CArbon-14 Source Term

CAST

Compilation and comparison of data on ^{14}C from spent ion-exchange resins (D4.8)

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CAST – Project Overview

The CAST project (CArbon-14 Source Term) aims to develop understanding of the potential release mechanisms of carbon-14 from radioactive waste materials under conditions relevant to waste packaging and disposal to underground geological disposal facilities. The project focuses on the release of carbon-14 as dissolved and gaseous species from irradiated metals (steels, zircaloys), irradiated graphite and from ion-exchange materials as dissolved and gaseous species.

The CAST consortium brings together 33 partners with a range of skills and competencies in the management of radioactive wastes containing carbon-14, geological disposal research, safety case development and experimental work on gas generation. The consortium consists of national waste management organisations, research institutes, universities and commercial organisations.

The objectives of the CAST project are to gain new scientific understanding of the rate of re-lease of carbon-14 from the corrosion of irradiated steels and Zircaloys and from the leaching of ion-exchange resins and irradiated graphite 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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Compilation and comparison of data on ^{14}C from spent ion-exchange resins

Executive Summary

This report summarizes and discusses the main results of the CAST WP4 activities on the quantification and speciation of ^{14}C fractions retained and released by spent ion-exchange resins (SIERs). Measured ^{14}C inventories in SIERs samples have shown to cover a wide range of specific activity depending on the reactor type — *i.e.* BWR, PWR, and CANDU — and on the corresponding cleaning circuit(s).

The ^{14}C retained in SIERs consisted mainly of inorganic carbonate form; as, *e.g.* observed in CANDU SIERs, whereas a small fraction of organic ^{14}C-bearing compounds bound to SIERs was detected. Their ratio was demonstrated to be influenced by the pre-treatment, cleaning circuit and storage conditions of the SIERs. In general, PWR SIERs are characterised by consistent amounts of retained ^{14}C-organics, descending in the following order PWR > CANDU > BWR. A more detailed speciation of the organic fraction revealed the presence of formic acid, which represents most of the retained organic ^{14}C.

A relatively fast kinetics and a saturation-like release of ^{14}C in the gaseous phase during storage of SIERs in a closed system was observed. Its speciation, similarly to the one retained in SIERs, was found to be inorganic (carbonate forms). The release is strongly dependent on the storage atmosphere, temperature, presence of water, and on the stability of the different ions bound to the resins. The presence of atmospheric air during storage allows an exchange of carbonate ions in presence of water and favours the release of ^{14}C. At elevated temperature, *e.g.* 50°C, the process is accompanied by a slow thermal degradation of the resins, providing for higher released ^{14}C fractions. Additionally, the various pH of the storage solution, affecting the stability of the ^{14}C-ions, *i.e.* HCO_3^- or CO_3^{2-}, influences the releases. A transient decrease in the pH may occur upon contact of SIERs with alkaline solutions after Na^+/H^+ and K^+/H^+ exchange, which could cause an instant ^{14}C release into the gas phase, presumably in form of $CO_2(g)$. The amount of unaccounted released ^{14}C increases with SIERs/solution ratio and with decreasing of the storage solution's molarity.

^{14}C in SIERs is rather labile and its release in form of CO_2 (the major fraction) can be caused by slight variations in the storage conditions. Therefore, a proper treatment and/or conditioning method — *e.g.* selective separation of ^{14}C, incineration, adoption of a stable matrix, etc. — is essential for the final disposal.

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1. Introduction

The WP4 of the project CAST deals with one type of radioactive waste containing ^{14}C: Spent Ion-Exchange Resins (SIERs). They are widely used in nuclear power plants (NPPs) for the purification of reactor cooling circuits or waste streams from activation products (*e.g.* ^{14}C or ^{60}Co) or some fission products (^{60}Co or ^{99}Tc) [RIZZATO *et al.*, 2014]. Particularly in pressurized water reactor (PWR) the major contribution of ^{14}C in the resins comes from the clean-up of the coolant circuits, whereas in boiling water reactor (BWR) it comes mainly from the condensate treatment circuit [Yim and Caron, 2006]. Generally, purification of the various circuits — *i.e.* primary circuit, secondary circuit or effluent treatment — is ensured by a chain of filters and demineralizers using ion exchange resins (IERs); these are required to be of high quality in order to remove the undesired soluble ionic species inducing corrosion, or radionuclides that affect local dose rates. A combination of cationic, anionic, and/or mixed bed resins are used depending on the physicochemical conditions of the circuits and on their specific needs.

At the end of the service, SIERs are discharged from the nuclear facility. At this stage SIERs are often mixed together, *e.g.* in French PWRs. Their ionic charge and activity depend on the following criteria:

- 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 due to unusual pressure drop behaviour, which is usually an indication of filter or resin degradation;
- SIERs may also need to be changed frequently depending on the fluid quality.

When the criteria thresholds are reached in a circuit, SIERs are discharged and stored under water in storage tanks. The storage delay may last some months until the dose rate induced by the radioactive decay of the short-lived activation products is low enough to allow handling; then SIERs are conditioned for further application or storage at the nuclear facility, or disposed of.

As SIERs are often planned to be disposed of in a subsurface storage, an uncontrolled release of ^{14}C from spent ion exchange resins (SIERs) is of high concern due to high risks of ^{14}C incorporation in the living organisms. Due to the variety of properties of SIERs and radionuclide inventories, presently there is no unified internationally accepted management option for this kind of waste. Few country-specific approaches have been implemented though, such as, *e.g.* cementation, fixation in epoxy resins, incineration, etc. An important step in every approach of SIERs´ management is the understanding of their behaviour in disposal-relevant conditions (*e.g.* stability of the waste form), and the release behaviour of the radionuclides of concern.

This report provides an overview of the results on ^{14}C retention and release from SIERs produced by all partners within the CAST WP4 and aims at comparing the results and finding commonalities in interpretation for the data obtained in different laboratories.

The contribution of FZJ here reported is part of an on-going RWTH Aachen PhD performed in FZJ [RIZZATO, in prep.].

2. Experimental Part

2.1 Samples

The WP4 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 regulations for the transportation [RIZZATO *et al.*, 2014]. Some partners could only have access to small quantities of samples — *e.g.* CEA-EDF, ENEA, as the main volume was already treated and stored —, others had access to the old resins — *e.g.* FZJ, RATEN-ICN, ÚJV —, and other to fresh ones, *e.g.* SKB, so it was not possible to have similar samples among the partners [BUCUR *et al.*, 2015]. The availability of a wide variety of samples enabled establishing some general understanding of SIERs properties in order to support the safety assessment of these wastes. Some samples of non-irradiated IERs (in case of ENEA) were also selected and used to support setting up and testing of analytical procedures.

Sample type and origin of SIERs used by each partner are listed in the Table 1: A more detailed information on the samples including characterization can be found in a previous CAST deliverable [BUCUR *et al.*, 2015]. It must be recalled that in the case of EDF-CEA samples, the SIERs were provided for research purposes and do not represent the final waste — see RIZZATO *et al.* [2014] for details.

- EDF SIERs samples were taken from storage tanks, and their origins were from different positions in the purification system of different PWR units.
- ENEA SIERs samples were taken from the purification systems of the PWR units.
- FZJ SIERs samples were taken from the Condensate Clean up (CCU) system of BWRs.
- RATEN-ICN SIERs samples were taken from purification systems of moderator (MOD) and of Primary Heat Transport System (PHTS) of CANDU reactor.
- SKB SIERS samples were taken from Reactor Water Clean-up systems (RWC) of PWR units and Condensed Clean up system (CCU) of BWR units.
- ÚJV SIERs samples were taken from purification systems of the PWR units and LVR research reactor.
- SKB analysed a considerable amount of data, consisting in hundreds of samples collected over 7 years (interval 2008-2015) and belonging to different units of the reactors (334 samples in the Reactor Water Clean-up systems of the PWR units and 335 in the condensate Clean-up systems of the BWR units). The detailed description of the sampling methodology for the sampling campaign is provided for CAST in ARONSSON *ET AL*. [2016].

Table 1. Description of the SIERs samples collected by the partner [RIZZO *et al.*, 2017] — More details in RIZZATO *et al.* [2014].

ORGANIZATION	SIERs type	Notes
EDF-CEA (F)	• SIERS from 5 different EDF nuclear reactors (PWR) • Non-irradiated IERs	Wet and dry beads (mixed anionic and cationic)
ENEA (I)	• IERS from PWR Trino NPP • non irradiated IERs stored for 10 years and of recent production	Wet beads (mixed anionic and cationic)
FZJ (D)	• SIERs from BWR (S)	Wet and dry powder (mixed anionic and cationic)
RATEN-ICN (RO)	• SIERs from Cernavoda NPP storage tanks or non-fuel contact purification system	Wet and dry beads (mixed anionic and cationic)
SKB (S)	• SIERS from Condensate Clean-up (BWR) • SIERS from Reactor Water Clean-up (PWR)	Wet and dry beads (mixed anionic and cationic)
ÚJV (CZ)	• SIERs from PWR and Research Reactor	Wet beads (mixed anionic and cationic)

2.2 Analytical techniques

2.2.1 ^{14}C inventory in SIERs

WP4 partners have chosen different analytical approaches for characterization of SIERs. Two principal methodologies for the determination of the total carbon content of the IERs were high pressure oxygen combustion (Parr Bomb) and non-catalytic/elemental combustion. The resulting gases (including $^{14}CO_2$) were let through washing bottles with different solutions, *e.g.* NaOH, Carbo-Sorb® E, and the total ^{14}C activity has been measured by liquid scintillation counting (LSC).

CEA applied high pressure combustion (Parr bomb) and optimized the parameters to obtain a complete combustion of the SIERs samples, resulting in 0.3 g SIERs mixed with 0.2 g carbon carrier [REILLER *et al.*, 2014; RIZZATO *et al.*, 2014; BUCUR *et al.*, 2015; COMTE *et al.*, 2017; RIZZO *et al.*, 2017].

Non-catalytic combustion by flame oxidation method was used at RATEN-ICN. By this method resins samples were combusted in an oxygen-enriched atmosphere with a continuous flow of oxygen. Some samples contained impurities, sediments and mud, due to the storage conditions and ageing. Therefore it was necessary to separate the resins beads from any impurities and mud by rinsing and decantation. The rinsing with distilled water was analysed to evaluate if any ^{14}C was released during the process: it was found that no ^{14}C species were released from SIERs [BUCUR *ET AL.*, 2015]. An optimization of the combustion process was performed with spiked resins, resulting in an optimal amount of 0.15 g SIERs and 0.2 ml of combustion enhancer — RIZZO *et al.* [2017] and references therein.

ENEA applied elemental combustion in a furnace at 930 °C in oxygen for the determination of the total carbon content of IERs. The CO_2 produced was analysed by a thermal conductivity detector (TCD).

FZJ applied non-catalytic combustion on FZJ-A SIERs samples in an electrical oven at about 900°C in synthetic air. For that *ca.* 0.2 g of sample was loaded in a ceramic crucible inside a quartz tube, inserted in the cylindrical oven´s chamber. The gas flow was let through a series of miniaturized washing bottles, similarly to what has been reported in BUCUR *et al.* [2015].

2.2.2 ^{14}C speciation

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 modified processes to collect the organic and inorganic fraction, optimizing their own methods according to the nature of their samples.

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

- 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).

To clarify the chemical form of ^{14}C, CAST partners have adopted the following approaches:

- direct measurement of the species released into solution after regeneration of the resins (quantification and qualification), *e.g.* by high performance liquid chromatography (HPLC);

- in order to find out whether ^{14}C is in ionic or non-ionic from, a modified procedure from MAGNUSSON AND STENSTRÖM [2005] was used: after acidic regeneration (the first step), the separation of the solution from the resins, with a subsequent separate wet oxidation of two fractions, *i.e.* resins and solution;

- to quantify the fraction of organic non-exchangeable ^{14}C, a combustion of SIERs after a complete regeneration was applied;

Set up at RATEN-ICN, SKB, CEA for ^{14}C speciation

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 1. It consists of a reaction vessel, a separation funnel, a nitrogen supply and a vacuum pump, two gas washing lines with a catalytic furnace between them.

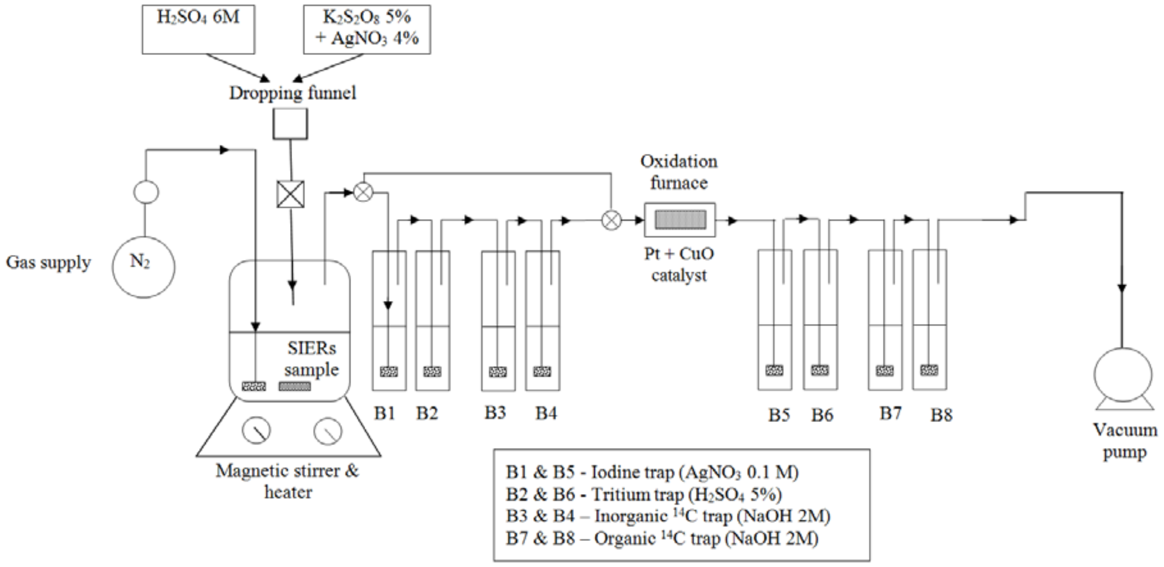


Figure 1. Scheme of experimental set-up for separation and purification of inorganic and organic ^{14}C compounds [Rizzo *et al.*, 2017].

The possible inorganic ^{14}C species in equilibrium are described by the following equilibria [Guillaumont *et al.*, 2003].

$$CO_2(g) \rightleftarrows CO_2(aq) \qquad \log_{10}k_h = -1.47 \tag{1}$$

$$CO_2(aq) + H_2O \rightleftarrows HCO_3^- + H^+ \qquad \log_{10}K_1 = -6.35 \tag{2}$$

$$HCO_3^- \rightleftarrows CO_3^{2-} + H^+ \qquad \log_{10}K_2 = -10.33 \tag{3}$$

Examples of the speciation of carbonate are given in Figure 2.

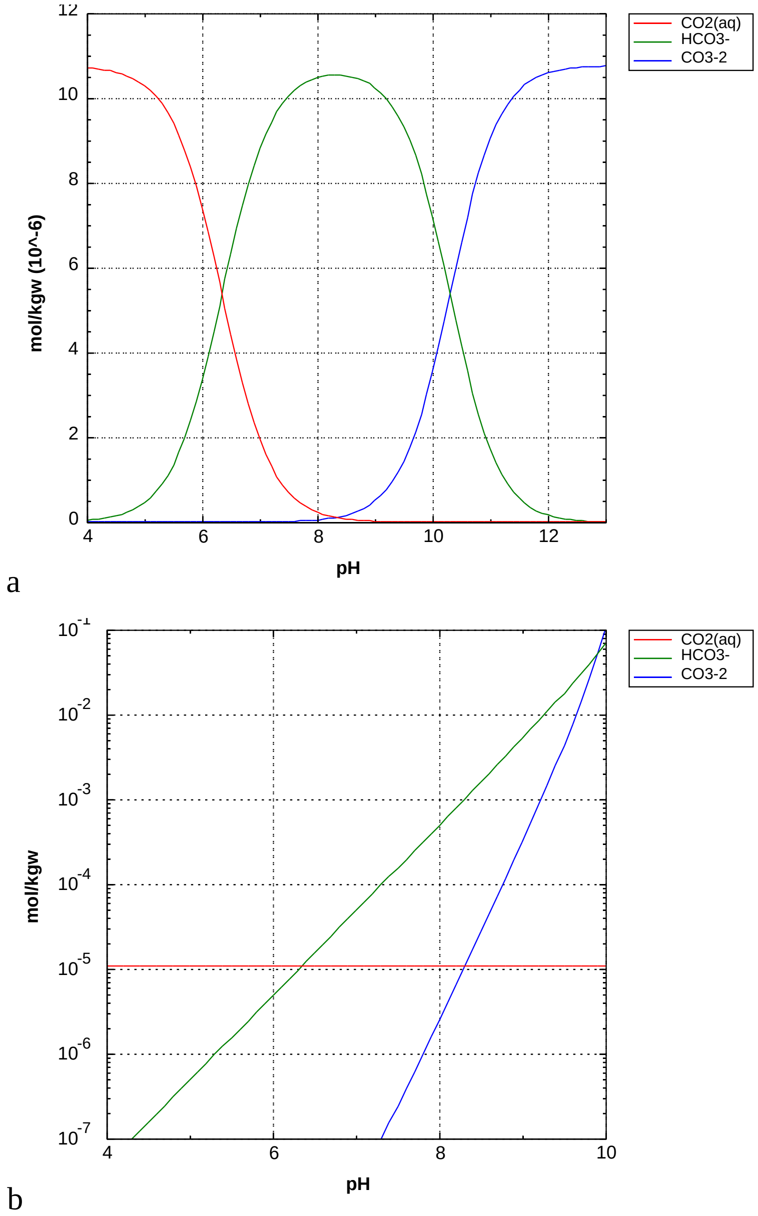


Figure 2. Carbonate system speciation in a closed (a) and an open (b) system at $pH_{initial} = 4$ and $P(CO_2) = 10^{-3.5}$ atm [GUILLAUMONT *et al.*, 2003].

Carbonates CO_3^{2-}, bicarbonates HCO_3^-, and dissolved $CO_2(aq)$ equilibria can be [GUILLAUMONT *et al.*, 2003] easily shifted by weak acids towards gaseous carbon dioxide. The inorganic ^{14}C is released during an acid stripping step resulting mainly in the release of $^{14}CO_2$ and the gases are carried by the carrier gas through the first gas washing line. If any ^{14}C is released as CO or other organic molecules, the flow is passed through the scrubbing bottles of the first gas washing line, and further through the catalytic furnace, where CO, or ^{14}C-org, is oxidized to CO_2, and is 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.

Since organic compounds have high bounding energies between atoms they are decomposed by strong oxidants such as potassium persulfate ($K_2S_2O_8$). 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.

Set up at FZJ for ^{14}C speciation

During the CAST project FZJ has optimized the sequence of washing bottles for the 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 (cf. Figure 3), with a reduced volume and, accordingly, a reduced dilution of the activity [BUCUR *ET AL.*, 2015].

The use 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 used as catalyser [COMTE *ET AL.*, 2017].

The experimental procedure for ^{14}C fractionation is based on the one reported by MAGNUSSON AND STENSTRÖM [2005], optimised to ensure the completeness of the releases in the gas phase. This approach, however, revealed to be time-consuming, but allowed a more accurate definition of every step — acidification with non-oxidising acid followed by wet oxidation — and, accordingly, the determination of the inorganic/organic ^{14}C retained in the SIERs.

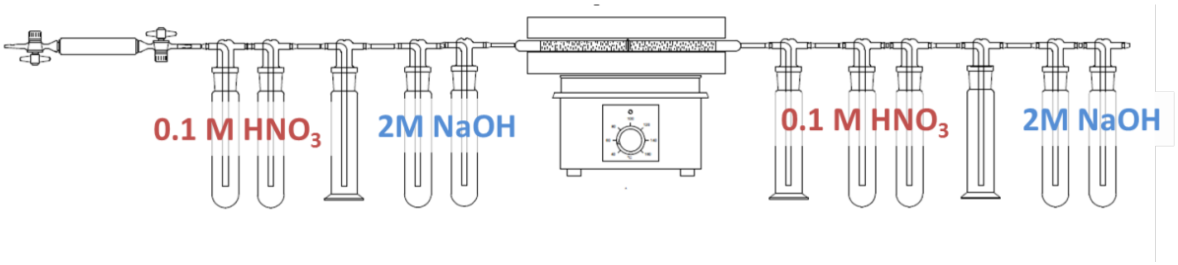


Figure 3. Experimental setup for the analysis of ^{14}C designed by FZJ, with a catalyser to convert HT to HTO, CO to CO_2, and organics to CO_2 [BUCUR *et al.*, 2017].

In addition to the ^{14}C fractionation with the system (*vide supra*), high performance liquid chromatography (HPLC) was used to qualify and quantify the eventual ^{14}C organic species bound to the SIERs in ionic form.

Set-up at ENEA for ^{14}C speciation

ENEA has designed and implemented a targeted device (Figure 4), with a double chamber combustion cell, in order to run stepped combustion of IERs samples to obtain different volatile/non-volatile fractions.

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

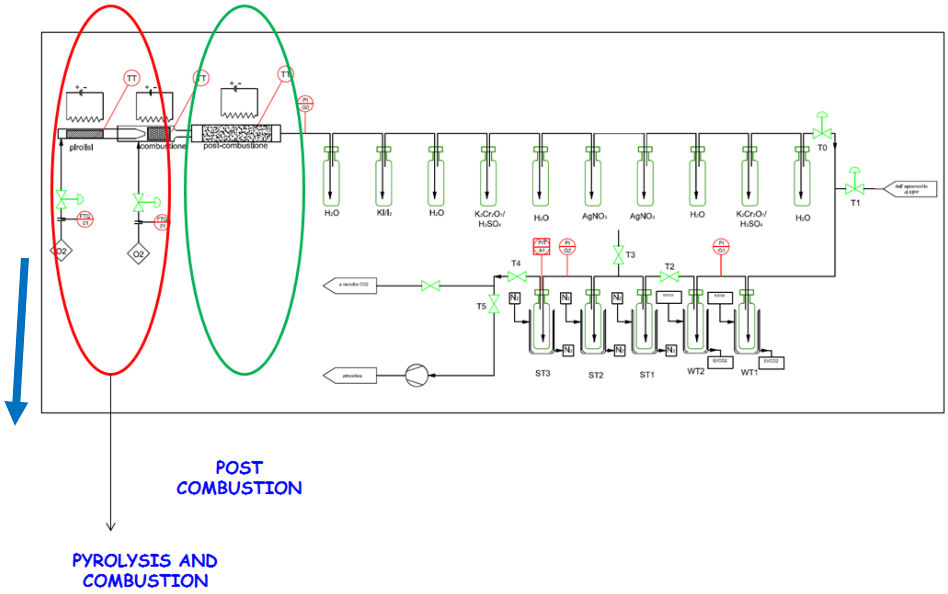


Figure 4. Equipment for stepwise combustion of organic materials for benzene LSC analysis at ENEA ^{14}C laboratory [Rizzo *et al.*, 2017].

2.2.3 ^{14}C released from SIERs

The release of ^{14}C from SIERs was investigated by FZJ and RATEN-ICN adopting the following approaches. FZJ investigated the release of ^{14}C into the gas phase from BWR SIERs during storage, taking into account effects of temperature, atmosphere and contact with high pH solutions. RATEN-ICN studied the release of ^{14}C from SIERs at high pH.

Effect of storage temperature and atmosphere

The generation of gases from BWR SIERs (FZJ-A/B) during storage was investigated in different experimental conditions (temperature, atmosphere) and the organic/inorganic ^{14}C released has been measured.

The ^{14}C release kinetics were investigated with small samples (about 1.5 g), stored in 15 mL vials furnished with a double access/valve to allow the exchange of the whole gas phase during analysis (Figure 5).

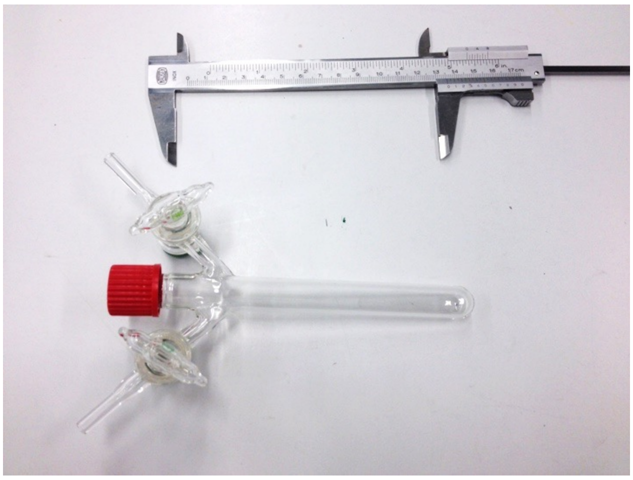


Figure 5. Example of vial used for the storage experiments of small FZJ-A/B samples [Bucur *et al.*, 2017].

The kinetics of ^{14}C release from SIERs has been investigated at room temperature and at 50°C, in aerobic atmosphere (air) and vacuum. Since any disturbances of the system would have affected the eventual releases of ^{14}C, several samples were prepared and analysed separately at well-defined time intervals: 3, 6, 9, and 12 weeks. The gas phase analyses consisted of a direct connection of the vial to the system represented in Figure 3 and by flushing the gas phase through the washing bottles and catalyser with an inert carrier gas (Ar) for 2 hours with a flow rate of about 6 mL/min.

Effect of alkaline media

Behaviour of SIERs and ^{14}C release kinetics in alkaline media was investigated, as conditioning in the cement represents one of the options for disposal of this type of waste. For this, ^{14}C releases in alkaline conditions simulating the cementitious environment were evaluated for BWR (FZJ), PWR (CEA), and CANDU (RATEN-ICN) SIERs. FZJ and RATEN-ICN focussed on the release of ^{14}C into the gas and liquid phase, while CEA focussed only on the on-line releases in solution.

An alkaline solution — 0.114 M NaOH and 0.18 M KOH supposedly representative of a cement pore water — was used in the experiments carried out on BWR SIERs, 0.1 M NaOH solution in the experiments performed on CANDU SIERs and LiOH solution for PWR SIERs. The determination of ^{14}C in solution was achieved by direct measurement with LSC, while the gas phase was let through washing bottles filled with alkaline solution that was then analysed by LSC.

In FZJ experiments, an on-line measurement of ^{14}C release using the equipment presented in Figure 3 was performed. A sample of about 1 g was weighed in the reactor vessel, 10 mL of alkaline water (0.114 M NaOH, 0.18 M KOH) was added, and the reactor vessel was connected to the analytical set-up (Figure 3). An inert gas carrier (Argon) was used to flush the vessel. The washing bottles were exchanged every 24 hours and new solution was added to the sample at every step, until the activity in the washing bottle solutions was below the detection limit of the LSC. A similar on-line approach was adopted to investigate the variations in the pH of the alkaline solution in contact with SIERs, in order to study the transient pH value at a well-defined sample-to-solution ratio (1 g SIERs and 10 mL of 0.1 M NaOH) and on the equilibrium pH value at different ionic strengths of the alkaline solution.

For CANDU SIER, the inorganic ^{14}C gaseous release was evaluated during desorption tests carried out in aerobic conditions, using two sub-samples from the SIERs received from Cernavoda NPP, in alkaline solution (NaOH 0.1 M). For the desorption tests (Test #1 and Test #2), 0.4 g of SIERs was contacted with 40 mL of NaOH 0.1 M in borosilicate glass bottles with polypropylene lids that were adapted to allow N_2 purging in the desorption vessels and outgas washing through alkaline gas washing bottles (Figure 6) to absorb the inorganic ^{14}C. Desorption tests were performed at room temperature (23 ± 3°C), for solid to liquid ratio of 0.01 g/mL (0.4 g of SIER + 40 mL of NaOH solution), in semi-dynamic conditions: 5 mL of leaching solution were sampled at each time step and 5 mL of fresh NaOH were added. The leaching solution was sampled daily within the first 4 days, and after 9, 17, 24, 45, 95, 122, and 174 days of desorption. At the end of the desorption tests not only ^{14}C activity in liquid phase was measured but also the residual ^{14}C activity in the SIER sample subject to desorption test.

Figure 6. The glass vessels used in desorption tests [Bucur *et al.*, 2017].

Before sampling the leaching solution, at each sampling time N_2 gas was purged in the space above the liquid level and the outgases were washed through gas bubblers using a similar experimental set-up as the one reported in Figure 3. At the beginning of the desorption tests it was not clear whether the ^{14}C released in gas phase could be measured by washing outgases through the alkaline bubblers. Therefore the nitrogen gas was introduced through both parallel desorption vessels at the same time. To get the amount of gaseous ^{14}C released from one vessel, the amount measured in the alkaline solutions from the gas bubblers was divided by two assuming the ^{14}C released in gas phase was equal from the two parallel tests.

Experiments of desorption of ^{14}C from PWR SIERs were performed at CEA to identify the organic molecules and check the analytical methodology for ^{14}C speciation by acidic mineralization. Around 1 g of wet resin was contacted with 10 mL of desorption solution for 30 min at room temperature. The PWR EDF-B SIERs sample has been used, the organic ^{14}C activity of which is the highest (around 1600 $Bq.g^{-1}$). No preliminary test has been carried out before. The initially chosen desorption solution was a 10^{-3} $mol.L^{-1}$ LiOH, *i.e.* pH *approx.* 11, solution for several reasons:

- lithium was the ionic form of the cationic resin and was maybe present on the real sample;

- solution with pH > 8.2 to avoid CO_2 release into the gas phase;
- solution with pH < 11 to avoid precipitation of metallic hydroxides that may cause the clogging of SIERs porosity.

The radiochemical analyses of the desorption solution showed that no ^{14}C was desorbed from the SIERs. The detection limit in the 10^{-3} M LiOH solution is 3 Bq in the 10 mL sampling sequence. In water the detection limit in 10 mL sampling sequence is 1 Bq. The concentration of the LiOH solution was increased up to 1 M, *i.e.* pH *ca.* 13.8, to increase the ionic exchange, which resulted in the detection of both inorganic and organic forms of ^{14}C in solution. Six desorption sequences were performed and the experiments were completed by two washings with water. These additional washings were performed to solubilize the hydroxides present in the pores of the resins.

3. Results and Discussion

3.1 Total ^{14}C

The total ^{14}C inventories of SIERs, obtained by all CAST WP4 partners, are summarized in Table 2. It is necessary to underline that EDF-CEA, FZJ, RATEN-ICN, and ÚJV selected batches of samples with very similar characteristic, so only the average values have been reported [RIZZO *et al.*, 2017]. On the other hand SKB have analysed a important amount of samples — 315 samples over a period of 7 years — for which ^{14}C inventory interval, *i.e.* min-max, was reported in RIZZO *et al.* [2017].

The source term determination from the measurement of the total ^{14}C content in SIERs cannot be directly compared among the partners, because of the differences in the reactor type, in the storage conditions, in the sampling, the ageing, etc. A summary of the results has been given in Table 2 in order to produce a reference database of the ^{14}C inventory for some common categories of SIERs; it can support for the evaluation of the safety cases and the performance assessment of the radioactive waste repository.

Table 2. ^{14}C total determination in SIERs [RIZZO *et al.*, 2017].

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
FZJ	CCU BWR (FZJA) wet resins	1770 ± 286 Bq/g dry
FZJ	CCU BWR (FZJB-1) dried resins	4241 Bq/g dry
FZJ	CCU BWR (FZJB-2) dried resins	626 Bq/g dry
FZJ	CCU BWR (FZJB-3) dried resins	2498 Bq/g dry
FZJ	CCU BWR (FZJB-4) dried resins	5275 Bq/g dry
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-ICN	CANDU SIERS wet	36500 ± 2220 Bq/g
ÚJV	PWR SIERS	45 ±5 Bq/g
ÚJV	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.

SKB results on wet and dried samples are based on a small number of samples, but they give a strong indication that drying reduces the concentration of ^{14}C and the main part of the ^{14}C activity has been released. This conclusion is supported by measurements of ^{14}C in the ventilation system [ARONSSON *ET AL.*, 2016]. Experiments performed in FZJ are pointing towards the same direction, *i.e.* anion-exchange resins are degraded at moderate temperatures during drying, resulting in the loss of exchange capacity and, consequently, in the release of ^{14}C, depending on the applied temperature, the amount of water, and the duration of the drying process.

3.2 ^{14}C speciation in SIERs

The results from MAGNUSSON AND STENSTRÖM [2005] and PARK *ET AL.* [2008] have shown that the majority of the ^{14}C activity in SIERs comes from the inorganic (ion exchangeable) compounds [RIZZATO *et al.*, 2014]. 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, probably under the form of metal carbonate [MOIR *et al.*, 1994; PARK *et al.*, 2008; RIZZATO *et al.*, 2014].

The first consideration for the speciation of ^{14}C content in SIERs is to differentiate between their organic and inorganic components. Furthermore, some partners (FZJ, SKB) focussed on the identification and quantification of the organic species.

3.2.1 Experimental data of ^{14}C speciation

The results on ^{14}C speciation (organic/inorganic) from all partners (Table 3) seem to show that in most samples the ^{14}C is released mainly in inorganic form, with some differences.

Table 3. ^{14}C speciation between inorganic and organic forms in SIERs [RIZZO *et al.*, 2017]

Partners	**Ref.**	**State**	**^{14}C form**	**^{14}C content (Bq/g)[*] (% of total)**
CEA	EDF–A PWR	Wet sample	Inorganic	76.6%
			Organic	23.4%
CEA	EDF–A PWR[†]	Dry sample	Inorganic	23.9% ÷ 60.3%
			Organic	39.7% ÷ 73.6%
CEA	EDF–B PWR	Wet sample	Inorganic	2.8%
			Organic	97.2%
RATEN-ICN	CANDU[*]	Wet samples	Inorganic	93.1%
			Organic	6.9%
SKB[§]	CCU BWR	Wet samples	Inorganic	95-99%
			Organic	1-5%
SKB[**]	CCU BWR	Dried samples	Inorganic	8%
			Organic	92%
SKB	RWCU PWR	Wet samples	Inorganic	70%
			Organic	30%
FZJ	CCU BWR (FZJA)	Wet samples	Inorganic	99.6%
			Organic	0.4%
FZJ	CCU BWR (FZJB-1)	Dried samples	Inorganic	99.4%
			Organic	0.6%
FZJ	CCU BWR (FZJB-2)	Dried samples	Inorganic	98.9%
			Organic	1.1%
FZJ	CCU BWR (FZJB-3)	Dried samples	Inorganic	99.5%
			Organic	0.5%
FZJ	CCU BWR (FZJB-4)	Dried samples	Inorganic	99.1%
			Organic	0.9%
ÚJV	EDU-PWR	Wet samples	Inorganic	29.2%
			Organic	70.8%
ÚJV	ETE-PWR	Wet samples	Inorganic	37.2%
			Organic	62.8%
ÚJV	ÚJV-PWR	Wet samples	Inorganic	96.2 - 100%
			Organic	3.8 – 0%

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

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

[§] For SKB samples the ^{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

RATEN-ICN CANDU samples

In CANDU reactors, the major part is retained in inorganic form, which is in agreement with the literature data. Regarding the repartition between inorganic and organic species, the results obtained show that the ^{14}C in the analysed CANDU SIERs is mainly in inorganic form and only less than 7% is present in organic form. Since the main source of the analysed CANDU SIERs is the moderator purification system, and in the CANDU moderator the major chemical form of ^{14}C is bicarbonate, the chemical form of ^{14}C absorbed on the resin is also most probably bicarbonate ($H^{14}CO_3^-$).

CEA-EDF PWR samples

However, results on the repartition between inorganic and organic molecules for PWRs and BWRs are contrasting. For PWR from EDF samples the results obtained with the acidic dissolution methods have been compared with the total ^{14}C measurements and they show some discrepancies (Table 4). ^{14}C measurements showed that activities — inorganic, organic, and total — are not similar. One reason for the discrepancy in the dry resin could be related to a possible loss of ^{14}C, mainly the inorganic form, during the analytical process.

Table 4. Comparison of the method for the effect of drying for total ^{14}C determination. Experiment on EDF-A sample [Rizzo *et al.*, 2017].

Measure	**Total ^{14}C combustion with oxygen**	**Total ^{14}C Acidic dissolution**
N°1	n/a	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%. One experiment gave a very low content of water, about 20%, which was not confirmed by the other sub-samples. This variation is probably due to the individual drying of each sub-sample before analysis. It seems difficult to have reproducible drying with such small samples.

To compare the mass before drying, the ^{14}C activities after drying were corrected by considering the weight of water. This result shows that the method developed for the total ^{14}C by combustion under oxygen gives individual results that 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 which can be improved by drying a larger amount of SIERs. However, the 'wet' average ^{14}C activity for the two determinations is very close to the reference result, *i.e.* 5710 $Bq \cdot g^{-1}$ compared to the reference result of 5630 $Bq \cdot g^{-1}$.

The results obtained through acidic dissolution method demonstrate significantly lower ^{14}C compared to the total combustion method. Furthermore, a poor reproducibility of the method was observed for the fractions of inorganic and organic ^{14}C, as well as for total ^{14}C. This method does not seem to be adapted for 'dry resin', presumably due to a partial loss of ^{14}C in inorganic form during the analytical process. This result is not entirely understood up to now, as measurement of ^{14}C inventory in the reference material ($NaH^{14}CO_3$) results in recovery of about 100% in all cases.

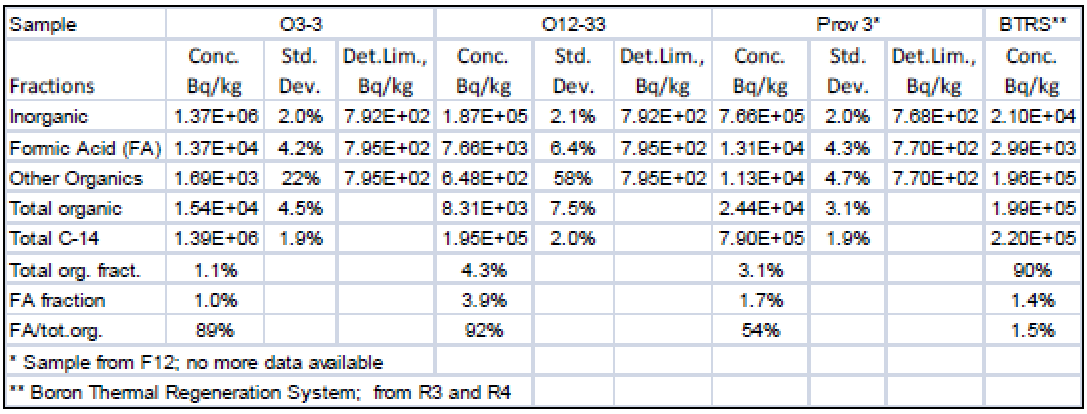
A similar test has been carried out on CEA CANDU SIERs and no discrepancies were found: the total ^{14}C content in the analysed samples are quite closed to the value determined by combustion, demonstrating the good recovery of the acid stripping/wet oxidation method.

SKB BWR and PWR samples

The results of SKB are based on investigation on a few samples and indicate that some loss of ^{14}C activity into the gas phase may take place. This conclusion is supported by measurements of ^{14}C in the ventilation system of the NPP's downstream line [ARONSSON *et al.*, 2016]. In particular, the factor that influences the ^{14}C content in the final waste form 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, a lot of the ^{14}C activity is lost under the form of $CO_2(g)$.

Several tests have been performed by SKB to investigate the presence of formic acid in SIERs. Details about the experimental set-up are described in RIZZO *et al.* [2017]. Tests were performed on three samples from BWR CCU and one sample from PWR BTRS (last column). The results obtained are shown in Table 5.

Table 5. Carbon speciation in organic ^{14}C-fraction in SIERs samples from SKB BWR and PWR [RIZZO *et al.*, 2017].



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
Fomic 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 mediating redox conditions in BTRS resins; at their position in the cleaning system, iron and iron oxides have already been separated. Another possible explanation may be that part of the ^{14}C in BTRS resins is present as elementary carbon.

ÚVJ PWR samples

For ÚJV samples [RIZZO *et al.*, 2017] the organic content was determined as a difference between the amount of total and inorganic ^{14}C in the material, measured by acidic dissolution, and they also exhibit contrasting results, *i.e.* from 3.8% to 70.8% of organic ^{14}C-fraction was found.

FZJ BWR samples

Total ^{14}C for FZJ-B SIERs was obtained through the two-step analysis, *i.e.* acid stripping followed by wet oxidation. Additionally, a verification of the methods' effectiveness was performed with FZJ-A samples by comparing the combustion's results to the two-step analysis aimed to determine the inorganic/organic ^{14}C fraction. All FZJ samples were characterised by similar fractions of organic ^{14}C, ranging from 0.4% to 0.9%, and are consistent with the data obtained for the SKB samples.

Another method for confirmation of the fact that organic ^{14}C could be present in ionic form is based on burning fully regenerated SIERs. In FZJ only one test with a small sample of about 0.2 g was performed, but no activity was measured. A possible improvement for the speciation of the organic ^{14}C fraction would be regenerating a sufficient amount of SIERs sample, separating the liquid phase from the SIERs by filtration and applying the acidification and wet-oxidation to the two fractions obtained.

HPLC analyses on NaCl solution (0.86 mol/L) in contact with FZJ-B SIERs revealed the presence of formic acid in small amounts (about 1.7 mmol/kg$_{resin}$). It is not clear whether such a molecule arises from the water circuit of the BWR or from the resins' degradation. A fractionation after chromatographic separation was, however, not possible, so an activity measurement was not performed.

Speciation of the organic fraction resulted in findings similar to SKB, confirming the presence of formic acid (or formate ions) bound to the SIERs. Experiments on gamma-irradiation performed on fresh IERs and loaded IERs in contact with 10 mL $NaHCO_3$ solution revealed the presence of formic acid in small amounts. In particular, fresh IERs were characterised by the presence of formic acid up to 0.2 mmol/kg$_{resin}$ at 1 MGy. Loaded IERs in contact with $NaHCO_3$ solution (to simulate real SIERs) showed significant amounts of formic acid, up to 0.9 mmol/kg$_{resin}$ at 0.5 MGy. Acetic acid was also detected for loaded IERs in the contacting solution only, increasing with the dose, up to about 0.7 mmol/kg$_{resin}$.

In conclusion, formic, and possibly acetic, acid could arise from the reactor coolant and/or from the degradation of SIERs due to, *e.g.* radiolytical effects caused by the retained beta/gamma emitters (self-irradiation). Direct analyses on the reactor coolant, however, are quite challenging, since the concentrations of the interesting compounds would be rather low and difficult to detect.

3.3 ^{14}C released from SIERs

Studies on the ^{14}C release behaviour of SIERs were conducted by FZJ and RATEN-ICN. Both partners focussed on the investigations of the SIERs' behaviour in alkaline solutions, as a proxy to cementitious conditions. FZJ focussed additionally on the effects of temperature and atmosphere during storage in a closed system, representative of, *e.g.* an intermediate storage of SIERs.

3.3.1 Effect of storage temperature, atmosphere and sample age

Experiments on samples FZJ-A resulted in undetectable — or close to the LSC detection limit, *i.e.* < 0.1 Bq/sample — releases of ^{14}C in the gas phase in all cases. Relatively low releases — not shown in this document but monitored in RIZZATO [in prep.] — could be explained by the fact that FZJ-A samples were probably stored in an open system in the NPP. So a partial release of ^{14}C could have already occurred by isotope-exchange and/or ion-exchange with the atmospheric air. However, analyses on the FZJ-A SIERs revealed consistent ^{14}C activities, mainly in inorganic form. Considering that an isotopic exchange and an ion-exchange process between SIERs and the ions from the carbonate system could take place, inorganic ^{14}C should be present in the gas phase. A possible explanation of the phenomenon could be linked to the number of groups interacting with the counter-ions, leading to a more stable CO_3^{2-} ion bound to the resin against a less stable HCO_3^- ion. However, such an hypothesis should be proven.

Storage experiments of FZJ-B samples were carried out in presence of small amounts of water (*ca.* 12%), retained in the resins as received, at room temperature and 50°C, under air or vacuum. The results on ^{14}C release kinetics are demonstrated in Figure 7. It can be noticed that most of the measured values are close to each other except for one sample FZJ-B2, which is out of the trend, supposedly due to hererogeneous sampling. During storage, ^{14}C was measured in the gas phase exclusively under the form of $^{14}CO_2$. Analyses of the samples stored at room temperature under air revealed some ^{14}C in the gas phase, ranging from 0.6% to 1.0% of the total ^{14}C (Figure 7).

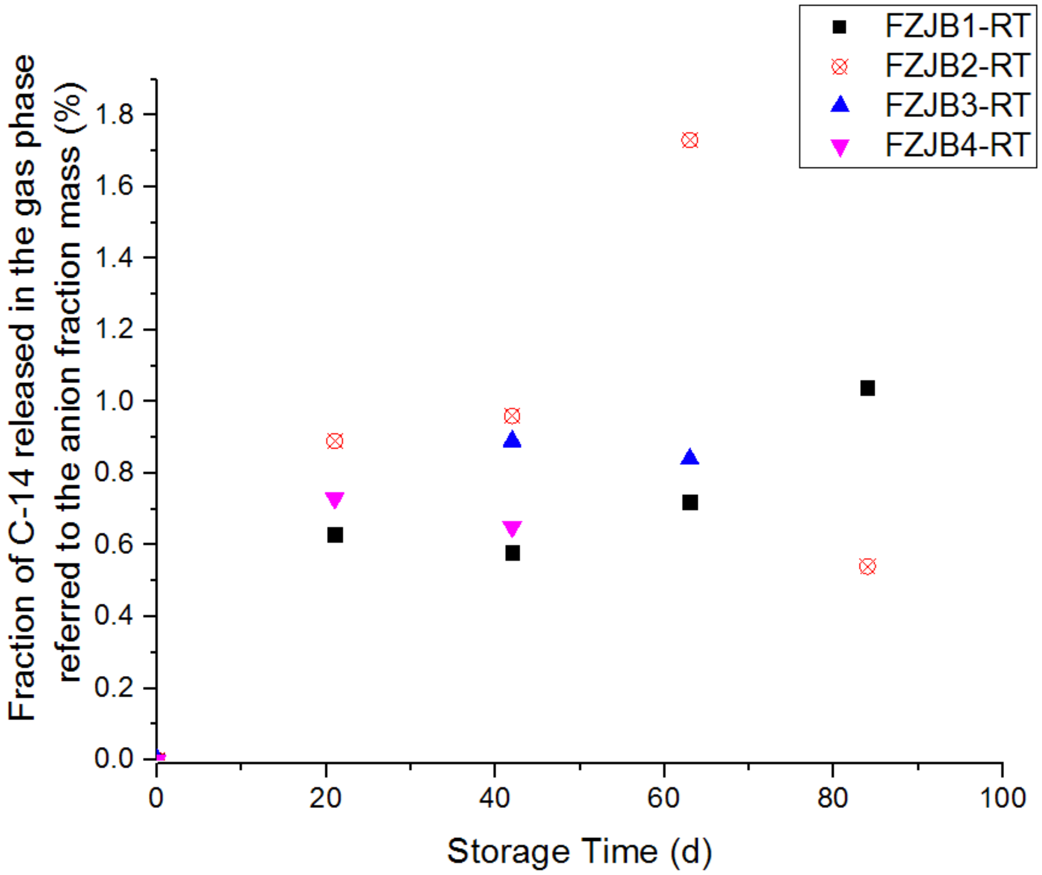


Figure 7. Kinetics of ^{14}C release into the gas phase in air at room temperature [Bucur *et al.*, 2017].

At 50°C in air, FZJ-B samples showed in general similar results, with slightly higher releases in some cases, with 0.6% to 3.0% of the total ^{14}C in the gas phase (see Figure 8). However, one can notice that some results from FZJ-B2 are out of the trend. This might be related to an inhomogeneous distribution of ^{14}C in a mixture of the SIERs (cation/anion fractions different from the other samples), or, *e.g.* an improver evaluation of the total ^{14}C.

All values in Figure 7 and Figure 8 are reported with reference to the dry anion-exchange fraction of the mixed resin, regenerated in a reference ionic form (-H and -Cl), assuming that ^{14}C is mainly retained by anionic SIERs. Results on the determination of the anion- and cation-exchange fractions will be reported in detail in Rizzato [in prep.].

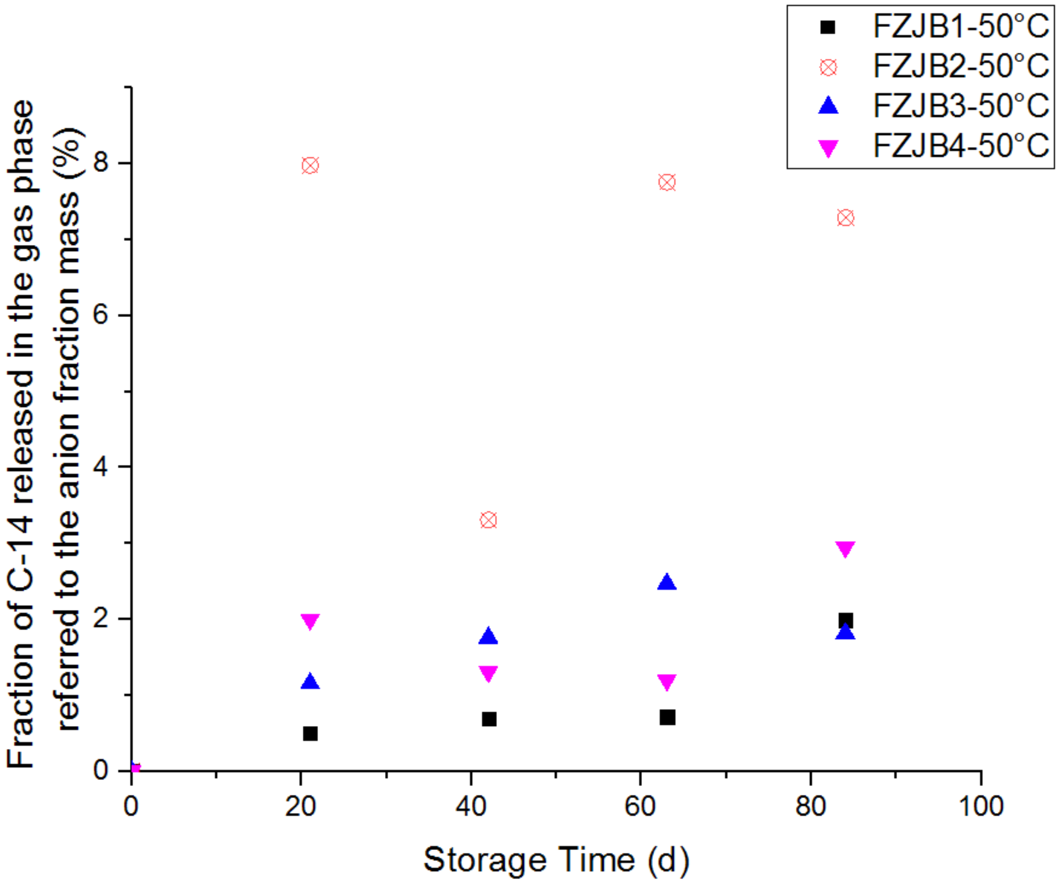


Figure 8. Kinetics of ^{14}C release into the gas phase in air at 50°C [Bucur *et al.*, 2017].

The results reported in Figure 7 and Figure 8 point out a relatively fast equilibration, *i.e.* within *ca.* 20 days, of ^{14}C partitioning between the SIERs and the gas phase, if stored in a closed system under aerobic atmosphere. Storage experiments at 50°C revealed higher fractions of volatile ^{14}C released, probably due to a slow temperature-related degradation of the SIERs. Release behaviour of ^{14}C from one sample (FZJ-B-2) was in most cases anomalously high with respect to the overall trend. The exact reason for this behaviour is unclear yet, and therefore this sample should be further investigated.

In parallel, storage experiments with FZJ-B samples were performed under vacuum. After vacuum was established in the vial, containing approximately 1.5 g of sample, samples were stored in absence of light. The vial was then flushed with argon and the ^{14}C activity in the gas phase was analysed, similarly to the previous case. All samples revealed no activity release. In fact, ion-exchange cannot take place in absence of water. Therefore, a vacuum drying of the resins and the absence of any humidity and gases in contact with the waste hindered any releases in the gas phase. This result can contribute to the development of a possible strategy for intermediate storage of SIERs.

Vacuum drying has been already partially applied, *e.g.* in Germany — see BMUB [2015]. However, some issues can be expected when SIERs are fully dried with vacuum, as, *e.g.* volatility due to the small particle sizes, and, *e.g.* regain of water due to contact with humid air, which can resume the release of ^{14}C. Therefore, a complete separation of ^{14}C could represent a solution to prevent uncontrolled releases in interim storage or final disposal.

Speciation of ^{14}C in the gas phase during the storage experiment demonstrated no measurable amount of organic ^{14}C. However, since the small samples investigated were retaining relatively low total ^{14}C activity, this observation could not exclude the presence of volatile organics in small amounts, resulting in released activities below the detection limits.

The different age and gamma activities of FZJ-B samples do not seem to represent a relevant effect for the present case. However, SIERs arising from, *e.g.* PWR, are expected to retain considerable amounts of gamma-emitters, causing a self-irradiation of the waste during storage, therefore such a conclusion may not be applied to SIERs from different reactor types.

In conclusion, in presence of air, the main release mechanism leading to the release of ^{14}C in the gas phase seems to be — in the short-term — ion-exchange and/or isotopic exchange with atmospheric CO_2. At elevated temperatures, a slow degradation of the resins was suggested to be responsible for enhanced release of volatile ^{14}C compounds. No organic ^{14}C-compounds were measured in the gas phase, *i.e.* a dominant fraction of released ^{14}C is under the form of $CO_2(g)$ [RIZZATO, in prep.].

3.3.2 Effect of contact with high pH solutions

The release of ^{14}C into solutions of different composition from PWR SIERs is shown in Figure 9 and Table 6, showing a comparison between inorganic and organic forms, as well as total ^{14}C release. To allow a comparison of the results, activities are normalized to 1 g of wet SIERs. Figure 9 presents the results of two parallel experiments, performed to verify the reproducibility of the experiment. Most of the ^{14}C is released during the first sequence in 1 M LiOH. The concentration decreases with successive washings. No activity is detected in the water washing solution. Final analysis of the ion exchange resin after desorption indicate that the remaining ^{14}C activity is quite low — around 10% or less of the initial activity — and mainly in organic carbon form.

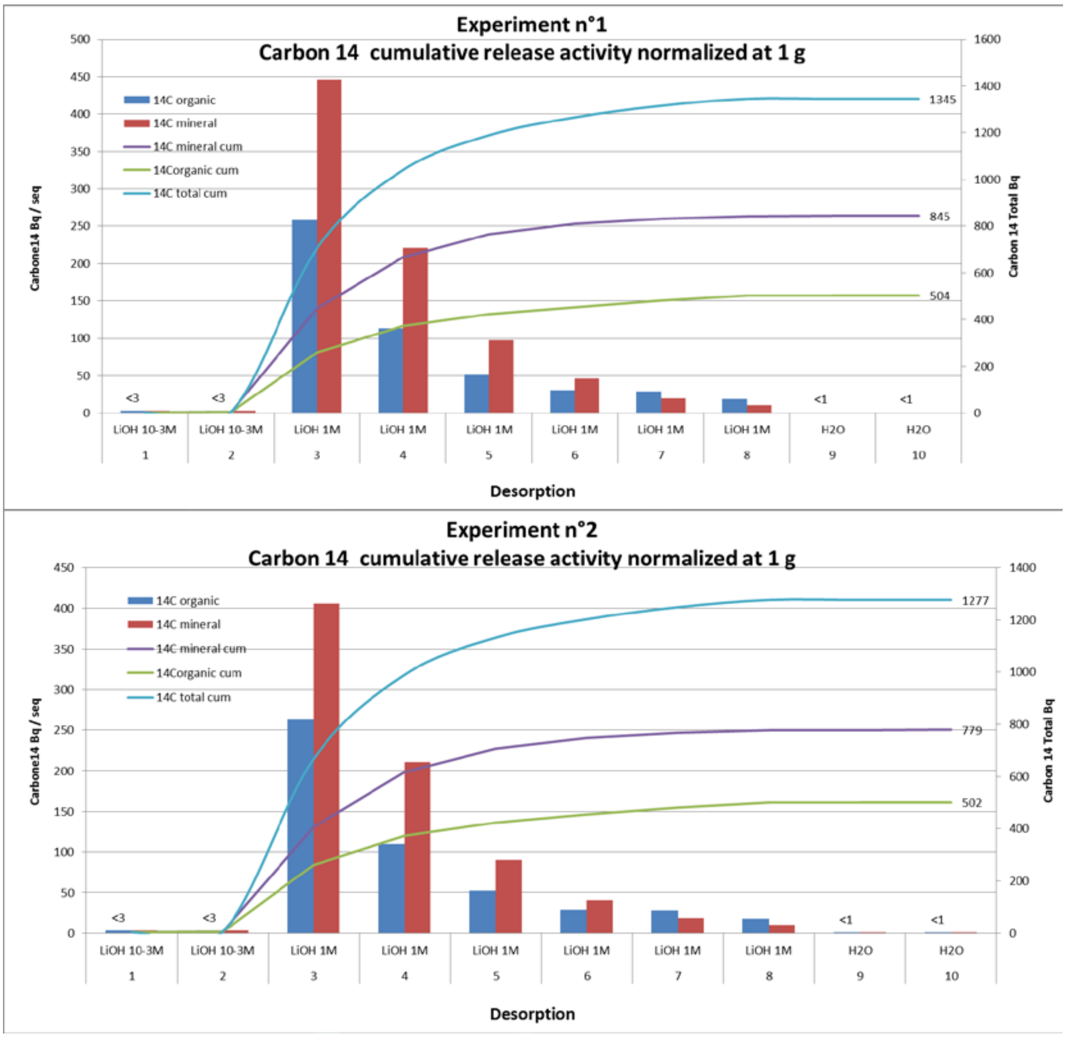


Figure 9. Differential and cumulative release of ^{14}C (total, inorganic, and organic forms) during desorption experiments for sample EDF-B [Comte *et al.*, 2017].

Table 6. Speciation of ^{14}C in fraction remaining in SIERs after desorption from sample EDF-B [Comte *et al.*, 2017].

Experiment N°		^{14}C Bq.g^{-1} total	Inorganic form (Bq.g^{-1})	Organic form (Bq.g^{-1})
1	Sub sample1	209 ± 12	<5	209 ± 12
	Sub sample2	153 ± 8	<5	153 ± 8
	Average	*180 ± 80*	*<5*	*180± 80*
2	Sub sample1	175 ±12	<5	175 ±12
	Sub sample2	150 ± 8	<5	150 ± 8
	Average	*162 ± 38*	*<5*	*162 ± 38*

These experiments show the good reproducibility of the desorption protocol: the results obtained are equivalent for the two tests. The influence of the concentration of the LiOH desorbing solution is also clear. A 1 M LiOH solution is needed to achieve ^{14}C desorption. The distribution between organic and inorganic forms and total activity are shown in Table 7.

Table 7. ^{14}C desorption assessment of the experiment with wet EDF-B SIER [Comte *et al.*, 2017].

Experiment Sample EDF-B	^{14}C	Total (Bq.g^{-1})	Inorganic form (Bq.g^{-1})	Organic form (Bq.g^{-1})
1	Total desorbed fraction	1345±120	845±160 (63%)	505±100 (37%)
	Final activity	180 ± 80	<5 Bq	180 ± 80 (100%)
	Estimated initial activity	**1525 ± 200**	**845±160 (55%)**	**680 ± 180 (45%)**
2	Total desorbed fraction	1280±100	780±130 (61%)	500±90 (39%)
	Final activity	160 ± 40	<5 Bq	160 ± 40 (100%)
	Estimated initial activity	**1440 ± 140**	**780±130 (54%)**	**660 ± 130 (46%)**

The comparison between total ^{14}C activity achieved through desorption experiments (*ca.* 1500 Bq.g^{-1}) and total ^{14}C activity achieved with the combustion method (2125 Bq.g^{-1}), evidences a loss of ^{14}C during the desorption experiments. A difference of about 30% is measured. The organic fraction determined by the summation of the desorbed fraction and that remaining in the SIERs represents around 45% of the total activity.

The aforementioned loss of ^{14}C might be due with its instant release into the gaseous phase. This could be linked with the experiments on release behaviour of ^{14}C performed by FZJ. An on-line analysis of the gas phase resulting from FZJ-B SIERs in contact with alkaline solution (0.114 M NaOH, 0.18 M KOH) revealed a consistent release of ^{14}C in few hours (see Figure 10).

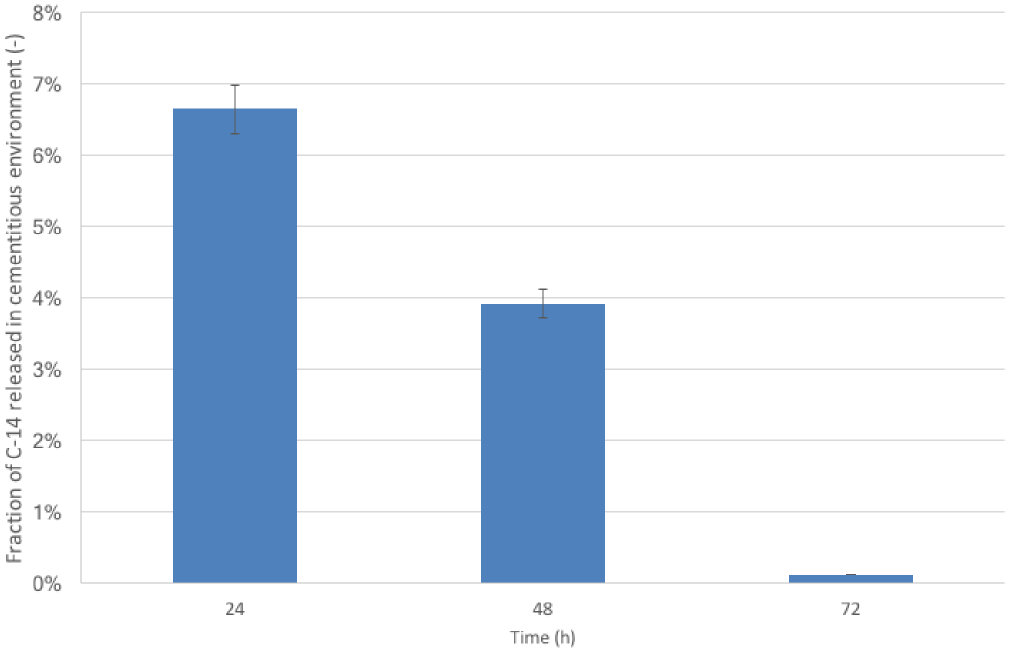


Figure 10. On-line release of inorganic ^{14}C from FZJ-B-2 SIERs in contact with alkaline solution. Values referred to the total mass of sample as delivered [BUCUR *et al.*, 2017].

Most of ^{14}C was retained exclusively in the third washing bottle of the analytic set-up (see Figure 3, page 9), which indicates the release under the form of $^{14}CO_2$ (no organic ^{14}C was detected). Thus, despite the expected effect of high pH favouring the retention of CO_2 in carbonate form, a release of *ca.* 10% of total ^{14}C occurred. A possible explanation of the observed phenomenon could arise from the fact that tested SIERs are mixed anion- and cation-exchange resins. A possible mechanism of CO_2 release could imply a decrease in the pH value, in a transient or permanent way. Once SIERs are in contact with an alkaline solution, cations like Na^+ or K^+ substitute H^+ in the cation-exchange resins, releasing H^+ in solution, which in turn transiently decrease the pH of the solution. At this moment the decrease in pH causes the release of ions from the carbonate system from the SIERs, with a consecutive release of gaseous CO_2. When the molarity of the alkaline solution is sufficient to compensate the instant release of H^+, the pH rises again, otherwise the decrease in pH of the solution becomes permanent.

A separate static experiment (open system in air) was carried out to confirm this suggested mechanism, mixing fixed amount of SIERs with different amounts of alkaline solution (XOH, with X=K, Na). Results are reported in Figure 11 and show that, in some cases, when SIERs/XOH ratio is above 1/15, *i.e.* with less solution, the pH value goes down to 4.14-4.82, which could favour degassing of CO_2 (Figure 2). By increasing the volume of added solution, the pH increases accordingly, up to the original pH of the alkaline solution, *i.e.* pH 13.2. This experiment demonstrates that, during sample preparation in an open system, a partial uncontrolled release of $^{14}CO_2$ may occur even if alkaline solution is used as a leaching solution.

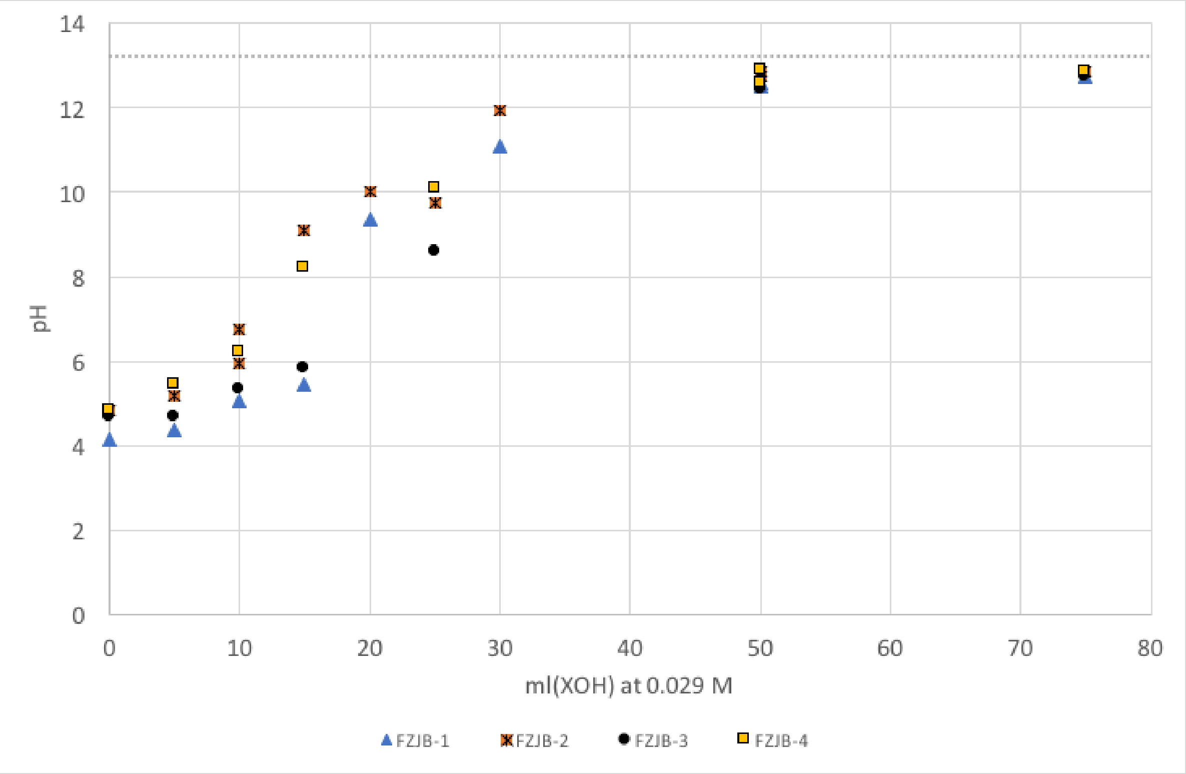


Figure 11. Static pH values of the solution in function of the equivalent volume in contact with FZJ-B SIERs. The initial point relates to the pH of deionised water in contact with SIERs [Bucur *et al.*, 2017].

Leaching experiments performed at RATEN-ICN with SIERs from CANDU demonstrated that the most fraction of ^{14}C is released as dissolved species, presumably as carbonate. The equilibrium in the solution is reached within the first 2 days (Figure 12), whereas the equilibrium level of inorganic ^{14}C released into the gas phase was instantly achieved and did not change until the end of experiment (*ca.* 300 days).

From the total ^{14}C present in the SIERs sample used for desorption test, around 7% was released as inorganic ^{14}C in the gas phase and around 79% as dissolved species. Around 94% of ^{14}C content in the SIER sample was recovered at the end of desorption test. The remaining ~ 6% was not found either as dissolved species or inorganic gas species, or as residual on the SIER sample after desorption test, and could represent an unaccounted ^{14}C fraction of instantly released CO_2, as in case of the FZJ tests. No organic ^{14}C released in gas phase was measured during these tests.

These results should nevertheless be further mitigated in view of the composition of actual cement pore water, which contains high concentration of dissolved calcium, and the possible precipitation of calcite [Berner, 1992; Pointeau *et al.*, 2004; Pointeau *et al.*, 2006; Pointeau *et al.*, 2008].

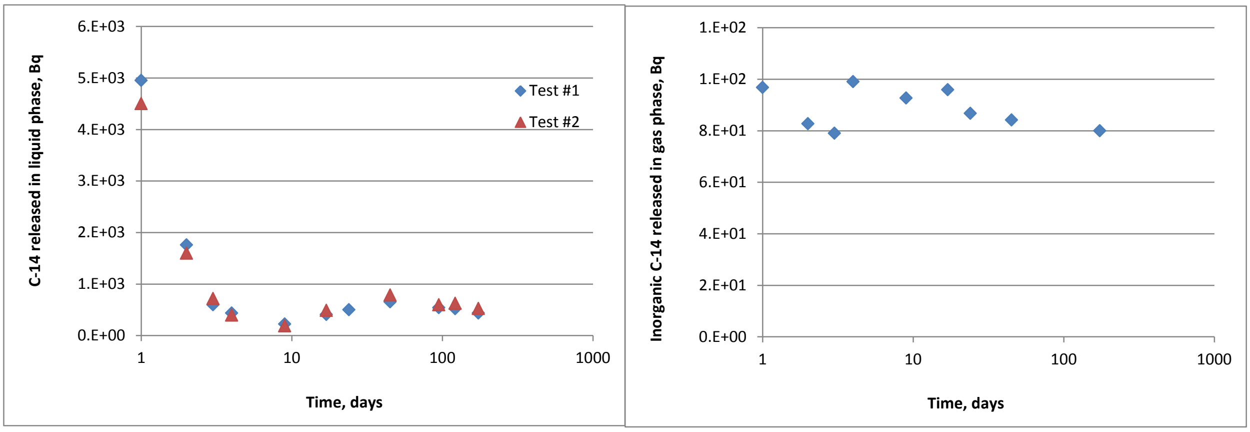


Figure 12. The kinetics of ^{14}C released into the solution (left) and gas phase (right) during desorption tests [Bucur *et al.*, 2017].

4. Conclusions and Outlook

The experiments with SIERs of different origin, *e.g.* BWR, PWR, and CANDU reactors, having a wide range of ^{14}C inventory, were investigated in WP4 for understanding of the ^{14}C source term.

The results on the speciation of ^{14}C originated from SIERs — partition between inorganic (carbonate) and organic fractions — seem to show that most ^{14}C is in inorganic form. In particular, for CANDU reactors, the major part is retained in the anion-exchange resins in inorganic form, whereas a minor fraction of ^{14}C-containing species were found fixed to cation-exchange resins and was presumably under the form of metal carbonate complexes. However, results on inorganic and organic fractions for PWRs were sometimes contrasting, spanning between 30% up to 99% for the inorganic fraction. The ^{14}C speciation for SIERs from BWR seems to be more consistent among WP4-partners, *e.g.* samples of SKB and FZJ, ranging between 0.4% and 5.0% of organic fraction. It has been also demonstrated that the drying procedure has strong influences on the speciation. The speciation ratio in the dried samples is completely reversed, *i.e.* 92% of organic form and 8% of inorganic form, pointing out that the major part of the inorganic ^{14}C might be released during the drying process, and the organic fraction remained on SIERs. A possibility of an uncontrolled loss of anion-exchange capacity in the resins during the process has been confirmed by FZJ.

The speciation of the organic fraction, performed with complementary approaches by SKB and FZJ, points towards the identification of formic acid as the main organic ionic compound bound to the SIERs, which could originate from the reactor coolant and/or from the degradation of the resins.

The presence of ^{14}C in non-ionic form, bound to the resins' backbone or in eventual particulate matter (BWR SIERs) could be tested and cannot be excluded. The ^{14}C activity of this fraction is, however, thought to be very limited.

The release of ^{14}C in storage experiments has proven the relatively fast release kinetics of ^{14}C, driven by ion-exchange and/or isotopic exchange processes. Enhanced temperatures favour a higher release of ^{14}C due to a (slow) thermal degradation of the SIERs. The nature of ^{14}C bound to the resins seems to play an important role during storage, as HCO_3^- ions, bound to one exchange group, are believed to be less stable than CO_3^{2-} ions, bound to two exchange groups.

Self-irradiation of SIERs seems to be irrelevant for ^{14}C release at the laboratory time scale, but cannot be excluded over the long-term storage and for high gamma activities. Investigation of the SIERs samples of different ages also did not reveal any measurable effect on the ^{14}C release.

A relatively fast kinetics of ^{14}C release in solution was measured, highlighting also the presence of organic ^{14}C in ionic form, *i.e.* from SIERs from PWR, as well as the release of soluble inorganic ^{14}C and gaseous $^{14}CO_2$. Gaseous releases from SIERs in alkaline conditions are caused by a transient decrease in the pH of storage solution, depending on the molarity and amount of the solution. Presumably, the transient pH drop is caused by H^+ ions released during the ion-exchange between SIERs and the alkaline solution.

A systematic collection and investigation of SIERs from different water-cleaning circuits would favour a better understanding of the source term for ^{14}C and could allow an optimization of the storage conditions in order to prevent uncontrolled release of ^{14}C. This could also support the development of an effective treatment process in order to transfer SIERs into more robust waste-forms for long-term disposal.

The mechanisms evidenced in the present work, however, have been obtained for unconditioned SIERs. National strategies for the management of SIERs are different and conditioned/treated SIERs may not reflect the same behaviour.

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Glossary

BWR

Boiling Water Reactor 1, 2, 3, 4, 10, 11, 12, 15, 17, 20, 21, 30, 31, 33

CANDU

Canadian Deuterium Uranium Pressurized Heavy Water Reactor... 2, 3, 12, 15, 16, 17, 18, 19, 29, 30, 31, 33, 34

CEA

Commissariat à l’Énergie Atomique et aux énergies alternatives.. 2, 3, 4, 6, 12, 13, 14, 15, 17, 19

EDF

Électricité de France 2, 3, 4, 13, 14, 15, 17, 18, 19, 26, 27

ENEA

Agenzia nazionale per le nuove tecnologie, l'energia e lo sviluppo economico sostenibile 2, 3, 4, 5, 10

FZJ

Forschungszentrum Jülich 2, 3, 4, 5, 9, 10, 11, 12, 14, 15, 16, 17, 21, 22, 23, 24, 25, 28, 29, 30, 31

HPLC

High Performance Liquid Chromatography 6, 10, 21

IERs

Ion-Exchange Resins 1, 2, 4, 5, 10, 21

LSC

Liquid Scintillation Counting 4, 10, 12, 22

NPP

Nuclear Power Plants 1, 4, 12, 19, 22

PWR

Pressurized Water Reactor 1, 2, 3, 4, 12, 13, 15, 17, 18, 20, 25, 30, 32

RATEN-ICN

Regia Autonoma Technologii pentru Energie Nucleara-Institutul de Cercetari Nucleare (Pitesti) 2, 3, 4, 5, 6, 10, 12, 14, 15, 17, 22, 29