.*, 2015] and the produced CO_2(g) was trapped in a activated charcoal trap and subsequently released for the measure by a TDC detector.

Six combustion cycles of each type of samples were run and the total carbon and nitrogen contents were as detailed in Table 12 and shown in figure 8.

Even if these are very preliminary data, we observed two opposite effects:

- in the anionic type the ageing cause an "apparent" uptake of carbon;
- in the cationic one the ageing cause a slight reduction of carbon content.

These results need further investigation in order to be assessed and to understand the underlying mechanism of carbon exchange.

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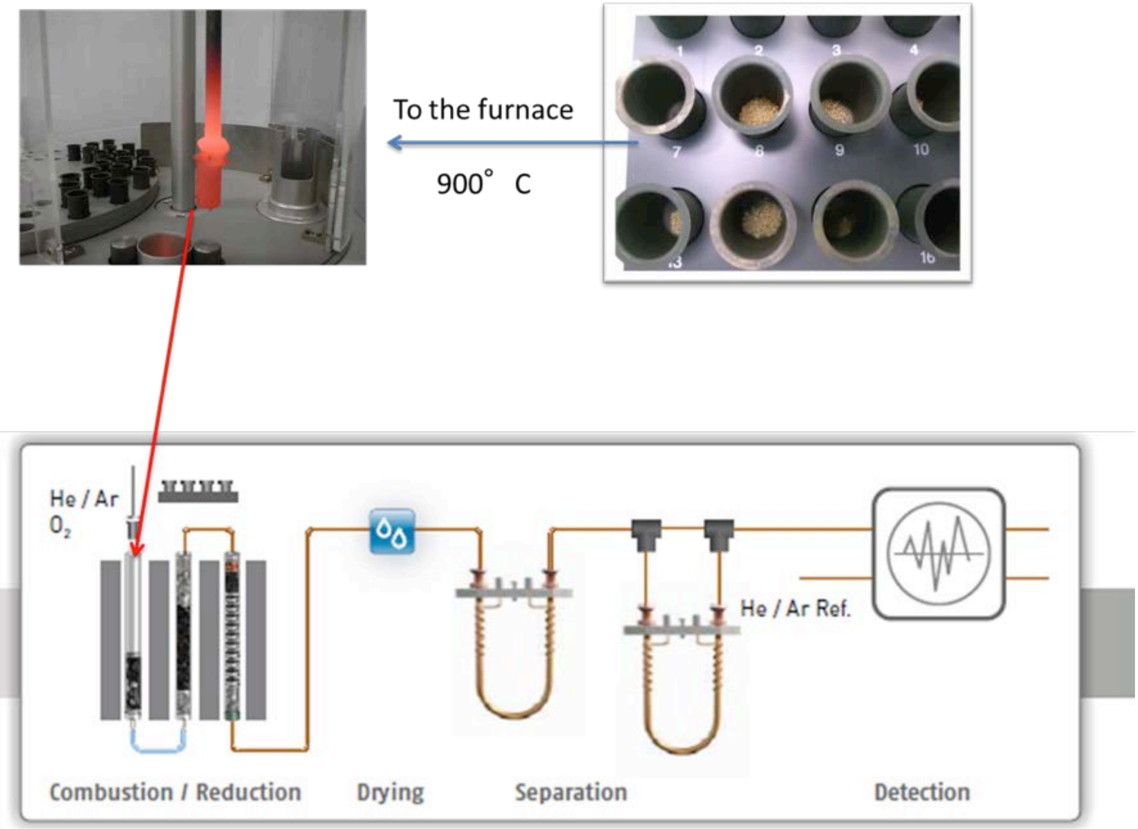

Figure 8. Combustion and separation systems for the total carbon content – samples in the Figure are inactivated resins

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.

The following data has been measured (Table 1).

The results show that the ageing in closed container caused a decrease in C content in the cationic resins that 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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Table 1

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

APPENDIX VI

CArbon-14 Source Term

CAST

SKB contribution to

Final report on the estimation of the source term and speciation (D4.5)

Author(s):

K. Kallstrom

APPENDIX VI

Executive Summary

Since the last annual report SKB has further analysed the available data from the Swedish ^{14}C sampling and analysis program. This is done in an attempt to find the reactor operating factors that influences the uptake of ^{14}C on the SIERs. The reactors in Sweden have been in operation for about 30-40 years.

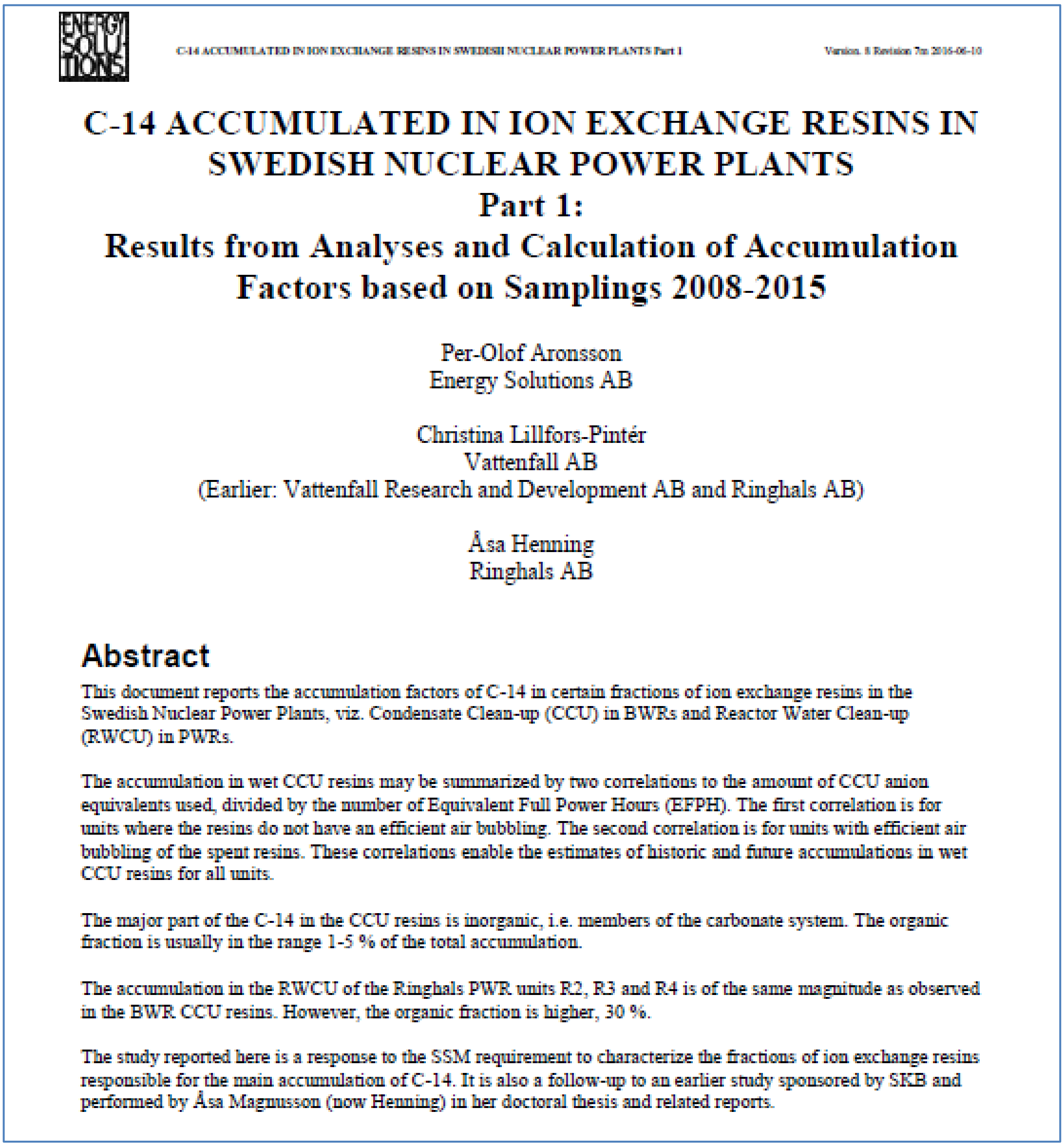
During these years the operation parameters such as SIERs operation times, anion equivalents used, reactor cooling water flow and condensate water flow has varied. The work has now been finalized and summarised in a separated report

This document reports the accumulation factors of C-14 in certain fractions of ion exchange resins in the Swedish Nuclear Power Plants. It includes data from samplings from 2008 up to and including 2015 (for one unit). The study reported here is a follow-up to an earlier study sponsored by SKB and performed by Åsa Magnusson (now Henning) in her doctoral thesis and related reports.

The ^{14}C content is divided into organic and inorganic form, which is essential for the safety assessments performed by SKB. The primary uptake of ^{14}C on the SIERs depends on the anion equivalents used in the IERs as well as the water flow through the IERs. Downstream processing such as wet storage and stirring techniques (air bubbling) influences the final amount of ^{14}C in waste packages. Downstream processing depends on the design of each reactor waste treatment facility hence it is reactor specific.

In this Appendix only a short summary of the results are reported, as the complete report "*SKB C-14 Accumulated in ion exchange resins in Swedish NPP*" is already available at https://www.projectcast.eu/cms-file/get/iFileId/2542

APPENDIX VI



C-14 ACCUMULATED IN ION EXCHANGE RESINS IN SWEDISH NUCLEAR POWER PLANTS

Part 1:

Results from Analyses and Calculation of Accumulation Factors based on Samplings 2008-2015

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Abstract

This document reports the accumulation factors of C-14 in certain fractions of ion exchange resins in the Swedish Nuclear Power Plants, viz. Condensate Clean-up (CCU) in BWRs and Reactor Water Clean-up (RWCU) in PWRs.

The accumulation in wet CCU resins may be summarized by two correlations to the amount of CCU anion equivalents used, divided by the number of Equivalent Full Power Hours (EFPH). The first correlation is for units where the resins do not have an efficient air bubbling. The second correlation is for units with efficient air bubbling of the spent resins. These correlations enable the estimates of historic and future accumulations in wet CCU resins for all units.

The major part of the C-14 in the CCU resins is inorganic, i.e. members of the carbonate system. The organic fraction is usually in the range 1-5 % of the total accumulation.

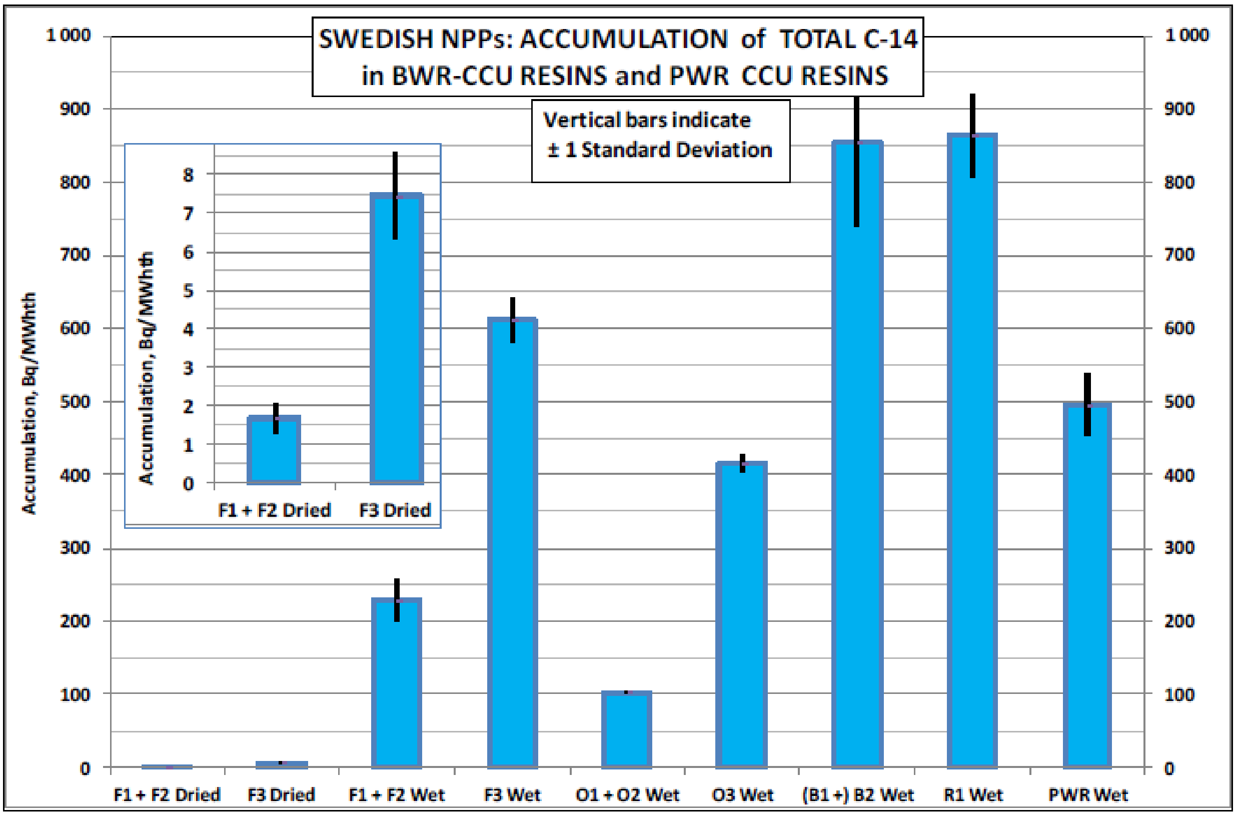
The accumulation in the RWCU of the Ringhals PWR units R2, R3 and R4 is of the same magnitude as observed in the BWR CCU resins. However, the organic fraction is higher, 30 %.

The study reported here is a response to the SSM requirement to characterize the fractions of ion exchange resins responsible for the main accumulation of C-14. It is also a follow-up to an earlier study sponsored by SKB and performed by Åsa Magnusson (now Henning) in her doctoral thesis and related reports.

APPENDIX VI

Summary of Results

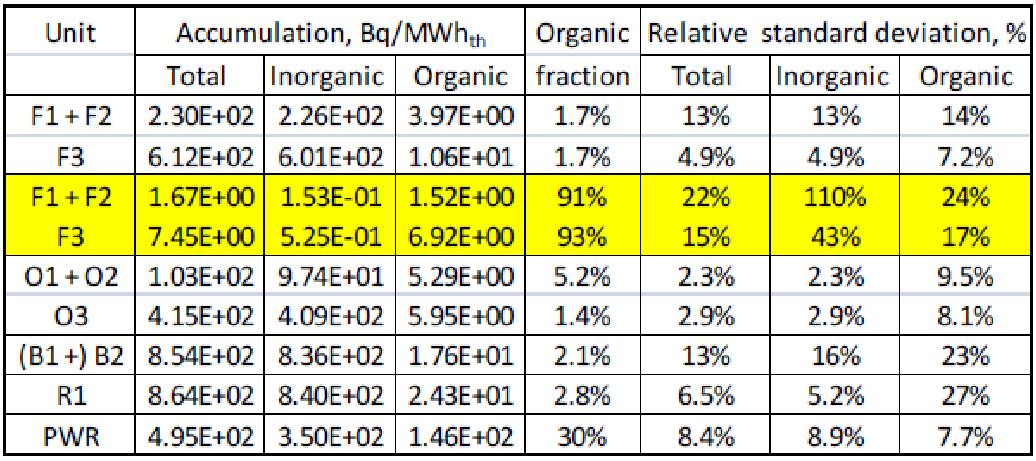
The accumulation factors are shown in *Summary Table 1* and *Summary Figures 1 and 2*, together with relative standard deviations. The accumulation is shown as Bq/MWh$_{th}$ for total, inorganic and organic C-14. The inorganic C-14 consists of species in the carbonate system, mainly hydrogen carbonate, 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.



Summary Figure 1. Accumulation factors for total C-14 expressed as Bq/MWh$_{th}$ for the Swedish NPPs. The inset is a zoom-in for dried resins from the Forsmark units. The vertical bars indicate ±1 standard deviation. O1+O2 have a standard deviation of 2.4 Bq/MWh$_{th}$. (A-2, sheet D Sum acc tot).

The organic fraction of the total accumulation is also given in Table 1. 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.

APPENDIX VI



Unit	Accumulation, Bq/MWh$_{th}$			Organic	Relative standard deviation, %		
	Total	Inorganic	Organic	fraction	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	1.67E+00	1.53E-01	1.52E+00	91%	22%	110%	24%
F3	7.45E+00	5.25E-01	6.92E+00	93%	15%	43%	17%
O1 + O2	1.03E+02	9.74E+01	5.29E+00	5.2%	2.3%	2.3%	9.5%
O3	4.15E+02	4.09E+02	5.95E+00	1.4%	2.9%	2.9%	8.1%
(B1 +) B2	8.54E+02	8.36E+02	1.76E+01	2.1%	13%	16%	23%
R1	8.64E+02	8.40E+02	2.43E+01	2.8%	6.5%	5.2%	27%
PWR	4.95E+02	3.50E+02	1.46E+02	30%	8.4%	8.9%	7.7%

Summary Table 1. Accumulation factors for C-14 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. (A-2, sheet SUMTAB).