CArbon-14 Source Term

CAST

State of the art review on sample choice, analytical techniques and current knowledge of release from spent ion-exchange resins (D4.1)

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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 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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Executive Summary

Seven partners (CEA, EDF, ENEA, FZJ, INR, SKB, ÚJV) from six countries (Czech Republic, France, Germany, Italy, Romania, Sweden) are involved in the fourth work package (WP4) of project CAST, dedicated to the study of speciation, source term, leaching, and gaseous release of ^{14}C from spent ion exchange resins. In several Reference Cases of disposal systems envisaged by waste management organizations, ^{14}C is one of the most important contributors to the dose. Ion exchange resins are widely used in nuclear facilities for the purification of liquid processes or wastes streams, and the fate of ^{14}C has to be addressed.

The WP4 partners' first task is to define on which relevant ion exchange resin samples they will construct their program based in the framework of their national constraints. Most of the partners will study spent ion exchange resins from pressurised water reactors – including CANDU reactors –, and two partners (FZJ, SKB) will study resins taken from boiling water reactors. A second aim is to provide a state of the art review of the different techniques used so far to address the different aspects of the questions asked within this work package. The partners involved will also develop analytical strategies.

A state of the art review on the different techniques used to characterize spent ion exchange resins is presented. A large part of the works that were done so far are based on liquid

scintillation counting, but an increasing amount of determination are now performed in accelerator mass spectrometry. Other non-conventional techniques are also reviewed.

Finally, a status of knowledge is provided on the possible chemical forms (speciation) under which ^{14}C can be released from spent ion exchange resins. Analytical strategies for speciation by partners are also described. Available estimations of the proportion of inorganic *vs.* organic forms are reviewed as well as the possibility of the different forms of organic molecules, and gaseous release.

Most of the ^{14}C determinations deal with the maximum activity determination, percentage of recovery and differentiation between organic and inorganic fractions. There are several studies of the acidic release of $H^{14}CO_3^-$ from inactive IERs, which implied the hypothesis that inorganic ^{14}C is adsorbed on the resins, for subsequent gasification. However, this does not bring any information about the actual speciation of ^{14}C in real SIERs.

There is only scarce information about the speciation of ^{14}C originated from SIERs. Most of the information is related to the partition between inorganic (carbonate) and organic fractions. Available results 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, after their separation from a mixed bed, and was probably in the form of metal carbonates. However, results on the partition of inorganic and organic molecules are contrasting. For SIERs from PWRs, around 20% was in the form of organic molecules and from 5% to 20 % for SIERs from CANDU reactors was found. The inorganic *vs.* organic partition in two actual cemented SIERs from RMBK graphite-moderated BWRs has been measured. An almost equal partition (48/52) of inorganic *vs.* organic ^{14}C was found for the first sample and slightly more inorganic than organic (59/41) ^{14}C was found in the second sample. These data may not be directly compared with other BWRs.

At present no determination of organic molecules in leachates from SIERs has been published. It has been hypothesized that acetate and formate are the possible organic forms of ^{14}C since they are expected in the reactor coolant of PWRs and BWRs. However, no direct measurements have been reported and the conditions of the coolant water going through the resins, *e.g.* 300°C and 72 bar for BWRs, are different from near-ambient conditions. The storage conditions for the SIERs are expected to affect the amount of ^{14}C released and its speciation depending on, for example, pH, temperature, microbial activity and radiolysis.

No published investigations on the release of gaseous ^{14}C from SIERs have been found. In general, inorganic releases in the gas phase are expected to be in form of $^{14}CO_2$. In general, a disturbance of the acid-base equilibrium of the solution in contact with the resins will result, directly or indirectly, in a release of ^{14}C present in the form of a carbonate. This could also arise through the ingress of foreign anions with selectivity on the resin higher than HCO_3^-, e.g. as chloride, nitrate, or hydrogenosulphate anions. Other less known effects leading to ^{14}C release from SIERs are the effects of service/storage temperatures and strong oxidants (thermal and chemical degradation), that could affect resin equilibrium and capacity. Microbial growth, which could convert some inorganic ^{14}C into an organic form or produce anions that may displace the ^{14}C from the resins; however, highly alkaline media ($pH > 12$) are not favourable for microbial activity.

Radiolysis could represent an important variable affecting the release and possibly the speciation of the released radionuclides. IERs are in most of the cases DVB-based resins, *i.e.*, they are particularly sensitive to radiation damage during and even after operation, compared to other materials like inorganic IERs or cement. Effects on the speciation of radionuclides due to the degradation of mixed bed IERs have been reported with releases of trimethylamine (TMA), $H_2(g)$ and $CO_2(g)$ from anion exchange resins (SBA type I) due to γ-irradiation. A distinction between anaerobic and aerobic conditions was made with $CO_2(g)$ detected only in the presence of oxygen. Studies on radiolytic and chemical degradation of strong acidic IERs underlined the formation of mainly sulphate and dissolved organic carbon in solution. Among these, only oxalate was identified, comprising 10-20% of the organic fraction. Other degradation products were CO_2 and H_2.

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1 Introduction and Context

In several Reference Cases of disposal systems envisaged by waste management organizations, ^{14}C is one of the most important contributor to the dose – see *e.g.*, JOHNSON AND SCHWYN [2008]. Ion exchange resins (IERs) are widely used in nuclear facilities for the purification of liquid processes or wastes streams. Particularly, significant amount of IERs are used in water clean-up systems in the reactor coolant. 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.

Typically, in boiling water reactors (BWRs) oxidizing conditions should lead mainly to the formation of more oxidized species, *i.e.*, end-product CO_2 and carbonate, whereas in pressurized water reactors (PWRs) less oxidized species should be obtained, *i.e.*, end-product CH_4. Particular situation can lead to intermediate cases, *e.g.*, hydrogen injection in BWRs. Depending on local redox conditions, alcohols, aldehydes, and acids can also be formed. As alcohols and aldehydes are not ionized in water at 25°C, only acids were thought to be retained in spent ion exchange resins (SIERs). The information on the repartition of species, *i.e.*, speciation, under which ^{14}C is fixed to SIERs is scarce. The main information exists under the form of repartition between inorganic and organic fractions – see *e.g.*, MAGNUSSON AND STENSTRÖM [2005].

The immobilization of resins in cement is a possible solution [LI AND WANG, 2006]. These matrices have the advantages to retain CO_2 under the form of carbonates ions, and also have the possibility to adsorb organic acids [VAN LOON *et al.*, 1997; YOSHIOKA *et al.*, 2002; POINTEAU *et al.*, 2008]. Hence, the interaction of SIERs in particular cementitious system is of interest and alkaline media will be particularly addressed within this work package.

Even if SIERs are not planned to be disposed in deep underground systems but in subsurface storage, the release of ^{14}C from SIERs is a major concern. This work package is thus dedicated to the study of the speciation of ^{14}C associated to the SIERs: from the repartition between organic and organic form, up to the more detailed speciation and content of organic acids, carbonate… The initial objective is to obtain further information on the repartition of molecules potentially fixed and/or released from SIERs during their storage in subsurface.

First, a status on the sample choice of each partner, within the framework of their national program, will be given. Second, as ^{14}C is a pure β-emitter, it belongs to the category of hard to measure radionuclides. Hence, the panel of possible analytical technique is not vast. A literature review will be proposed to better ascertain to possibilities of each techniques and the possible information that can be retrieved from this work package. Finally, the status of knowledge on the possible release from SIERs will be presented.

2 Sample Choice

2.1 *Pressurized Water Reactors*

2.1.1 EDF-CEA program

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.

2.1.1.1 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 1**:

- the chemical and volume control system (1);
- the primary effluent treatment system (2);
- the reactor pool and spent fuel pool cooling and treatment system (3);
- the steam generator blow down system (4);
- the stator water purification system (5);
- the liquid waste treatment system (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 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.

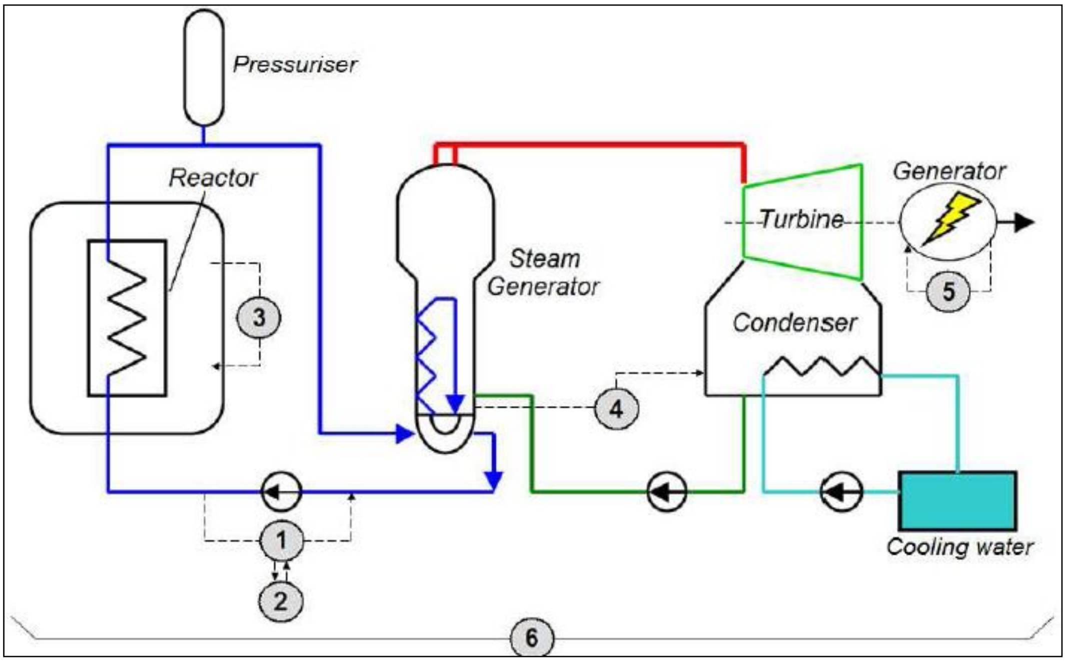

Figure 1. General location of the key purification systems on an EDF PWR.

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 spent ion exchange resins (SIERs) produced in EDF nuclear facilities are a mixture of IERs of different origins and characteristics. The radioactive content depends on the criteria for discharging used resin. 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 till 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.

2.1.1.2 On-site conditioning of EDF spent ion exchange resins

The “Mercure” process uses an epoxy matrix for resin encapsulation. The resins are conditioned in shielded concrete packages. For carrying out the “Mercure” process a mobile device used onsite includes 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 two IP2 containers for conditioning contaminated equipment;
- two office bungalows;
- a cold container.

The process is implemented onsite by SOCODEI[1]. The resins are conditioned in shielded C1PG type concrete shells manufactured by CDB[2] in compliance with ANDRA specifications on the encapsulation of waste intended for surface storage (LLW).

Figure 2: Cross section of a "Mercure" C1PG package (SOCODEI).

2.1.1.3 Samples choice

As previously explained, it is not possible defining 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

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[1] http://www.socodei.fr/en/

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

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 in a non-leachable epoxy matrix, contained in a metallic shield protected by a durable concrete shell.

EDF will provide 1 sample from 5 different EDF nuclear reactors to CEA in the framework of the CAST project as described in Table 1. The sampling will be 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 characteristics of these samples are summarized in Table 1.

Table 1. Characteristics of the EDF samples.

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

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

2.1.1.4 Transfer and analyses at CEA facilities

The work in CEA will be divided on two sites: the inventory of ^{14}C in SIERs will be performed in Cadarache Centre, and speciation of organic molecules will be performed in Saclay Centre. The total ^{14}C activity and the distribution between mineral and organic forms, will be based on methodology from previous work [MAGNUSSON AND STENSTRÖM, 2005; MAGNUSSON, 2007; MAGNUSSON *et al.*, 2008] and previous knowledge of the laboratory.

The first sample was received 06/19/14. It consists of a 10 g sample of wet SIER (Sample EDF-A, sampled 02/18/14).

2.1.2 ENEA

ENEA has been in contact with the Italian SOGIN and has received the information regarding the actual inventory of the SIERs. The SIERs consist in granulometric particles, the volume (wet samples) of which is more than 60,100 litres. The SIERs are stored in a temporary repository, under the management of SOGIN.

The IERs used during the operational phases are both cationic and anionic type and most of them are mixed bed, according to their specific utilization for the purification and treatment processes.

Table 2. Type and properties of IERs used in Italian context.

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

The total activity of the full amount of SIERs is in the range of 1.4 10^{13} Bq. As most of the SIERs have been already stored, only small amounts are still available for further investigation. ENEA is making arrangements with SOGIN in order to receive 9 samples (3.5-10.0 g for each sample) of SIERs. The samples will undergo ^{14}C measurement analysis and, if feasible, due to the small available amounts, also some morphological characterization.

ENEA has planned to have the availability of the SIERs from the PWR power plant in Trino by September 2014.

2.1.3 INR

Romania has two Canadian Deuterium Uranium Pressurized Heavy Water Reactor (CANDU) reactors in operation at Cernavoda NPP – U1 in operation since December 1996 and U2 since November 2007 – and two more CANDU units are foreseen to be constructed.

Around 6.65 m^3 of spent ion exchange resins (SIERs) are yearly generated at each CANDU reactor. 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 2055. Around 580 m^3 of non-fuel contact SIERs will be generated from the four CANDU units for an operational period of 40 years – the Cernavoda units 1&2 are designed to be operational for 30 years but reactor refurbishment is planned to extend its life-time to 40 years. These resins could contain approx. 2 10^{15} Bq of ^{14}C [SEDOR, 2012].

Up to now no real measurements on Cernavoda SIERs were performed. IRN will perform experiments for ^{14}C measurement and its inorganic and organic fractions in CANDU spent ion exchange resins (SIERs) from Cernavoda nuclear power plant Unit 1. The two units in operation at Cernavoda are 700 MW pressurized heavy water CANDU-6 reactors with nuclear fuel based on natural uranium and heavy water as moderator and cooling fluid. Cernavoda Unit 1 is designed for an average burn-up of 156 MWh/kg U. The values of burn-up registered at Cernavoda Unit 1 from 2007 to 2013 are presented in Table 3.

Table 3. The burn-up recorded at Cernavoda Unit 1 [NUCLEARELECTRICA, 2013].

	2007	**2008**	**2009**	**2010**	**2011**	**2012**	**2013$^{(*)}$**
Burn-up [MWh/kg U]	169.57	152.86	167.78	168.51	168.19	168.55	169.05

(*) the burn-up for 2013 was calculated based on the reported values for the first 9 months.

At Cernavoda, the SIERs are generated during routine operation and maintenance activities. The SIERs are collected in concrete vaults, under light water, based on their origin: non-fuel contact systems and fuel contact systems.

The non-fuel contact SIERs are those spent resins generated from the purification of water circuits which were not in contact with the fuel assembly, such as:

- moderator purification system;
- heavy water clean-up system;
- liquid zone control system;
- end shield cooling system.

For moderator purification system a mixed resin type Amberlite IRN-150 is used. 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. The same type of resin is also used in the liquid zone control system and in the heavy water clean-up system but combined with activated charcoal in the last system. In the end shield cooling system IRN-154 resin is used, a similar mixture of acid and base resins, but with Li^+ substituted for around 75% of H^+ on the strong acid cation-exchange resin.

Other type of ion exchange resins used in the end shield cooling system is IRN 217, also a mixed resin containing a stoichiometric equivalent of the strong acid cation resins, fully converted in the $^7Li^+$ form, and the strong basic anion exchange resins.

Once the resins are used they are removed from the purification system and transferred to the storage vaults in the form of slurry in demineralised water. Cernavoda SIERs are stored in three reinforced concrete vaults, lined with epoxy resin, with capacity of 200 m^3 each. No SIERs sampling from the Cernavoda storage tank were performed up to now. INR designed and realized a sampling device that was tested in the presence of the Cernavoda NPP representatives, in simulating conditions. It shall be tested at Cernavoda, after some modifications to improve the radiological safety of the workers. The SIERs sampled will be transferred to INR to be used in the experimental program developed under CAST project.

If SIERs from storage tanks cannot be sampled: there are available fresh SIERs from different non-fuel contact purification systems of Cernavoda NPP that will be analysed in the frame of CAST project. These resins are removed from purification systems during routine maintenance work.

2.1.4 SKB

For the three Swedish PWRs, the reactor water clean-up IERs accumulate most of the ^{14}C activity. Therefore samples are withdrawn from these resins when they have been discharged and transported to the waste handling facility. This means that the samples are taken earlier in the downstream processing of the spent ion exchange resins than for the BWR units. However the results will be on the pessimistic side and it has been deemed that this is the only practical way of retrieving samples without jeopardising the dose budget for the operational personnel. The sampling frequency depends on the practical arrangements but a number of samples have been withdrawn from fuel cycles as far back as 2009.

Table 4 gives an overview of the sampling campaigns performed in the Swedish PWRs over the last years. For the Ringhals 2, 3 and 4 units, one resin bed/fuel cycle is sampled; however, the sample from each bed is composed of several subsamples. At the Ringhals 1 reactor, the storage tank receiving spent resin batches and delivering resin to waste solidification is sampled.

Table 4. The amount of samples that have been withdrawn and analysed for ^{14}C from Swedish PWRs during the last years.

Year	2008				2009				2010				2011				2012				2013				2014			
Unit	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
R1					11				6	18	16	1		19	21	8	12	6	8	8	8	2	3	5	10	1		
R2		1					1							1					1				1					
R3			1				1					1				1		1					1					
R4		1												1					1			1						

2.1.5 ÚJV

There is relatively low information and data about the composition of spent ion exchange resins produced in Czech nuclear power plants. In both Temelín and Dukovany nuclear power plants, VVER reactor types (Water-Water Power Reactor) are installed. IERs are used in operation of all of them. Moreover, the trademarks used ion exchangers at the Dukovany nuclear power plant changed over time (at least 3 types of cation exchangers and 2 types of anion exchangers). These sorbents showed varied provenance; fundamentally, they were always a strongly acidic cation and strongly basic anion exchangers. Real SIERs are in the form of small spheres/beads with maximum of 10 % shape failure and small amount of admixtures. These admixtures could be mainly organic impurities, oils and precipitated borates. Composition of cations and anions is quite variable, spent resins contain mainly sodium, potassium and borate, nitrate ions.

In both Czech nuclear power plants the IERs are mainly based on divinyl benzene (catex:anex = approx. 2:1). After usage, SIERs are stored in tanks for radioactive waste without any regeneration. Ion exchange groups are substituted by ions from radioactive wastes.

Specimen from Temelín nuclear power plant was obtained for the purpose of this project. Preliminary analysis of ^{14}C shows the content approximately 600 Bq.kg^{-1}. Detailed analysis of this spent resin will follow together with the analysis of second resin type specimen.

The second spent resin will be obtained from services of research reactors, which are operated by Research Centre Řež. The research reactor LVR-15 is a light water tank-type research reactor placed in a stainless steel vessel under a shielding cover. The maximum reactor power is 10 MW thermal power. The LR-0 research reactor is a light-water, zero-power, pool-type reactor. It serves as an experimental reactor for measuring neutron-physical characteristics of VVER type reactors.

For preparation of laboratory samples, to compare with real spent ion exchange resins, strongly basic and strongly acidic Amberlite type resins, artificially contaminated with ^{14}C are proposed.

2.2 Boiling Water Reactors

In Figure 3, a typical configuration of boiling water reactors is shown. Figure 4 shows schematically the main circuits, highlighting the water purification/treatment systems.

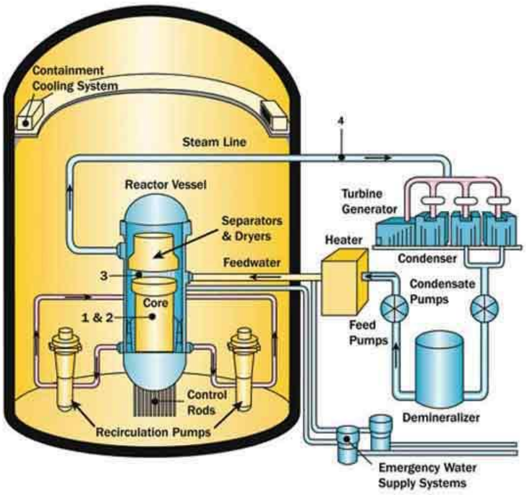

Figure 3: Typical Boiling Water Reactor Configuration (Source: US Nuclear Regulatory Commission).

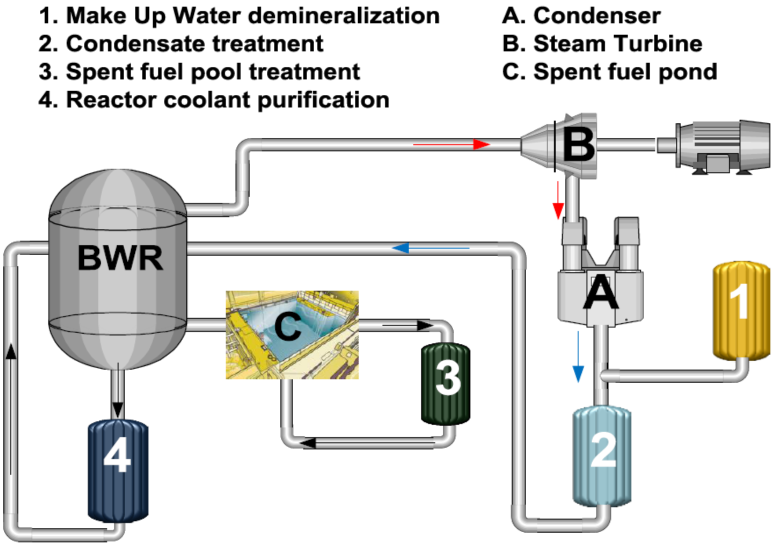

Figure 4: Water Treatment Circuits with IERs in a BWR [Wolff, 2012]

2.2.1 FZJ

Forschungszentrum Jülich (FZJ) is focusing its research on Ion Exchange Resins (IERs) adopted in water cleaning circuits of BWRs. The work will be part of a PhD thesis.[3] FZJ is in contact with German and other European BWR operators. Following the requests of the operators, in parallel to the agreement within CAST, the samples have been anonymized.

In contrast to PWR, powder IERs are also used, in particular in the condensate polishing circuit (CCU): this is due to the fact that the water in BWRs requires much higher pureness compared to the primary water of PWRs, because of the direct contact with the steam turbine. Table 5 reports the typical amounts of SIERs generated by the different types of reactors. From a chemical point of view, IERs in different forms (powder or beads) are substantially the same; in fact, the powder resins are obtained from the beads, after a milling process. Successively, a flocculation is necessary to reach the right mean dimension of the

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[3] The contribution here reported is going to be included in a Doctoral Thesis in FZJ. In case of external use please report a citation with reference: Rizzato, C. Predicted Defense in 2016. Radiocarbon and other Radionuclides Released by Spent Ion Exchange Resins Arising from Nuclear Power Plants. RWTH Aachen University.

agglomerates. More details will be reported in a dedicated section. The forms in which (S-)IERs are available can be observed in **Figure 5**.

Table 5. Spent organic ion exchange resin generation by reactor type [I.A.E.A., 2002].

Reactor Type	**SIERs generation [$m^3 \cdot unit^{-1} \cdot year^{-1}$]**
PWR	4-7
PHWR	5-7
BWR	20

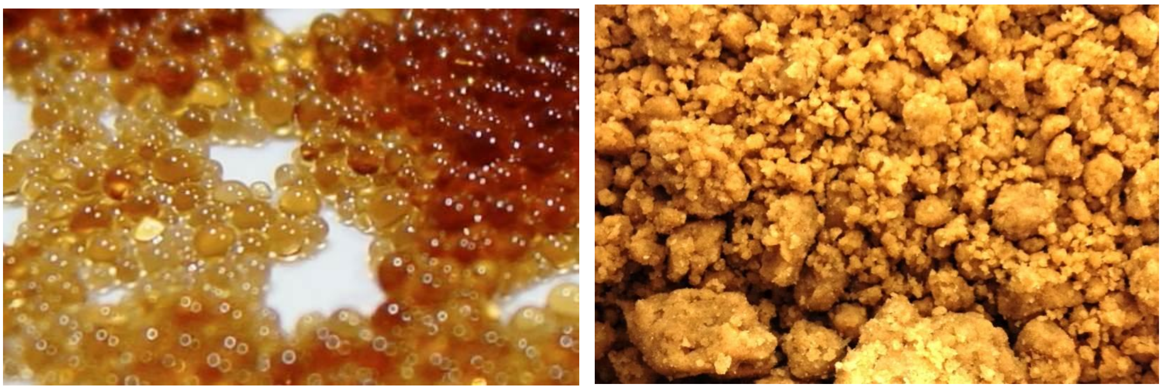

Figure 5. Comparison among IERs in bead form (left) and powder form (right, flocculated).

The water treatment circuits where ^{14}C is expected to be found are:

- Condensate Clean-Up System (CCU);
- Reactor Water Clean-Up System (RWCU);
- Spent Fuel Pond Clean-Up (SFPCU).

The resins of major interest, from the point of view of the ^{14}C content, are the ones used in the Condensate Clean-Up (CCU, circuit no. 2 in Figure 4) System and the Reactor Water Clean-Up (RWCU, circuit no. 4 in Figure 4) System, in descending order: former studies on BWRs [MAGNUSSON, 2007, p.34] showed that the ^{14}C is, in general, significantly higher in SIERs coming from the CCU system. Accordingly, FZJ is concentrating on the CCU SIERs, also due to the fact that RWCU SIERs are showing generally rather high ^{60}Co activities (up to tens of MBq.g^{-1}, depending on the specific reactor and boundary conditions), resulting in a more difficult and expensive transport, handling, and storage. A comparison of the ^{60}Co and total γ/β activities, in the case of FZJ-B, can be observed in Figure 6 and Figure 7.

SIERs coming from the different water clean-up systems are sometimes mixed all together generating a mixed waste. In order to have a systematic approach, only SIERs coming from the condensate clean-up system that were not mixed with other resins have been considered.

A further distinction is related to fresh/legacy samples: the first ones can be retrieved only in nuclear power plant under current operation, while the second ones can be retrieved independently on the operational status of the nuclear power plant, where an intermediate storage has taken place. In some cases the intermediate storage requested a (pre-)conditioning method (FZJ-B,C). In other cases, no intermediate storage took place and the SIERs were directly conditioned (cemented or even bituminized). More details on the standard conditioning methods will be reported in the related section.

The general criteria adopted during the sample selection, where a sample choice was possible (case FZJ-B), are explained hereafter.

I. Low γ-radiation: a selection of SIERs has been performed according to the licensed dose rate limitations for handling and storage in the FZJ’s radiochemical laboratory. An additional condition regarded the transport costs, limited as far as possible to reasonable amounts, according to the waste package classification (contact dose rate lower than 5 µSv.h^{-1}).

II. High estimated ^{14}C content: analysis on ^{14}C were not available. In some cases preliminary activity estimations (^{60}Co and total γ/β activities) have been made. The ratios A(total β,γ)/A(^{60}Co) have been considered for the different samples, in order to select the maximum β- and probably ^{14}C-containing samples with a concomitant low dose rate. This will result in easier transport, storage and handling. However, this selection criteria will be confirmed after laboratory analyses, since the amount of ^{14}C may not follow the ratios A(total β,γ)/A(^{60}Co). Optionally, a selection based on scaling factors referred to ^{60}Co could have led to unacceptably high dose rates and, in addition, would not have guaranteed high ^{14}C activities. Scaling factors, discussed in MAGNUSSON [2007], could lead to high uncertainties, when they are not reactor-specific and waste-stream-specific.

III. Effect of storage time: similar γ activities of the SIERs, stored for different periods, were selected. The aim is to extrapolate the ^{14}C behaviour during storage by considering at least 3 points in time.

IV. Self-irradiation effects: different γ activities of SIERs, stored for a similar period in similar conditions, were considered. The aim is to understand the effect of γ-irradiation on the ^{14}C behaviour during storage.

V. Type of samples: SIERs have been considered as priority samples. Successively, also water and gaseous samples (secondary samples) have been taken into account, when made available.

In the cases where a sample choice was not possible (case FZJ-A/C), the adopted criteria are exposed hereafter.

A. Evaluation of preliminary analyses: γ activity, total γ/β activity, contact dose rate.

B. Optimization of the sample amounts, according to the transport costs, storage and handling limitations.

C. Secondary samples – *e.g.*, water in solution, from the primary circuit or from the conditioning method, gases from the storage vessels/treatment line –, in addition to primary samples (SIERs), have been considered, when made available.

In the following, a more detailed approach to the sample choice for every selected BWR (named FZJ-A, -B, -C, etc.) is described.

In the case of FZJ-A, SIERs coming from the CCU system were collected in a dedicated vessel: the waste is, then, not mixed. However, the vessel has not been emptied up-to-now and it was flushed by air. Therefore all the time-related information on releases of ^{14}C and other radionuclides have been lost. Nevertheless, this powder SIER sample as it is could be considered as an average one, accounting the entire lifetime of the nuclear power plant. In January 2013, water was added to the vessel in order to keep the resins in wet conditions and, accordingly, to facilitate their removal afterwards. This precaution was not sufficient, resulting in an insufficient fluidity of the suspension: a first attempt to gather samples failed due to the blockage of the extraction device, most probably caused also by the presence of the flocculation material (usually Acrysorb®). A second sampling attempt succeeded and both SIERs and suspension water (criteria C) were collected and delivered to FZJ. The amounts have been optimized following criteria A and B.

In the case of FZJ-B, SIERs were systematically collected along the lifetime of the reactor, in dewatered conditions. Resins coming from different circuits were stored, in most of the cases, separately. This approach allowed a systematic sample choice. However, the limiting factor that played an important role in the collection of samples is represented by the dose rate. As mentioned above, only CCU SIERs have been considered following the criteria I, due to the high ^{60}Co activities of the RWCU SIERs: a comparison of the ^{60}Co and total γ/β activities can be observed in Figure 5 and Figure 6. The sample selection process, for what concerns the CCU SIERs from FZJ-B, dealt with a large number of resins, collected along power plant operation (see Figure 7). The adoptions of criteria II, III and IV allowed the choice of 4 samples (see Figure 7).

As previously mentioned, the most problematic radionuclide for transport and handling is generally ^{60}Co, which represents the highest contribution to the dose rate from SIERs in most of the cases. After the optimization of the minimum amounts needed for the planned analyses, together with the limitation of the transport costs and the licenced activities for storage/handling, samples from three drums, collected in a range of about 8 years, were selected. This will allow an evaluation of the degradation/release effects on the resins during interim storage. A fourth drum has been considered with a particularly high γ activity, with a storage period similar to another selected drum: an evaluation of the self-irradiation effects at two different ^{60}Co activities along a similar storage period in similar conditions will be possible.

Gas samples, coming from drums stored up to some decades, would have given significant contribution to the scientific understanding of the time-related ^{14}C release in gaseous form during (interim) storage. However, the ALARA[4] principle did not permit operations on the drums without a mechanical manipulator. This fact hindered the collection of gaseous samples due to the unsuitability of the manipulator for this task.

Sample delivery (SIERs) from FZJ-B is expected within October 2014.

The available radiological data of the selected samples is reported in Figure 8. The ratios total/^{60}Co of the different samples are reported in Figure 9 (criteria II).

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[4] As low as reasonably achievable

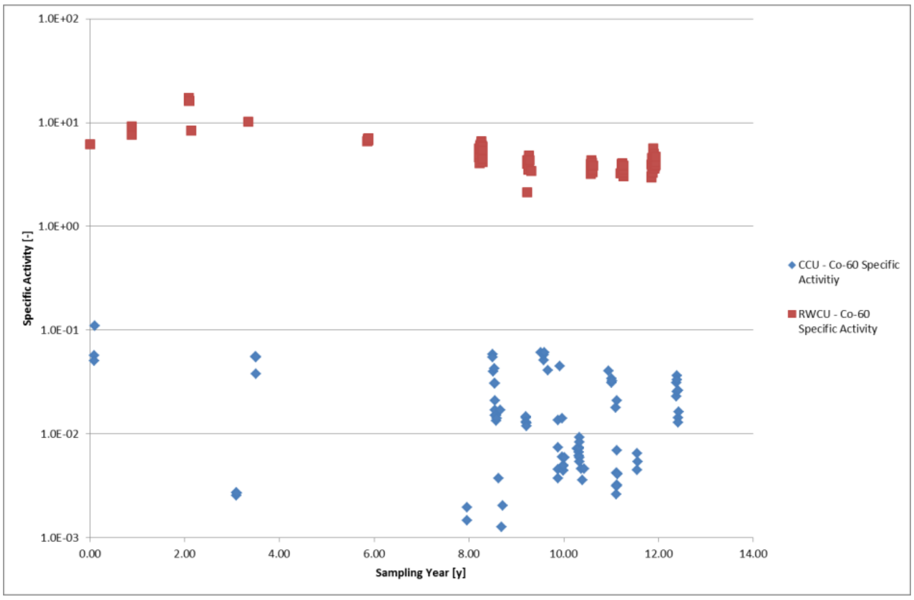

Figure 6. Comparison among ^{60}Co specific activities (relative values) between CCU and RWCU SIERs.

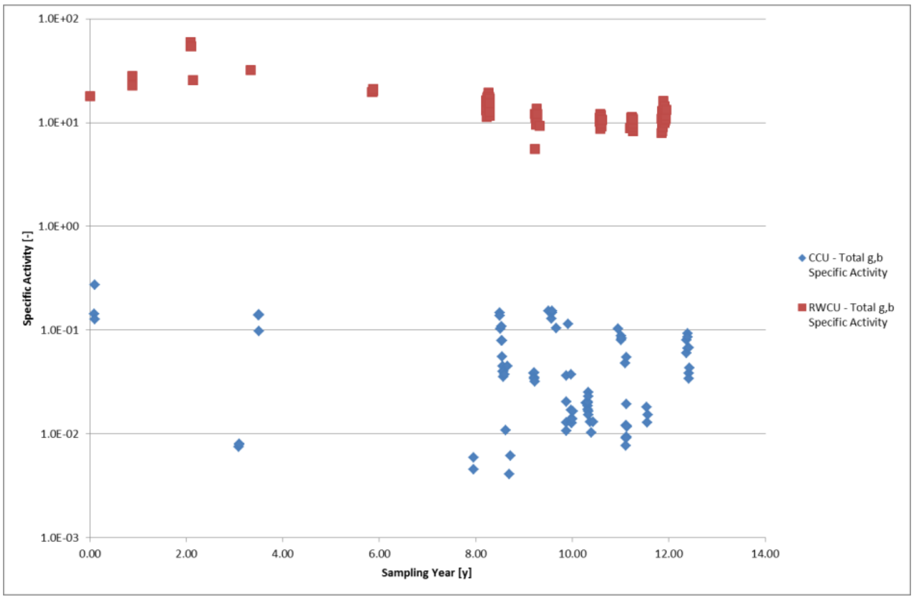

Figure 7. Comparison among total γ/β activities (relative values) of CCU and RWCU SIERs.

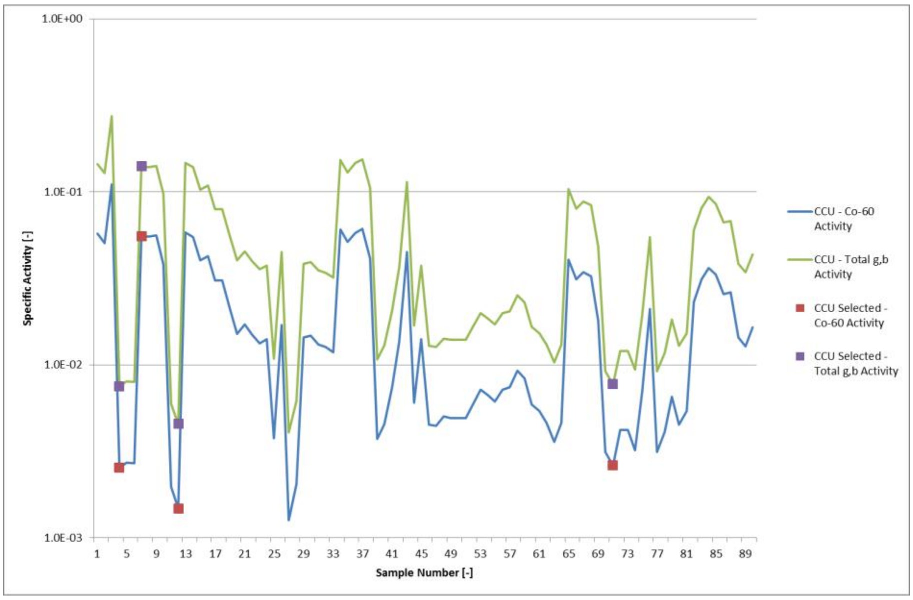

Figure 8. Comparison among total γ/β and ^{60}Co specific activities (relative values) of the available samples.

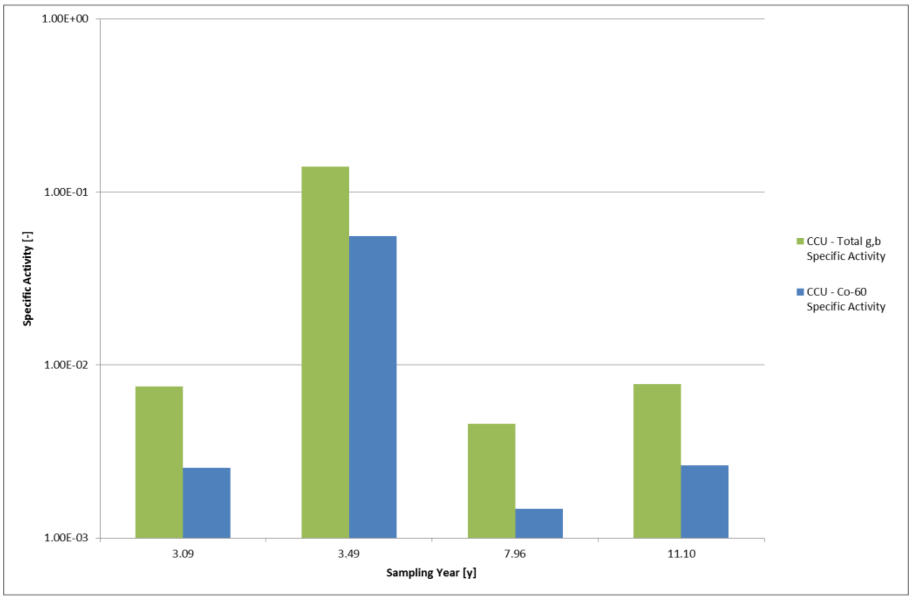

Figure 9. ^{60}Co and total γ,β activities (relative values) of the selected samples.

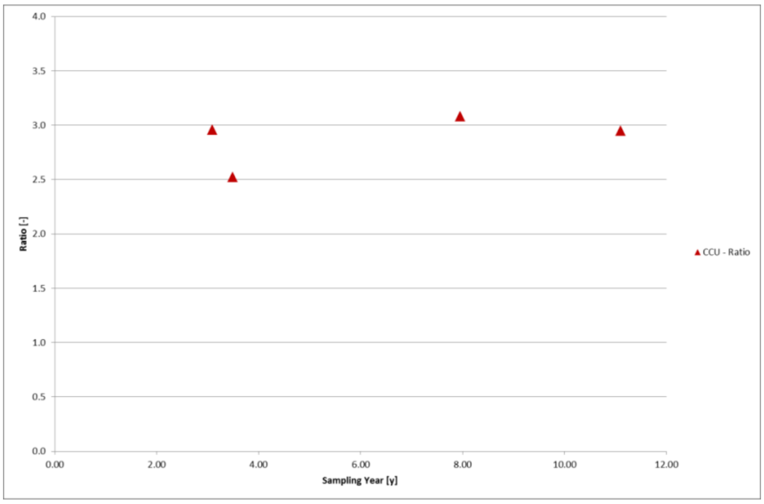

Figure 10. Ratio of the total γ,β and ^{60}Co specific activities of the selected samples.

In the case of FZJ-C, legacy and fresh samples have been taken into account. Some drums, containing SIERs, have been collected, designated to investigations on the gaseous releases during storage. Gas samples are expected from those drums in the next future. Concerning the “fresh” samples, a collection campaign is planned in the power plant FZJ-C within the next months: samples of SIERs, suspension water and possibly gaseous samples from the storage vessel are expected within October 2014.

The cases FZJ-D and FZJ-E are still under discussion with the respective operators. Samples will be available depending on the required/available budget for the transport.

Table 6. Summary of the different samples received/expected by FZJ.

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

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

2.2.1.1 Additional samples for parallel/complementary investigations: fresh IERs

Radiation protection and laboratory licensing are limiting the amounts of SIERs that can be considered. In addition, handling of radioactive material is allowed only in controlled areas. In most cases not all the analyses are possible with the equipment available inside these areas, while a large variety of investigation techniques could be possible in normal laboratories, without the restrictions related to radioactive samples. For this reasons, together with the easiness of handling inactive material, non-radioactive IERs may be considered. The purpose is to widen the spectra of available investigations and to facilitate the understanding of several mechanisms leading to the release of ^{14}C.

In many cases, fresh IERs have been provided directly by the nuclear power plant operators. However, in order to attain completeness of information, the producer (IDRECO s.p.a.) has been directly contacted to obtain samples, information on the fabrication process, and characteristics of the resins. The selected IERs are of the same grade and form than the selected SIERs. It would then be possible for instance to:

- investigate the degradation of the IERs caused by several factors;
- verify the different parameters and kinetics before/after usage;
- simulate leaching experiments with non-active material loaded with targeted species.

In addition, a dedicated γ-irradiation campaign could be performed, if further funds were made available by budget modifications, in order to investigate systematically the release of carbon (in this case ^{13}C, loaded on the resins in various forms) under several boundary conditions (pH, different atmospheres, different radiation doses, etc.), both in solution and gaseous form.

2.2.1.2 Additional considerations:

Different water chemistries, i.e. neutral water chemistry (NWC), and hydrogen water chemistry (HWC) affect the ^{14}C organic fraction in the SIERs [MAGNUSSON, 2007]: the consideration of this effect could extend the investigations to SIERs coming from reactors with different water chemistries. However, the transport costs for the related samples are expected to exceed the related budget agreed within CAST. It is foreseen to shift some cost (within the FZJ's budget) to allow for investigations of the water chemistry effects on the ^{14}C speciation and release from SIERs.

Efforts on lowering the detection limits and development of the analytical techniques are under way, but the application of Accelerator Mass Spectrometry (AMS), in particular for gaseous samples, could be the key factor for the detection/speciation of the ^{14}C, or ^{13}C loaded on –and released by – fresh resins. A sample exchange routine could be established with those CAST partners operating AMS capable of measuring also gaseous samples.

2.2.2 SKB

From the seven BWRs, samples are taken from the condensate clean up units (CCU) as it has been shown in earlier investigations that most of the ^{14}C content resides at these ion exchange resins. In order to get an "as comprehensive" picture as possible of the ^{14}C activity that is taken up by the resins and deposited of in the repository for short lived intermediate level waste, samples are withdrawn and analysed as late in the waste processing facility as possible. In many cases this corresponds to a sample just before waste immobilisation, *i.e.*, bitumen or cement solidification of the SIERs.

Table 7 gives an overview of the sampling campaigns performed in the Swedish BWRs over the last years. The Forsmark 1and 2 reactors and the Oskarshamn 1 and 2 reactors are sampled in pairs, named F1,2 and O1,2, respectively. For O1+O2 each collection tank is sampled prior to the preparation of the waste containers that will be deposited of in the final storage for operational low- and intermediate level waste (SFR). At the Oskarshamn 3 reactor, the sampling is done in connection with transfer to the waste containers. For F1+F2, the corresponding interim storage tank, may be sampled when the tank contents is recirculated and when resin is brought to drying before solidification.

Table 7. The amount of samples that have been withdrawn and analysed for ^{14}C from Swedish BWRs during the last years.

year	2008				2009				2010				2011				2012				2013				2014			
Unit	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
F1+F2					1	4	2			1	3	2						4	4	2	1		3					
F3							1	1	6	1	3		3	1					1	2			5					
O1+O2				2	4	3						5	7	2	1	5	6	5	4	2	3	6	1					
O3													1		2		1		1	1	2	1	1					

3 Analytical Techniques

As ^{14}C is a weak β-emitter, it has to be isolated from all the other radionuclides, when it needs to be analysed in materials from nuclear processes. Most of the existing data on the quantification and characterization of ^{14}C in process water – generally reactor water – and SIERs from LWRs are from investigations performed in the 1980's and the beginning of the 1990's [MAGNUSSON *et al.*, 2008].

The general objective of the performed analysis was to measure the total ^{14}C content, so the analytical methods didn't take into consideration the chemical forms of the carbon within the analysed matrix.

However, the chemical form of ^{14}C (organic or inorganic) is an important factor when estimating doses arising from releases to the environment. The chemical form of ^{14}C in process systems determines its behaviour, *e.g.*, degree of adsorption on ion-exchange resins. The characterization is therefore important to model and predict its fate.

In water, inorganic carbon undergoes through chemical equilibrium simple and complex carbonates, but organic compounds like methane could be affected by different pathways [GARNETT *et al.*, 2011]. As an example if CH_4 passes through mineral layers enriched in sulphate, it is transformed again in carbonate/bicarbonate compounds, resulting in a higher retention mechanism and lower diffusion into the biosphere (Figure 11).

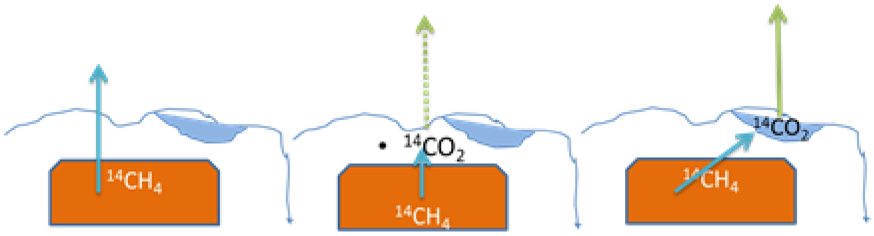

Figure 11. Schematic representation of diffusion of methane or carbonation of methane.

The chemistry of carbon is strictly linked to its electronic configuration $1s^2$ $2s^2$ $2p^2$ that causes it to form more compounds than any other element in the periodic table. Its chemical forms are controlled by pH, redox potential, and temperature. Carbon has different oxidation states, –IV, 0 or +IV, and forms covalent chemical bonds. In its elemental form carbon has oxidation state 0 and it exists in nature as diamond or graphite. In aqueous solution, carbon is in equilibrium with different chemical forms: carbon dioxide $CO_2(g)$, and ions from the carbonate system, *i.e.*, CO_3^{2-}, HCO_3^-, H_2CO_3, each of these forms being governed by pH of the solution. Carbonate system plays an important role in controlling other radionuclide speciation.

H_2CO_3 and $CH_4(aq)$ are the most stable chemical species in acid conditions, whereas carbonate ion CO_3^{2-} is the stable form in alkaline media. At standard temperature and pressure conditions (equilibrium with air) the prevalent species are the ions from the carbonate system. In strongly reducing environment the reduced form $CH_4(aq)$ and $CH_4(g)$ are stable in a wide range of pH (see Figure 12a). The formation of alcohols and acids (CH_3OH, C_2H_5OH, $HCOOH$, CH_3COOH) as intermediate reduced species requires strongly reducing conditions. A complementary Pourbaix diagram excluding the formation of CH_4 and the formation of small organic molecules up to C_2 is proposed in Figure 12b [Shock and Helgeson, 1990].

The chemical forms of ^{14}C in the material that will eventually become low level waste will be different from those existing at the source, *e.g.*, coolant/moderator system, as the temperature and redox potential of the system environment change. During a water-reactor operation, the coolant temperature is on the order of 300 °C, and pressure is high (155 bar for PWR; 72 bar for BWR; 89 bar for CANDU). The condition for filters and ion exchange resins represent what is closer to ambient conditions. As the temperature of the system is lowered and the system becomes more oxidizing by being exposed to the ambient atmosphere, the ^{14}C could experience a series of oxidation processes.

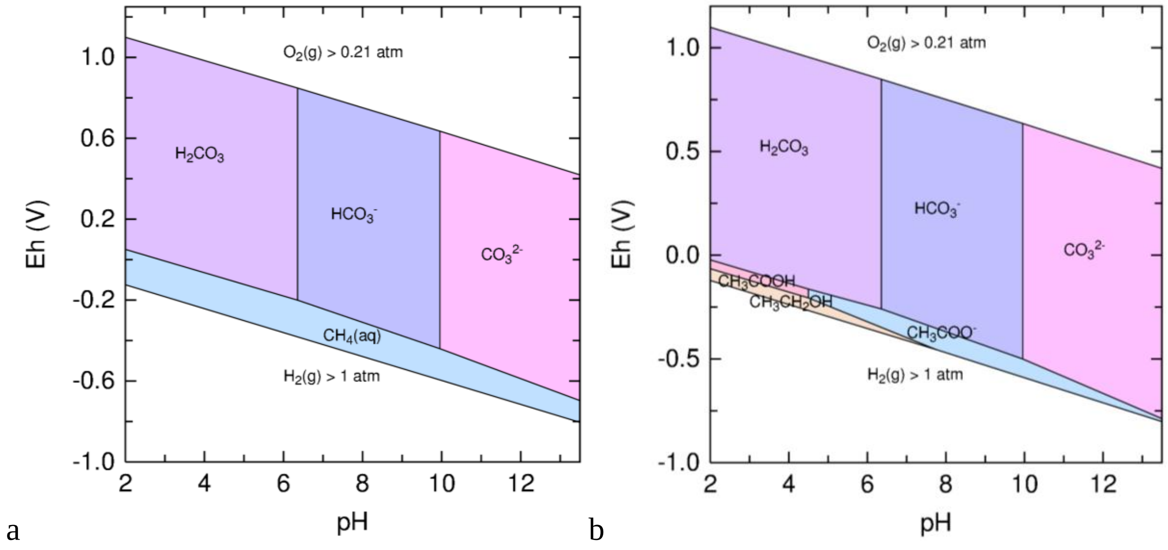

Figure 12. Pourbaix diagrams of the major carbon species at 25 °C and standard conditions at 10^{-3} mol.L^{-1}, (a) accounting for CH_4 formation, and (b) limiting to the formation of C_2 molecules – graphs created with PhreePlot [Kinniburgh and Cooper, 2011], from data in Shock and Helgeson [1990].

3.1 *Total ^{14}C*

The major chemical form of ^{14}C available for release in nuclear industries is as bicarbonate adsorbed into the ion exchange resins ($H^{14}CO_3^-$). ^{14}C produced in the coolant of all types of LWRs and HWRs, and especially in the moderator of HWRs, is removed by ion exchange resins in a purification system [Lundgren *et al.*, 2002]. The chemical form on the resins is still bicarbonate. This anion can still be chemically displaced by other anions present in natural waters, hence, it is considered as available.

Methods providing information on the chemical form of ^{14}C in different process media of nuclear reactors are generally based on measuring the total and inorganic ^{14}C in separate subsamples, whereby the organic fraction is estimated by subtraction (*i.e.*, indirect measurement). This procedure led to some intrinsic uncertainties. In order to perform direct measurements of both fractions the analytical methodology should consider the chemical-physical separation of different forms.

The first step for measurement of total ^{14}C is to efficiently extract the carbon content from the samples. This step is usually done by oxidative combustion (Figure 13), heating the sample in air or oxygen atmosphere and obtaining carbon monoxide (CO) and carbon dioxide (CO_2) as by-products.

$$^{12,13,14}\mathrm{C\text{-}X\ (sample)} + \mathrm{O}_{2(g)} \rightarrow {}^{12,13,14}\mathrm{CO}_2 + {}^{12,13,14}\mathrm{CO}$$

Where $^{12,13,14}C$ means that all the carbon isotopes are involved in the chemical reaction and they will maintain, as a first approximation, their constant ratio also in the byproducts of the combustion. Usually a catalytic furnace is used to ensure complete oxidation to CO_2.

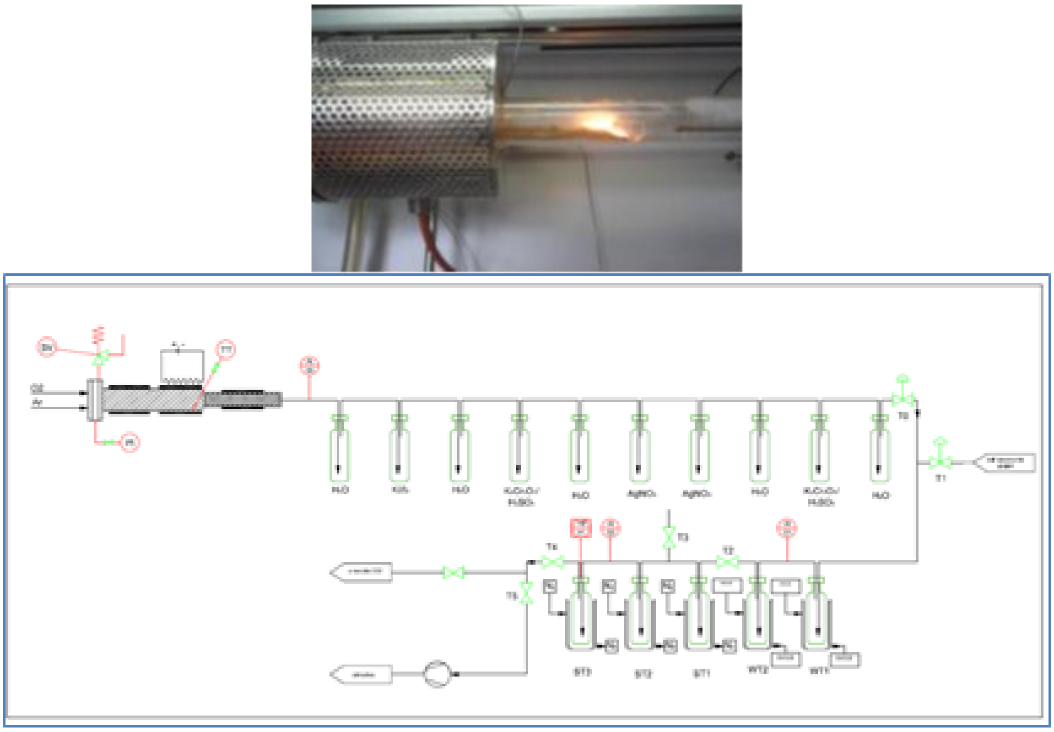

Figure 13. Schematic representation and photo of a typical combustion chamber for CO_2 transformation of the sample – photo courtesy provided by ENEA ^{14}C laboratory.

As the main purpose in this step is to extract the carbon content from the samples, the following step will be the trapping of the CO_2 in a suitable form for measuring the beta radioactivity, due to the ^{14}C. This purpose can be achieved by three main techniques that have in common the necessity to obtain CO_2 gas from the sample: accelerator mass spectrometry (AMS), liquid scintillation counting either after benzene formation, or precipitation in CO_2 cocktail.

The three methods differentiate from their detection limit that increases from AMS to CO_2 cocktail-LSC technique. AMS and benzene-LSC are well-known and successful methods used by many laboratories worldwide. Until recently, almost all quantitation of ^{14}C content was made by scintillation detection of the low energy β particle emitted in its decay, a low efficiency method as only one β particle is emitted per minute for every 5 billion ^{14}C atoms present. Only AMS has been able to achieve the specificity and sensitivity required for ^{14}C atom counting for low level activity.

3.1.1 Accelerator mass spectrometry

AMS is specifically devoted to relatively low ^{14}C levels in environmental and archaeological samples, as it measures the actual number of atoms of a certain radionuclide instead of the statistic of its radioactive decay. This technique is a particular upgrading of the conventional mass spectrometry but instead of accelerating the ions to keV energies, the ions are accelerated to MeV energies using an electrostatic tandem accelerator [TUNIZ, 1998]. In the AMS method the CO_2 is trapped in liquid nitrogen cooled trap and converted into graphite, using Fe catalyst and H_2 gas. The graphite is used as a solid target sample for a sputtering process by an external ion source such as Cs^+ ions that are focused to a small spot on the sample. The sputtered ions (with a negative charge) are extracted from the ion source and sent towards a first magnetic mass analyzer. The negative ions are then pre-accelerated and analyzed according to their isotopic mass in the injector magnet by a bending angle of 90 degrees to select the mass of interest. The mass analyzed negative ions are then directed to the tandem accelerator, consisting in two accelerator gaps with positive voltage in the middle. Passing through an electron stripper, the ions are converted in positive charged ions and they are rejected by the positive terminal causing a further acceleration step. The positively charge ions passed finally through a magnetic analyzer and they are selected according to the combination of their charge and energy. The AMS technique usually delivered a relative analysis, *i.e.*, determine the ratio between two isotopes of an element; for carbon the isotopic ratio $^{14}C/^{12}C$ is measured and the detection limit for the ratio is 10^{-15}, corresponding to a ^{14}C activity as low as 10^{-7} Bq. A typical analytical precision for AMS measurement is < 0.2 % and it is actually the highest precision techniques for ^{14}C analysis.

The wider use of AMS for many studies, however, are constrained by the size, cost and complexity of the analysis system as well as the fact that samples must contain at least 0.5 mg of total carbon.

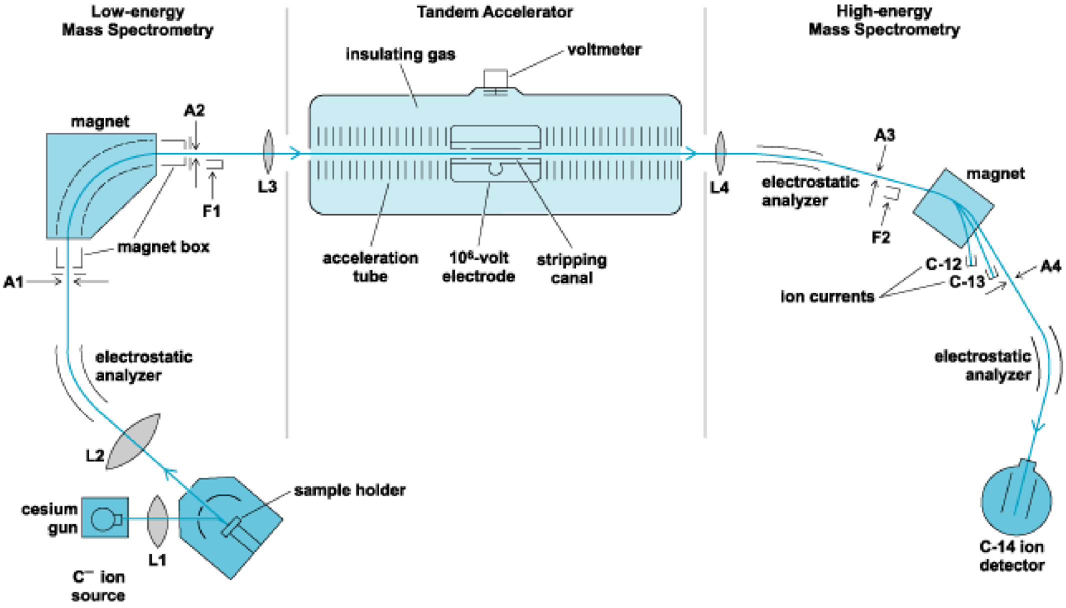

Figure 14. Schematic drawing of an accelerator mass spectrometer (AMS) used for radiocarbon dating. The equipment is divided into three sections. Electric lenses L1–L4 are used to focus the ion beams; apertures A1–A4 and charge collection cups F1 and F2 are used for setting up the equipment [McGraw-Hill, 2007].

3.1.2 Benzene-LSC

When the ^{14}C content is relatively high – as in biological and nuclear materials –, the liquid scintillation counting technique [Libby *et al.*, 1949] has been used to determine the ^{14}C concentrations [Mäkinen, 1995]. There are different LSC techniques for ^{14}C measurement. First of all the carbon content of the sample is transformed in CO_2 gas and then it is either trapped in adsorption media such as alkaline solutions (NaOH/KOH) or amines and converted respectively in carbonate $CaCO_3$ or carbamate R-NH(CO)O-R' , or directly converted in benzene C_6H_6 by a catalyzed chemical reaction.

3.1.2.1 Direct measurement in alkaline solution

In alkaline solution (NaOH/KOH), the efficiency curve can be realized and calculated with a ^{14}C standard solution and established as a function of a quench index parameter (SQPE).

The quenching curve is established by adding increasing amounts of acetone quenching agent to seven vials containing the same activity of the ^{14}C standard.

3.1.2.2 Measurement after conversion to benzene

The conversion into benzene is the most advanced techniques in LSC determination as the sample itself is transformed in a scintillation molecule, the benzene, which contains over 90 % (w/w) of carbon atoms. The sample to be measured is burned in a furnace in oxidizing conditions and, after drying, the CO_2 is transformed into lithium carbide Li_2C_2 by a chemical reaction with molten lithium metal, at 600 °C.

$$2\ ^{12}CO_2 + 4Li \rightarrow Li_2C_2 + 4Li_2O$$

The lithium carbide is then decomposed by the addition of water and transformed into acetylene C_2H_2 (see Figure 15)

$$Li_2C_2 + 2H_2O \rightarrow C_2H_2 + 2LiOH$$

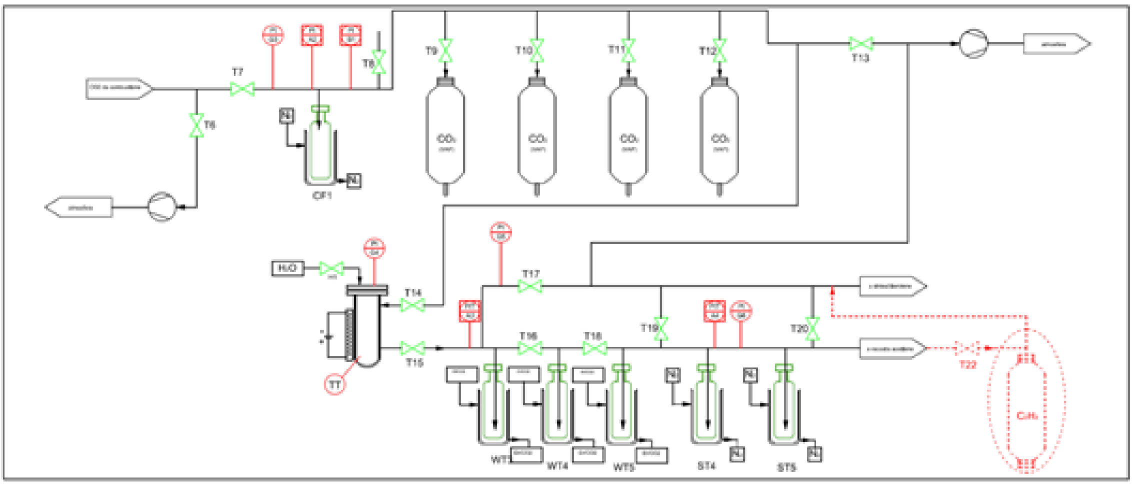

Figure 15. Schematic representation of the synthesis of acetylene at ENEA ^{14}C laboratory.

Finally the acetylene is transformed in a catalysis tube (filled by trimerization catalyst beads) into benzene C_6H_6 at 90 °C (Figure 16).

$$3C_2H_2 \rightarrow C_6H_6$$

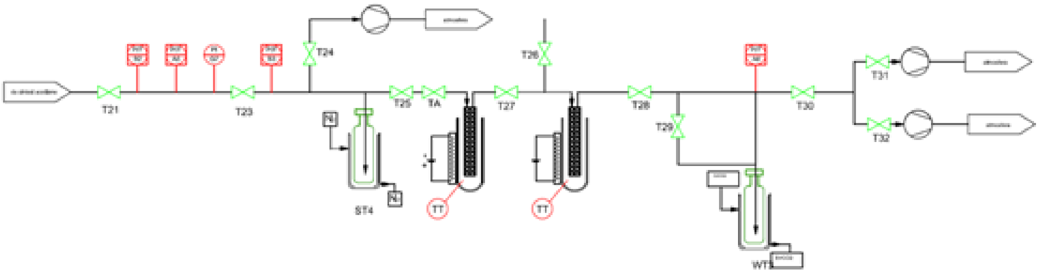

Figure 16. Schematic representation of the synthesis of benzene at ENEA ^{14}C laboratory.

The benzene sample is then mixed with scintillation cocktail, consisting in a solvent and a scintillator, which is an organic liquid that fluoresce when energized. The vial containing the benzene sample is stored for a few hours before counting in order to avoid chemi-luminescence effects that could interfere with ^{14}C spectrum especially at the lowest energies.

The measure of ^{14}C content is made by LSC equipment that analyses the β radiation emitted by ^{14}C. The β-particle from the sample will generate numerous of scintillator photons which can be detected by photomultiplier tubes (PMT), where an electrical pulse is generated. The number of generated pulses corresponds to the number of disintegrations, *i.e.*, the activity of the measured sample.

In the most advanced LSC instruments a double shielding system is implemented in order to lower the background signals and the false positive spikes.

In Figure 17 a typical detection system is represented: one for the coincidence counting and the other one in anti-coincidence mode from the first one. The use of two photomultiplier tubes and the coincidence circuit allow lowering the instrumental background down to 30 counts.min^{-1}. An active shielding is provided by a liquid scintillator surrounding the two sample PMTs; the other two PMTs being placed outside the active shielding but inside the passive one, made by an asymmetric shield of lead. The technique with benzene is very accurate, but requires a great expenditure of time and costs.

A typical ^{14}C spectrum is shown in Figure 18.

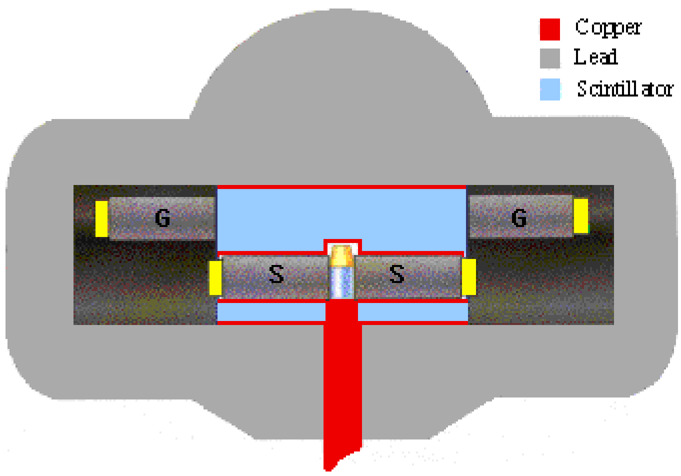

Figure 17. Internal shielding (active and passive) in a commercial LSC instrument.

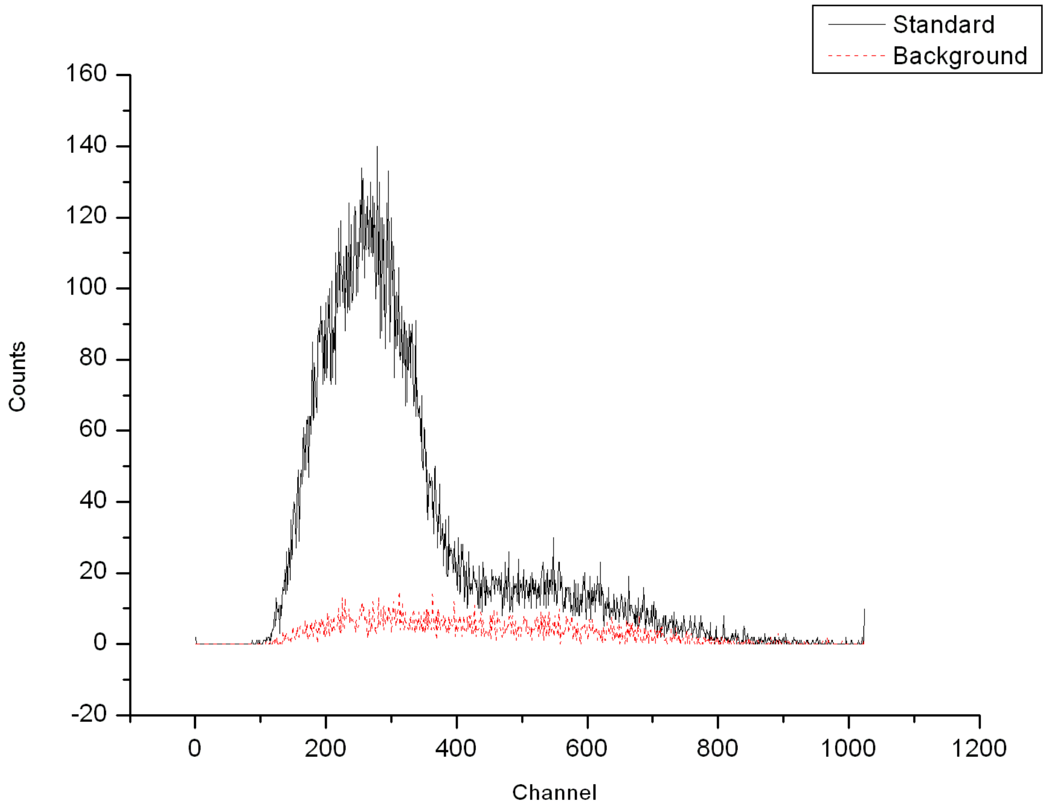

Figure 18. Typical ^{14}C spectrum obtained by standard (black curve) and background sample (red curve) [CANDUCCI *et al.*, 2013].

3.1.3 CO_2 cocktail-LSC

3.1.3.1 Direct measurement after precipitation

The third approach is based on the same basic principle of benzene-LSC method [VITA-FINZI AND LEANEY, 2006]. The main difference is that once CO_2 is produced from the sample, it is directly absorbed by a chemical/physical adsorption in specific liquid solutions. The simpler, but least accurate method is to precipitate the carbonate by fluxing CO_2 in an alkaline (NaOH/KOH trap) and adding calcium chloride $CaCl_{2.}$ The carbonate is then filtered, dried (in order to be weighted for the determination of the yield) and added by a scintillation cocktail for the LSC measurement. The most adverse problem with this technique is the self-absorption (physical quenching) and the inhomogeneity of the suspension that could affect the counting efficiency.

3.1.3.2 Measurement with a specific scintillation liquid

A more advanced method uses the CO_2-absorbing properties of a class of molecules such as the functionalized amines. Carbon dioxide is chemically trapped as a carbamate in a suitable absorbing solution, *i.e.*, 3-methoxy-propyl-amine, added of methanol – in order to avoid phase separation and occurrence of high viscosity colloidal suspension, see difference in Figure 19 and Figure 20 – and scintillator and then analyzed by LSC to determine the content of ^{14}C. Studies on the efficiency comparison of the two methods are reported in TAKAHASHI *et al.* [2014].

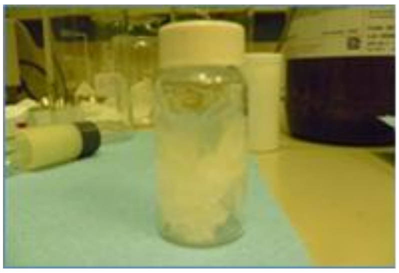

Figure 19. Formation of gel colloidal during the adsorption of CO_2 in amine without the addition of methanol.

Figure 20. Vial containing carbamate solution ready to be counted by LSC.

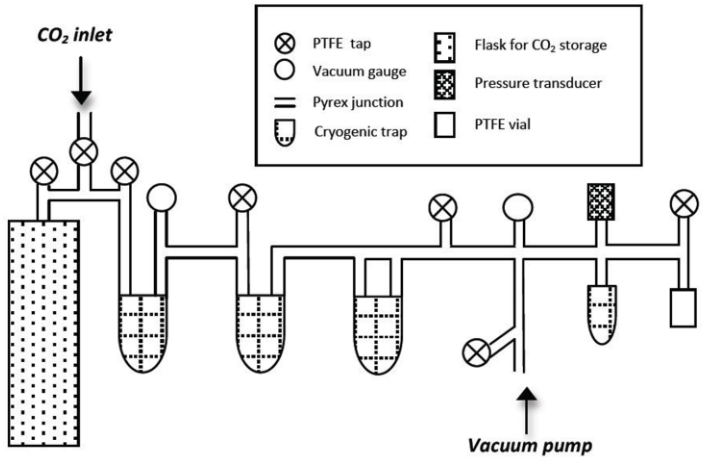

Figure 21. Equipment for the CO_2 direct absorption method at ENEA ^{14}C laboratory

3.1.4 Comparison between LSC and AMS methods

Currently, worldwide there are about 120 traditional radiocarbon laboratories that mainly use LSC, and 44 AMS laboratories. The only operator that has an industrial dimension is the Beta Analytic of Miami (USA) with an output of tens of thousands of samples per year, while all the others are research laboratories, with limited productivity.

Table 8. Principal parameters for LSC and AMS.

Parameters	**Radiometric methods (LSC)**	**Mass spectrometric method (AMS)**
Detection limit	30 mBq	10^{-4} mBq
Sensitivity	Low	Very high
Accuracy with small amount of sample	Low	Medium
Accuracy with big amount of sample	Very high	Good
Price for analysis	Low (200-800 €)	High (500-2000 €)
Equipment expenditure	Low-medium	Very high
Maintenance	Low	Very high
Equipment dimension	Small	Big
Time per analysis	Long	Short

3.1.5 Other techniques

3.1.5.1 Gas proportional counter (GPC)

Gas Proportional Counter (GPC) is historically the first technique used for the determination of the content of ^{14}C. It consists in the transformation of the carbon content sample in CO_2 (or even methane CH_4); after that the gas is led into the detection chamber, which is a gas proportional counter measuring the ionization produced by the radioactive decay of ^{14}C. The detection limit is typically about 30 mBq and the counting efficiency for ^{14}C could reach 24%. Actually it is a technique not used so frequently.

3.1.5.2 Laser spectroscopy technology

New developments in ^{14}C measurement are based on laser spectroscopy technology, and have the potential to provide a low-cost and easy-to-operate table-top experimental setup. In recent years, two new laser-based techniques have been reported: intracavity optogalvanic spectroscopy (ICOGS) [MURNICK *et al.*, 2010] and cavity ring down spectroscopy (CRDS) GALLI *et al.* [2011]. Both these techniques are based on high-resolution, ultrasensitive infrared absorption spectroscopy. The sample is oxidized to CO_2 and the isotopic species of the gas are distinguished from the shift in the infrared absorption spectra due to the difference in the mass of the carbon atoms [LABRIE AND REID, 1981].

These techniques require the use of highly stable, single-frequency lasers. Unlike AMS, the laser based measurement techniques do not destroy the CO_2 sample, so that it can be stored and used in repetitive measurements.

ICOGS is based on the optogalvanic (OG) effect. The interaction of the incident laser with atoms or molecules present in a glow discharge (plasma) induces changes in the electrical properties (impedance) of the plasma, which can be measured electrically. The measured impedance change is proportional to the number of interacting molecules, but also will depend on the plasma parameters, *e.g.*, pressure, as well as the laser intensity and gas composition in the discharge. In ICOGS, the plasma cell containing the sample, is placed inside the laser cavity [MURNICK *et al.*, 2008], where two stabilized single-frequency lasers with the active lasing media being $^{12}CO_2$ and $^{14}CO_2$, respectively, were used to perturb the plasma in the sample cell. A special $^{14}CO_2$ laser replaces the tandem accelerator of the AMS. High sensitivity was reported down to isotope ratios in the 10^{-13} range. However, the technique suffers from problems with calibration over a wide $^{14}CO_2$ concentration range. One of the main limitations of ICOGS is its non-linear calibration for concentrations higher than 1.5 ppt, as well as a large background.

GALLI *et al.* [2013] have recently reported another technique in which saturated-absorption CRD spectroscopy is used to measure the $^{14}C/^{12}C$ ratio. In CRDS, the gas sample cell is placed between two highly reflective mirrors that form a Fabry-Perot cavity. The infrared light from a laser, tuned to a specific roto-vibrational transition of CO_2, enters the cavity and will undergo multiple reflections between the cavity mirrors. The high reflectivity of the mirrors ensures that photons can make many round trips resulting in a long effective path, and consequently an ultrasensitive absorption measurement. The authors report a linear response in concentration down to 43 parts per quadrillion. However, this method requires a rather complicated laser system to obtain stable single-frequency operation at 4.5 µm. Furthermore, a relatively large sample size of about 70 mg is required, which may limit its applications.

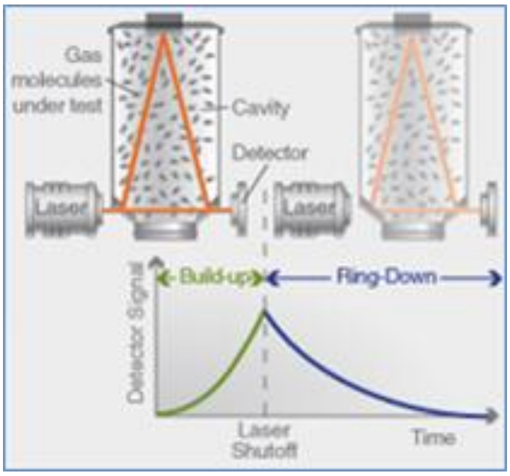

Figure 22. Basic principle of the Cavity ring-down spectroscopy

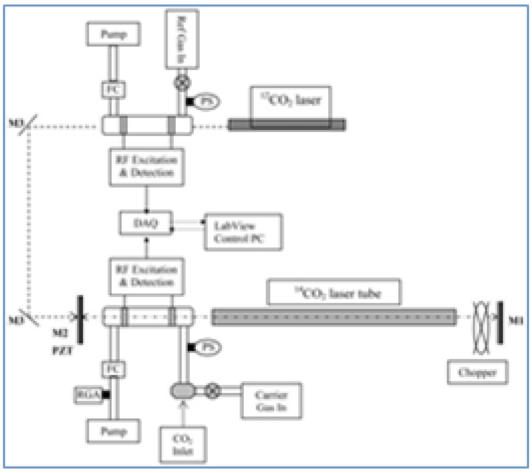

Figure 23. Scheme of the ICOGS technique

3.1.6 Comparison of total ^{14}C detection techniques

Table 9 proposes a comparison of the different techniques used to determine total ^{14}C content. If AMS is clearly the most sensitive technique, its low availability, its cost, and possibility to analyze high activity samples are clearly limiting factors.

As organic and inorganic carbon compounds are governed by different retention mechanisms during migration within the waste package, it is necessary to develop, test, and assess reliable separation procedures in order to make direct measurements of chemical forms of ^{14}C.

Table 9. Comparison of LSC, AMS, and CRDS methods.

	LSC	AMS	CRDS
^{14}C detection method	β-decay counting	^{14}C ion counting	Absorbed Photons
Sample material	CO_2, C_6H_6	C + Fe	CO_2
Measurement time (h)	~ 17	~ 1	~ 3
Preparation time (h)	8-24	~ 8	~ 4
Measurement repeatability	Same technique	Same technique	Any technique
Interferences and/or background	Cosmic rays	^{14}N, ^{13}CH, $^{12}CH_2$	$^{13}C^{16}O_2$ (T > 170 K) N_2O (> 0.3 ppb) O_3 (> 10 ppm)
Precision for modern	~ 0.5	~ 0.3	~ 2
Limiting factor	Poisson statistics	Poisson statistics	α_{min}
Footprint (m^2) (sample preparation excluded)	~ 1	~ 7-200	~ 2
Cost (k€)	~ 120	~ 500-3000	~ 300

3.2 *Inorganic Carbon (CO_2-carbonate ions)*

A great variety of carbon compounds is expected to be found in the SIERs, among them carbonates, organic acids, aldehydes, etc. [I.A.E.A., 2004]. Inorganic carbon is mainly composed of CO_2 and carbonate ions. The following section presents the techniques that have been used to analyse inorganic carbon.

3.2.1 Acid stripping

Acid stripping consists in promoting an acid-alkaline reaction between an added acid solution and the carbonate adsorbed in the SIER. It extracts mainly the inorganic fraction. A schematic of a typical experimental setup is outlined in the Figure 24 [AITTOLA AND OLSSON, 1980]. Concentrated HCl is added to the resin sample in order to evolve carbon dioxide, which was carried by streaming air to the NaOH flasks, where it was absorbed as soluble Na_2CO_3. A further flask containing $Ca(OH)_2$ could be used in order to check the presence of unabsorbed CO_2. The Na_2CO_3 salt is then transformed in solid $BaCO_3$ by the addition of $BaCl_2$ and cleaned and solved for LSC analysis. The recovery yield is around 40%, it decreases to <35% if amine is used instead of NaOH and it could be raised to 85% if the process is temperature assisted (50-70° C).

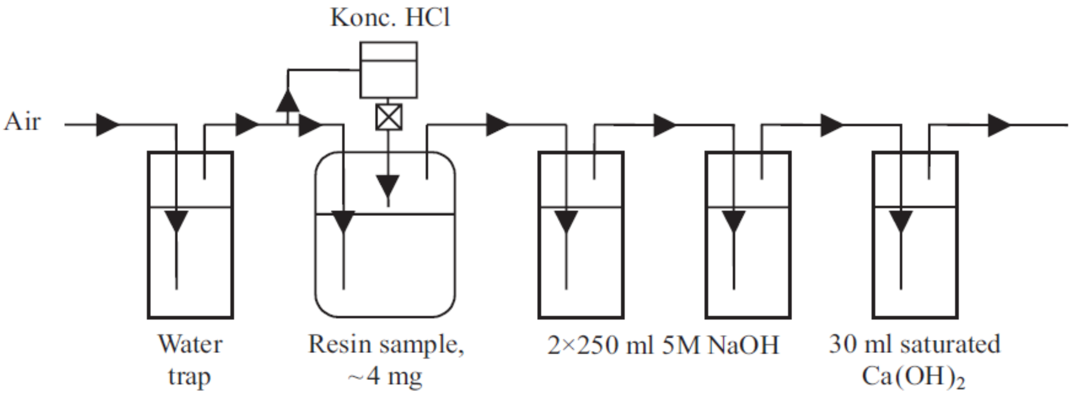

Figure 24. Schematic representation of an acid stripping system [AITTOLA AND OLSSON, 1980].

An alternative methods was developed by NOTT [1982], consisting in a stripping column with an ultrasonic mixing probe and an acid circulation pumping system. The system was kept under slight vacuum to prevent $^{14}CO_2$ leakage. The mean recovery yield is around 97%.

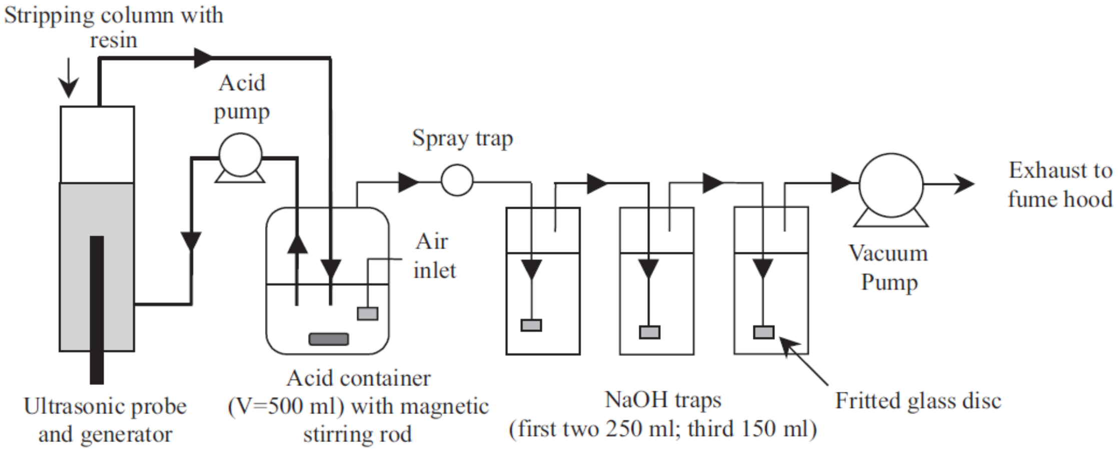

Figure 25. Schematic representation of an acid stripping system with acid circulation pumping [NOTT, 1982].

Recoveries near to 99% were obtained by agitating the resins in aerated acid solution, combining air bubbling and mechanical agitation [CHANG *et al.*, 1989].

3.2.2 Combustion methods

The combustion method uses high temperatures (600- 700°C) in oxidizing atmosphere in order to convert the carbon content in CO_2. In this method it's difficult to separate the inorganic and organic fraction. At the end of the combustion, small amount of acid could be added in order to assure release of any residual carbonate [MARTIN *et al.*, 1993]. This process usually need an additional oxidizing step (by catalytic furnace) in order to convert CO in CO_2. Recovery yield was found to be 63%.

Other method consists in the Parr bomb, where the samples is inserted in a pressurized vessel with oxygen (2.5 MPa) and let it combusted [MOIR *et al.*, 1994]. The gaseous products are released using a carrier gas (N_2) and then trapped in NaOH solution for LSC determination (recovery 100%).

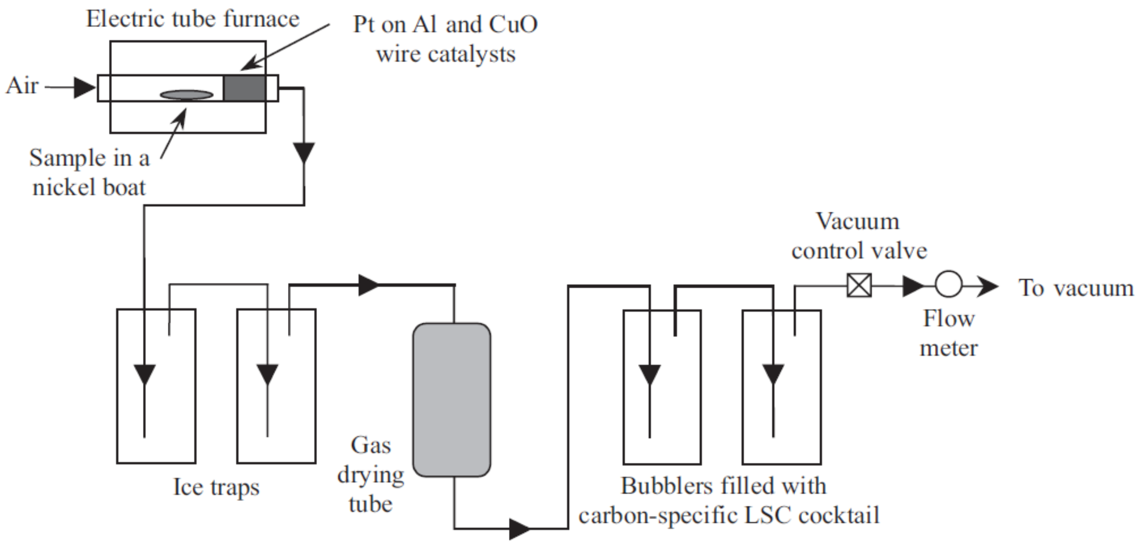

Figure 26. Schematic of a typical combustion method [MARTIN *et al.*, 1993]

A slight modification of the combustion process can be achieved by heating the sample in oxygen flux at higher temperature (1200°C) with PbO_2 as catalyst.

The following scheme was adopted by SPERANZINI AND BUCKLEY [1981] in order to release ^{14}C at lower temperature (*ca.* 500°C), which is the decomposition temperature for the resins. With this system it was possible to observe that the carbonate forms contained in the ionic resins are not thermally stable as they start to decompose at 440°C, *i.e.* well below their decomposition temperature (900° C for $CaCO_3$, 1430°C for $BaCO_3$). This mechanism could be due to the presence of sulfonic groups in the ionic resins that start to decompose at 300°C to produce SO_2 that reacts with carbonate to release CO_2:

$$CaCO_3 + SO_2 + \frac{1}{2} O_2 \rightarrow CaSO_4 + CO_2$$

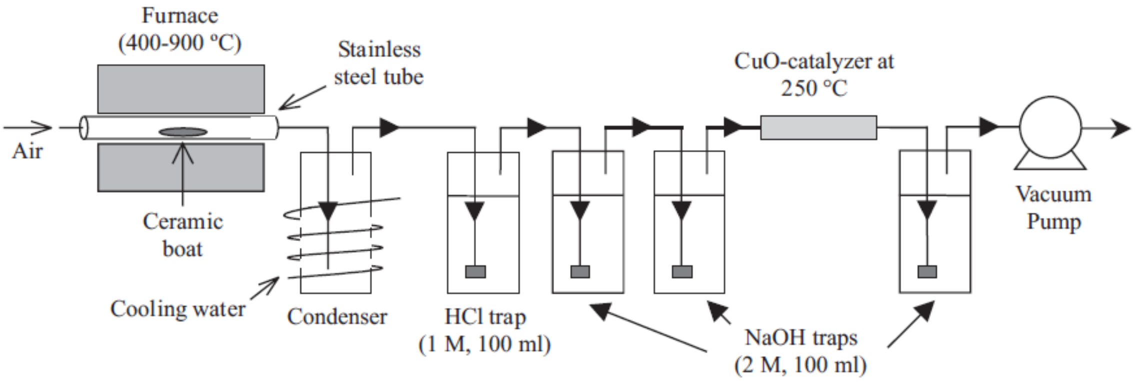

Figure 27. Combustion scheme used by SPERANZINI AND BUCKLEY [1981].

3.2.3 Resin regeneration technique

A typical method for the regeneration of ionic resins (acid/base washing) has been also used as a protocol to replace the adsorbed inorganic carbon compounds, with recovery around 85% [MARTIN *et al.*, 1993].

3.3 *Organic Carbon*

In the past, the ^{14}C organic fraction was estimated by subtraction, after determination of the total ^{14}C content and the inorganic fraction one, but this method inevitably lead to uncertainties. A direct measurement of both fractions can be achieved only providing that the separation of the chemical form is performed efficiently.

As the ion exchange resin is a very resistant organic material, it is possible to extract the inorganic fraction with the methods above described and then to destroy organic material by using several oxidative treatment procedures.

3.3.1 Acid stripping combined with catalytic oxidation

One method accomplishes the separation of the different chemical forms by using two absorbers with a catalyst (CuO at 800°C) in between. With this arrangement CO_2 was absorbed in the first absorber, whereas hydrocarbons and CO passed it, then they were oxidized in the catalyst and absorbed in the second absorber. After completing the collection, the absorbed CO_2 was precipitated as $BaCO_3$, which was filtered, washed, dried, weighed, and measured by LSC.

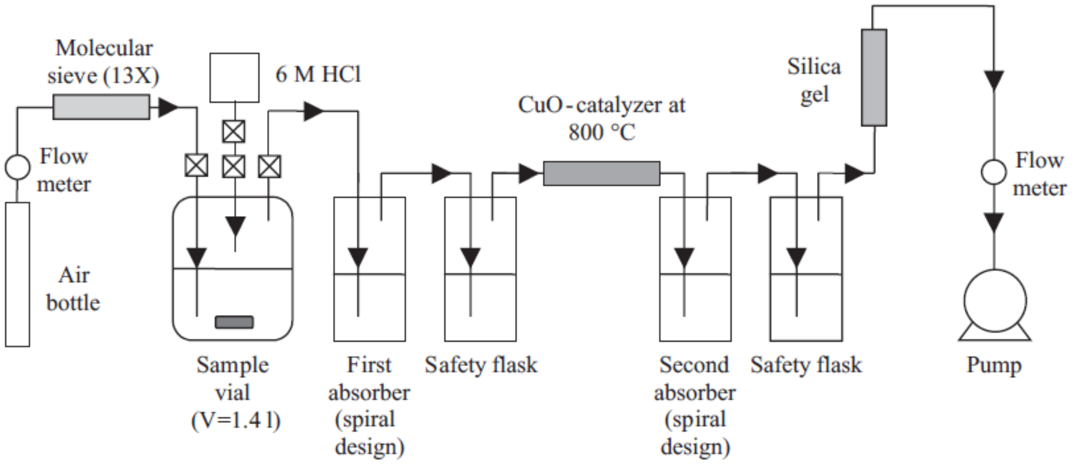

Figure 28. Schematic representation of a two steps absorption process [Salonen and Snellman, 1981].

3.3.2 Wet oxidation

This process relies on the reaction occurring in the presence of water into which an oxidant, (usually a gas) is dissolved. At higher temperatures the process is run under pressure to ensure that the gas remains dissolved and this also improves the solubility of waste breakdown products. Higher temperatures have the capability to destroy the most resistant carbonaceous material. There are three main types of wet oxidation processes, based on temperature : Cold Wet Oxidation, High Temperature Oxidation and Super-Critical Thermal Oxidation.

3.3.2.1 Cold wet oxidation

An example of cold wet oxidation is in Figure 29. 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 [MAGNUSSON *et al.*, 2008]. A catalytic furnace, located between the two sets of washing bottles, ensures oxidation of reduced compounds. The carrier gas is nitrogen so the catalytic furnace should have good performance in oxidizing carbon compounds using the oxygen coming from the chemical wet oxidation. 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% [MAGNUSSON *et al.*, 2008].

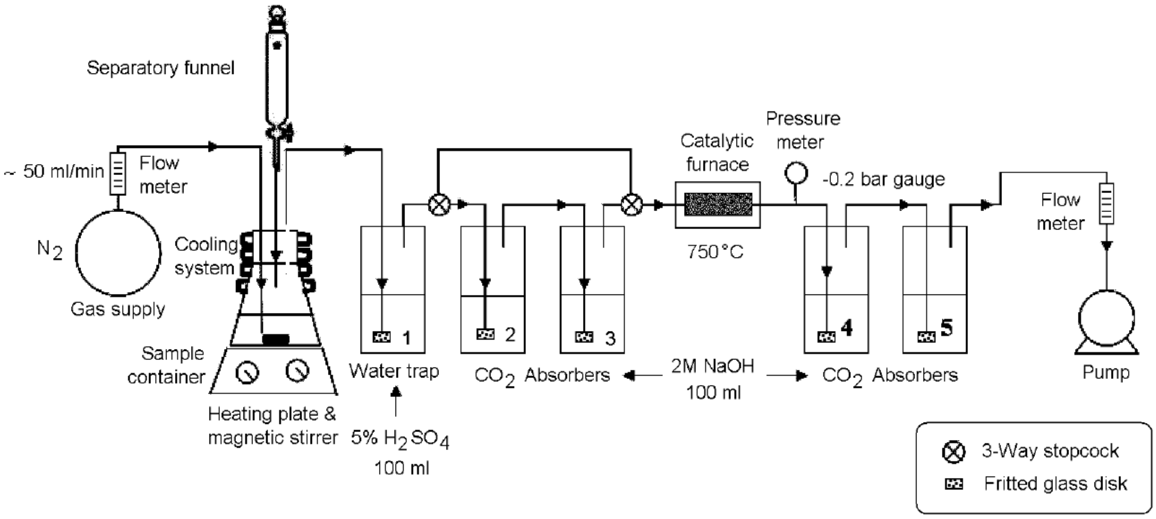

Figure 29. Schematic representation of double step separation equipment [MAGNUSSON *et al.*, 2008].

3.3.2.2 High temperature oxidation

This process also uses soluble oxidants such as hydrogen peroxide, a catalyst and a range of inorganic oxidants such as nitric acid, permanganate and dichromate ions at elevated temperatures. It is a process conducted at temperatures above 100°C in an autoclave to allow batch processing. More resilient materials can be treated in such a way.

3.3.2.3 Super-critical thermal oxidation

Super-Critical Thermal Oxidation (SCWO) technology uses the beneficial characteristics of supercritical fluids such as high solubility, fast mass and heat transfer, low viscosity, high diffusion coefficient, and low surface tension. Super-critical water (T_c = 374°C, P_c = 22.1 MPa) is completely miscible with oxygen and most of organic materials so thanks to high mass transfer rate in super-critical water, it is possible to decompose organic materials, as IERs in a short residence time [RHU *et al.*, 2003].

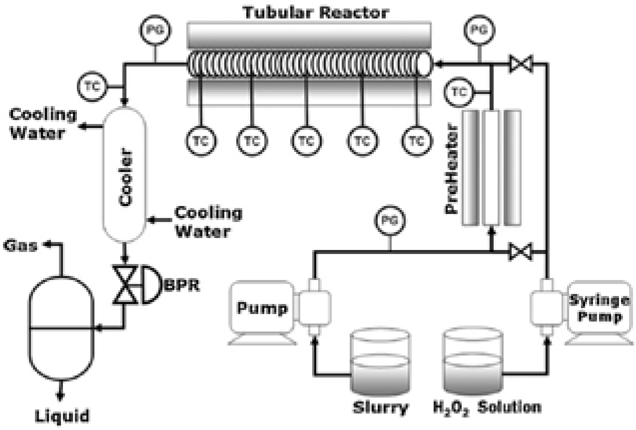

Figure 30. Schematic representation of a Super-Critical Thermal Oxidation system [RHU *et al.*, 2003]**.**

3.3.3 Pyrolysis

Pyrolysis (thermal decomposition) requires a reducing atmosphere maintained by restricting air supply to less than stoichiometric levels. The pyrolysis of organic materials causes thermal degradation to occur and a distillation of the volatile fraction, forming combustible liquids and vapours. These vapours are composed mostly of methane, hydrogen, carbon monoxide, water and hydrocarbons such as ethane, propane, oils and tars. This is an endothermic process, which requires a constant source of heat to maintain temperature. Usually, the heat is generated in local burning of the feed material.

The initial part of the process does not require an oxidant, but is performed in the presence of an inert gas without the need for a flame. The process operates at a reduced pressure to ensure the removal of the volatiles. Adding oxygen in the second step of the process oxidises the char left behind. The initial products can be combustible hydrocarbons such as methane or aromatics. CO_2 is only produced if there is a sufficient amount of oxygenated compounds in the waste.

The recovery of the distinct fractions pyrolyzed at different temperatures and with increasing oxidising gases content could lead to the separation of three different fractions: volatile, high boiling organic and inorganic compounds.

3.4 *Speciation*

A large part of the data is on the distribution between organic and inorganic forms, without direct speciation of the organic molecules.

3.4.1 Total ^{14}C, and distribution between mineral and organic forms

The study of the distribution of inorganic and organic forms is typically carried out by acidic dissolution of the IER.

For instance in CEA, about 0.2 - 0.5 g of wet ion exchange resins is introduced into a little quartz vessel mixed with a “Stable Carbon” carrier. Mineralization is carried out under O_2 pressure in a closed system (Parr bomb, IKA AOD 1). The combustion of the ions exchange resin produced CO_2, which is trapped in sodium hydroxide solution as carbonate. 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.

^{14}C present in the KOH/NaOH solutions is oxidized to CO_2 by adding acidic solutions and trapped in three washing bottles that contain ^{14}C-liquid scintillation cocktail. Parameters (Volume of sample / LSC-cocktail…) will be studied also in function of the ^{14}C activity level.

The study of the distribution of inorganic and organic forms will be carried out by acidic dissolution of the ion exchange resin. A first step consists in introducing the sample in a glass reactor and mixing it with acidic solutions to provide the degasing of CO_2 and to catch the 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 will be performed by a hot acidic dissolution with oxidant reagent (H_2SO_4/HNO_3). At the end of this step, additional H_2O_2 solution can be used to accelerate/finish the dissolution.

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

3.4.2 Ion chromatography

One of the most convenient methods that permit attaining the speciation of small organic molecules in aqueous solution is ion chromatography. CEA has already developed a protocol for the detection of carboxylic acids from C_1 to C_5 in solution [LEGAND *et al.*, 2014], that can be adapted to alkaline solutions. An example of a real sample chromatogram in NaOH solution and the ion chromatography (IC) in glove box are presented in Figure 31.

As the CEA IC set-up is equipped with a conductimetric detector, which means that total carboxylic acids (^{12}C and ^{14}C) will be detected. A new scintillator counter will be added in 2015.

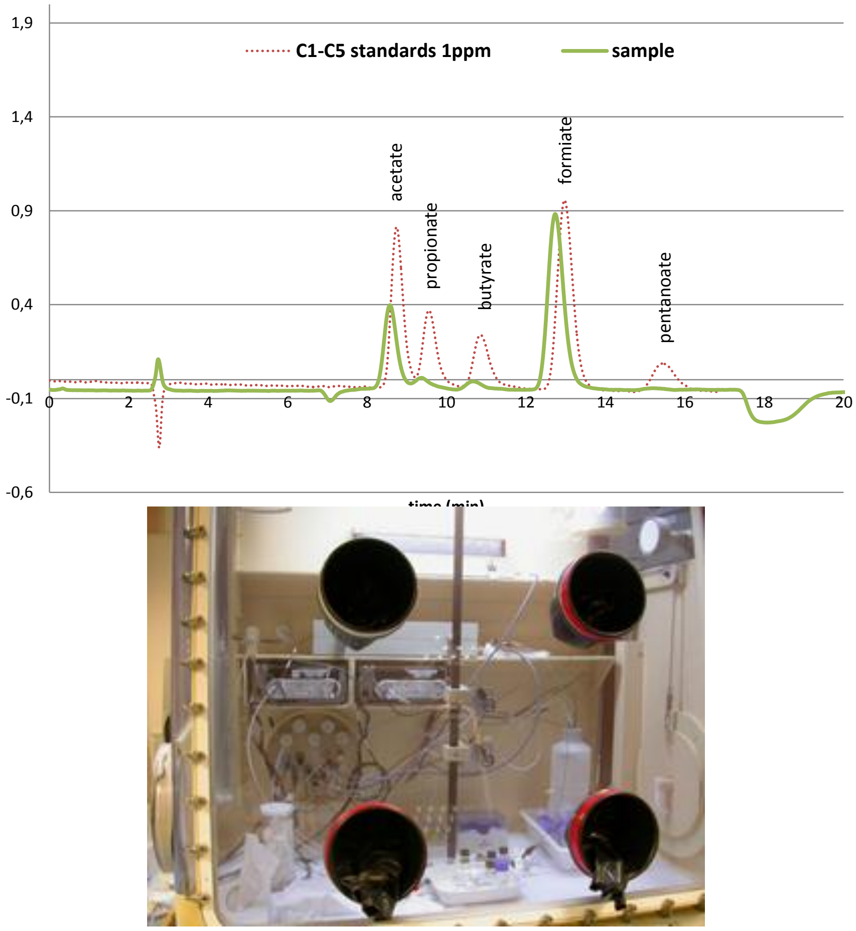

Figure 31. Example of a chromatogram obtained in cementitious conditions (a), and photograph of the ion chromatography set-up in glove box (CEA).

3.4.3 Gas chromatography

Identification of low volatile molecules could be done by gas-chromatography coupled with mass spectrometry (GC/MS, Figure 32). Different capillary columns with different polarities can be used to increase of number of identified molecules.

Ion source used in CEA for mass spectrometry detector is an electronic impact. The analytical conditions are standard conditions in order to be able to used mass spectra library for molecules identification.

Figure 32. Gas chromatography-coupled with mass spectrometry in CEA laboratory.

To increase the number of identified molecules, selective extraction of molecules families can be realized before GC/MS analysis. For this, after the evaporation process, the sample can be solubilized in different solvent, *e.g.*, polar solvent for extraction of more polar molecules or hexane for extraction of non-polar molecules.

When molecules or families of molecules of interest are detected, semi-quantification can be realized under the same analytical conditions by gas chromatography but here, coupled with flame ionization detector (FID). The semi-quantification can be realized with internal or external standards if chromatograms are too complex. Thus, gas chromatography analysis will help for molecule identification after coupling with mass spectrometry and for quantification after coupling with FID.

3.4.4 Electrospray-mass spectrometry analysis

Electrospray ionization mass spectrometry (ESI-MS, Figure 33) technique can be used for the detection of molecules with molecular weight higher than some hundreds of g.mol^{-1}. This soft ionization technique allows detecting intact polar molecules [PLANCQUE *et al.*, 2001]. Like for gas chromatography technique, different solvent can be used for selective extraction of molecules in different solvents. Electrospray technique can help identifying molecules in solution. For molecules with molecular weight lower than 1000 g.mol^{-1}, the resolution on the mass spectrum can be sufficient to obtain a good resolution on mass spectra and allow determining the $^{12}C/^{14}C$ ratio. The detection of molecules marked with ^{14}C can also be realized. However, the concentration of ^{14}C has to be quite high and different tests for limit of detection on standard and ^{14}C-labelled molecules have to be realized beforehand.

Figure 33. Electrospray-Mass spectrometry set-up available in CEA.

3.4.5 High performance liquid chromatography

The identification and quantification of small organic molecules in solution can be performed *via* high performance liquid chromatography (HPLC). The equipment in FZJ is furnished with an UV detector, a Refractive Index detector (RID), and a Scintillation Counter. The analytical method, with the relative parameters, needs to be optimized. Two methods of detection/quantification are possible:

1) direct speciation through calibration of the method with standards;

2) separation and concentration of the interesting fractions of the solution under investigation, *e.g.*, in correspondence of the hypothesized peaks (small organic

acids). Successive mass spectrometric analyses and/or capillary electrophoresis could be performed on the separated/concentrated solution fractions to further lower the detection limit or to confirm what has been directly measured with the HPLC.

A combination of ion exchange, HPLC and mass spectrometry has been proposed in TAKAHASHI *et al.* [2014] as improved identification method: the use of ion exchange resins, prior to analyse the solution with an HPLC, allows fractionating the solution into anion and neutral species, leading to the identification of the species with a mass spectrometer. Additionally, nuclear magnetic resonance has been proposed for the chemical speciation of the organic compounds.

In case of very low activities/concentrations in solution, HPLC-AMS could represent a suitable method for separation, concentration and speciation of small organic molecules [VAN HEES *et al.*, 1999; BUCHHOLZ *et al.*, 2000].

3.4.6 Fourier-Transform Infrared Spectroscopy (FTIR) and Raman Spectroscopy

The vibrational information obtained from a molecule could help to identify the speciation of carbon-containing species (included ^{14}C) directly on the (S-)IERs or released in solution. However, the typical structure of a DVB-based IER is quite complex; in addition, imperfections – *e.g.*, due to radiation damage – in the styrene chains and/or DVB could lead to spectra, whose interpretation could not be trivial. However, with a systematic approach, starting from database information, testing fresh-unused resins, going through resins loaded with target molecules, considering possibly the radiation damages and investigating at last the real waste, the speciation of ^{14}C on the SIERs could be also performed directly. FTIR (Figure 34) is not able to distinguish different isotopes, but it would provide some information on the chemical form of the retained species, measured directly on the resins; in addition, measurements of species released in solution can be performed.

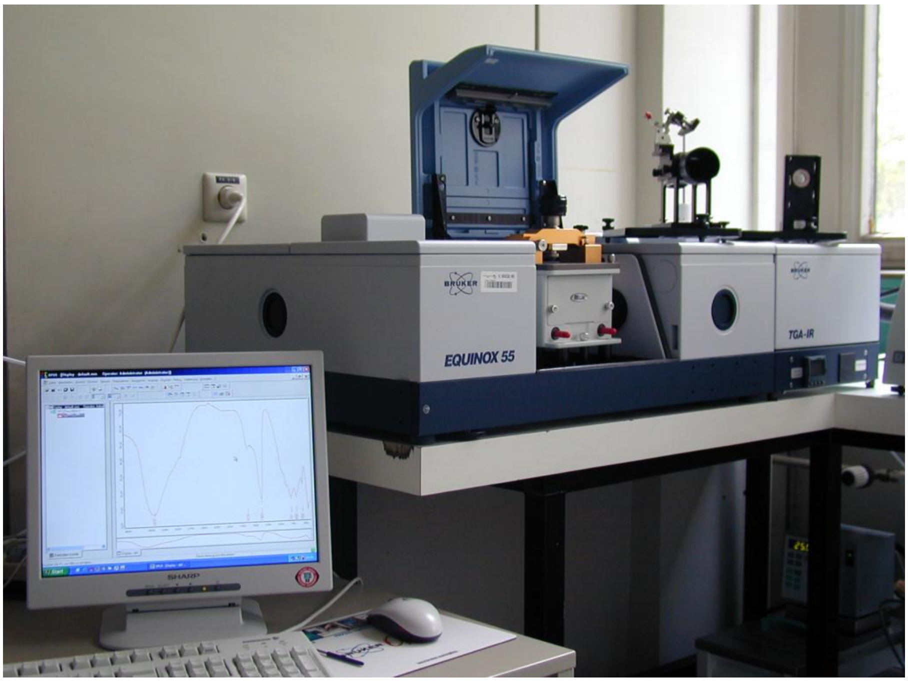

Figure 34: FTIR Spectrometer coupled with a TGA, available in FZJ.

3.4.7 X-Ray Photoelectron Spectroscopy

A surface-sensitive technique like XPS could provide additional/complementary information to the ones obtained by vibrational spectroscopy, with a local identification and quantification of the different species retained in (S-)IERs. However, in FZJ such an analysis can be performed only on inactive samples or specimens with activities below the clearance level. Techniques like FTIR and XPS have been used for investigating the interactions of metal ions with IERs by CHEN *et al.* [2012].

4 Release from SIERs

Most of the ^{14}C determinations deal with the maximum activity determination, percentage of recovery and differentiation between organic and inorganic fractions [PARK *et al.*, 2006; MAGNUSSON *et al.*, 2008]. Several authors studied the acidic release of $H^{14}CO_3^-$ from inactive IERs – which implied the hypothesis that inorganic ^{14}C is adsorbed on the resins – , for subsequent gasification. However, this does not bring any information about the actual speciation of ^{14}C in the SIERs [NOTT, 1982; YANG *et al.*, 2010].

4.1 *Speciation of ^{14}C Released in Solution*

There is only scarce information about the speciation of ^{14}C originated from SIERs. Most of the information is related to the repartition between inorganic (carbonate) and organic fractions [MAGNUSSON AND STENSTRÖM, 2005; PARK *et al.*, 2008; VAITKEVIČIENE *et al.*, 2013].

Results from MAGNUSSON AND STENSTRÖM [2005] and PARK *et al.* [2008] results seem to show that the majority of the ^{14}C activity comes from the inorganic part. Particularly, in CANDU reactors, the major part is retained in anionic resins under 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].

Results on the repartition of inorganic and organic molecules are contrasted. For SIERs from PWRs, if MAGNUSSON AND STENSTRÖM [2005] showed that around 20% was under the form of organic molecules (Figure 35a), PARK *et al.* [2008] obtained from 0 to 20% for CANDU PWRs (Figure 35b).

More recently, VAITKEVIČIENE *et al.* [2013] estimated the inorganic *vs.* organic repartition in two actual cemented SIERs using the same experimental protocol validated on ^{14}C-doped inactive IERs is giving an almost equal repartition (48/52) of the inorganic *vs.* organic compartments for the first sample, and slightly more inorganic than organic (59/41) for the second sample. These data on RMBK graphite-moderated BWRs may not be directly compared with other BWRs situation.

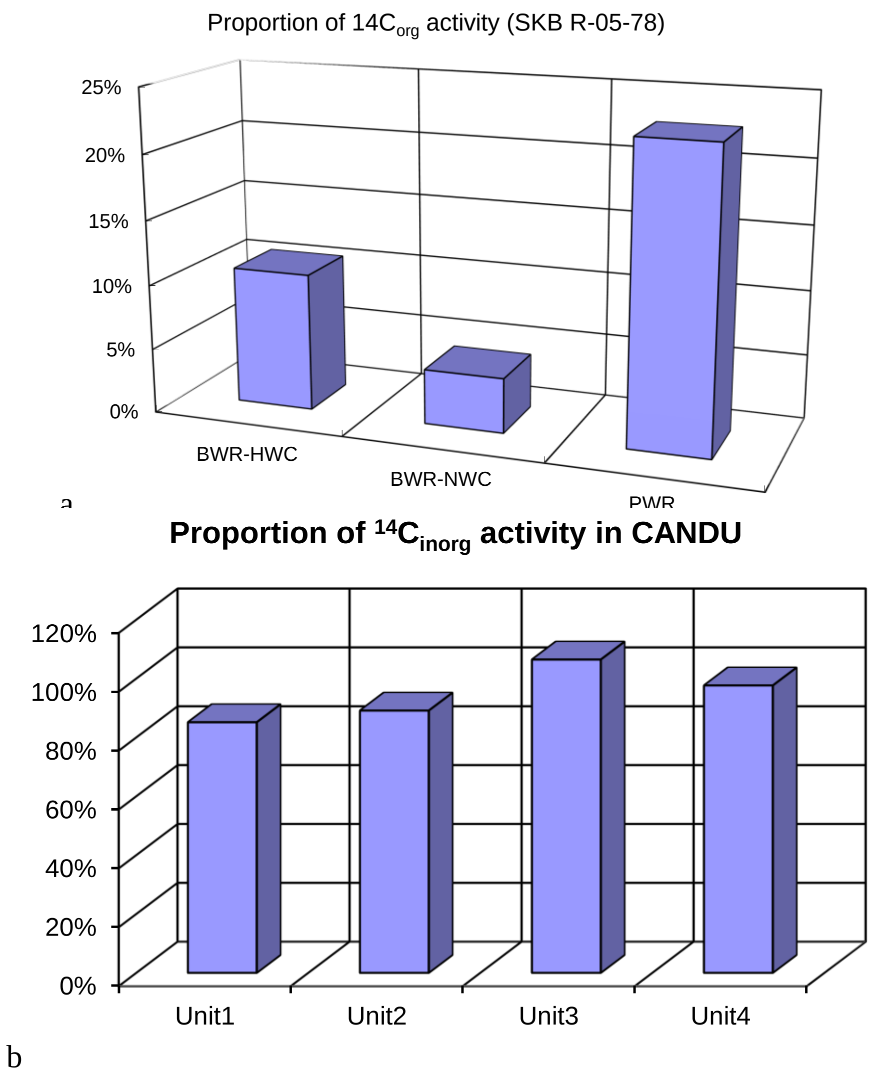

Figure 35. Proportion of the ^{14}C activity contained in (a) the organic fraction of the SIERs in PWRs [aggregated from the data in MAGNUSSON AND STENSTRÖM, 2005], (b) the inorganic fraction of the SIERs from CANDU PWRs [PARK *et al.*, 2008].

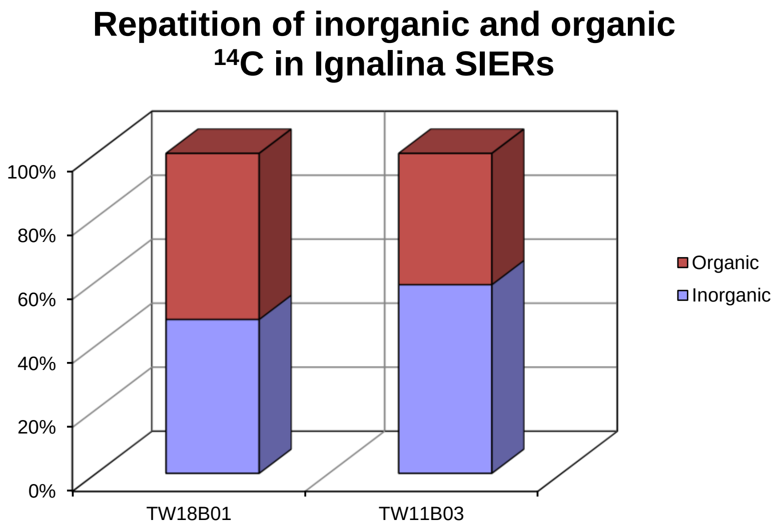

Figure 36. Repartition between organic and inorganic fraction of ^{14}C in SIERs from RMBK [VAITKEVIČIENE *et al.*, 2013]

At the present state, no determination of organic molecules in SIERs leachates has been published. However, the detection/separation of organic molecules has been reported by TAKAHASHI *et al.* [2014], in particular in leachates from graphite, zirconium alloys and stainless steel. In a first step, organic and inorganic fractions were measured, both in gas and liquid phase. More in detail, the liquid phase was investigated with HPLC+LSC, but this method, in some cases, did not provide sufficient information to identify the organic compounds. The speciation of organic ^{14}C in solution showed to be dependent on the material used, with releases from few percent up to 100%. The chemical species could not be identified by direct comparison of the retention values with the considered standards: formate, acetate, formaldehyde, methanol, and ethanol. MAGNUSSON [2007] hypothesized acetate and formate as possible organic speciation of ^{14}C, since they are expected in the reactor coolant of PWRs and BWRs. However, no direct measurements were reported. In addition, the conditions of the water going through the resins in MAGNUSSON [2007] are different than the reference ones – *e.g.*, 300°C and 72 bar for BWRs compared to near-ambient conditions –, leading to different redox potential and, accordingly, different speciation – see § 3 for more details. Finally, the storage conditions are expected to affect the ^{14}C amount and speciation on/released by the SIERs, depending on *e.g.*, pH, temperature, microbial activity, radiolysis – see § 4.2 for more details.

4.2 Speciation of ^{14}C in Gaseous Releases

No literature reporting ^{14}C released from SIERs in the gas phase was found.

In general, inorganic releases in the gas phase are expected to be in form of $^{14}CO_2$, whenever any factor will affect the bicarbonate-loaded resin or the acid-base equilibria in the solution, releasing at first bicarbonate that will lead to forming $^{14}CO_2$(g) [YIM AND CARON, 2006]. MAGNUSSON [2007] addressed CH_4(g), and more in general volatile organic carbon, released by liquid waste, but no data was reported on the actual speciation. In the gas phase one can expect to measure organic radiocarbon, coming directly from the degradation (of different nature) of the resin or either from secondary reactions due to the concomitant presence of H_2 and other gases (see § 4.3).

Releases in the gas phase could be investigated following three approaches:

i. direct measurement and speciation;

ii. application of ultra-sensitive techniques;

iii. concentration techniques.

The total ^{14}C released in the gas phase must be quantified, in relation to the boundary conditions – *e.g.* temperature, dry/wet storage, pH, *etc*. In the case of a detectable amount with radiometric methods (Scintillation Counter), approach i.) can be applied and a direct speciation of ^{14}C in the gas phase could be performed through radio-gas chromatography (R-GC) / radio-gas chromatography coupled with mass spectrometry (R-GC-MS), as reported in § 3.4.3. In the cases where the ^{14}C activity will be below the detection limit, the species determination is not possible, at least with a direct method. Ultra-sensitive mass spectrometric and/or vibrational techniques, *e.g.*, AMS (see § 3.1.1), ICOGS and CRDS (see § 3.1.5) could represent a solution. The latter option iii.) consists on applying/developing concentration techniques, based *e.g.*, upon distillation, molecular sieves and pressure/temperature swing adsorption (PSA/TSA).

4.3 Factors influencing the release of Radiocarbon from SIERs

In general, any disturbance of the acid-base equilibrium of the solution in contact with the resins will result, directly or indirectly, in a release of ^{14}C. This includes the increased CO_2 partial pressure, which will shift the acid-base equilibria of the solution, affecting indirectly the resin through an isotope exchange process [YIM AND CARON, 2006]; an example of this case is represented by the exposure to the atmosphere. Also the ingress of foreign anions with selectivity higher than the one of HCO_3^-, as *e.g.*, chloride, nitrate, or hydrogenosulphate anions; this case could be also accounted for the mixed bed case, where anionic and cationic resins are used and then stored together.

Other less known effects leading to ^{14}C release from SIERs as the effects of service/storage temperatures and strong oxidants (thermal and chemical degradation), that could affect resin equilibrium and capacity. The bacterial growth, which could convert some inorganic ^{14}C into organic form or produce anions that will displace the ^{14}C from the resins [MOIR *et al.*, 1994; YIM AND CARON, 2006]; however, high alkaline media (pH > 12) are not favourable for microorganisms. In case of samples coming from a wet storage, a BART (Biological Activity Reaction Test) analysis could reveal the presence of microbes, indication that a prior release could have already taken place [MOIR *et al.*, 1994].

Radiolysis could represent an important variable affecting the release and even the speciation of the released radionuclides [YIM AND CARON, 2006]. IERs are in most of the cases DVB-based resins, *i.e.*, they are particularly sensitive to radiation damage during and even after operation, compared to other materials like inorganic IERs or cement. Most of the γ-emitters are found in the cation exchange resins. PARK *et al.* [2008] reported more than 80% of the total γ-activity in the cation fraction. IERs are often used in mixed bed – cationic and anionic form –, so the ^{14}C, mainly present in the anionic fraction, is sometimes in contact with high γ-activities: a correlation between ^{14}C releases and γ-emitters in SIERs could clarify this point. Effects on the radionuclides speciation due to the degradation of mixed bed IERs were reported by VAN LOON AND HUMMEL [1999b]. TRABOULSI *et al.* [2013] reported releases of trimethylamine (TMA), $H_2(g)$ and $CO_2(g)$ from anion exchange resins (SBA type I) due to γ-irradiation. A distinction between anaerobic and aerobic conditions was made: $CO_2(g)$ was detected only in the presence of oxygen. Other gases such as methane and ethane were detected in very small quantities in all the cases. In the presence of liquid water, TMA(aq) was associated with dimethyamine (DMA(aq)), monomethyl-amine (MMA(aq)) and ammonia. Similar results were reported by VAN LOON AND HUMMEL [1999b]. $CO_2(g)$ was detected under oxidizing conditions, mainly due to the oxidation of the degradation products such as TMA(g) [TRABOULSI *et al.*, 2013]. BAIDAK AND LAVERNE [2010] showed that the yield of $H_2(g)$ is strictly dependent on the water content, on the presence of various electron scavengers – *e.g.*, NO_3^-, O_2, N_2O – and on the ionic form of the resins, *e.g.*, Cl^-, OH^-. Studies on radiolytic and chemical degradation of strong acidic IERs reported by VAN LOON AND HUMMEL [1999a], underlined the formation of mainly sulphate and dissolved organic carbon in solution. Among these, only oxalate was identified, constituting 10-20% of the organic fraction. Other degradation products were CO_2 and H_2. Chemical degradation of IERs revealed to be very limited compared to the radiolytic effect, in a similar time scale. The mixture of anion and cation exchange resins, subjected to γ-radiation, revealed the formation of other degradation products compared to the single-bed resin [VAN LOON AND HUMMEL, 1999b].

5 Conclusions

In this document, the reasons of the choice of the SIERs samples that will be used in the WP4 of CAST are presented. The major part of the SIERs samples are from PWR NPP from different technologies.

Most of the existing ^{14}C determinations for SIERs deal with the maximum activity determination, percentage of recovery and differentiation between organic and inorganic fractions. Several authors have studied the acidic release of $H^{14}CO_3^-$ from inactive IERs – which implied the hypothesis that inorganic ^{14}C is adsorbed on the resins – for subsequent gasification. However, this does not bring any information about the actual speciation of ^{14}C in the SIERs.

There is only scarce information about the speciation of ^{14}C originated from SIERs. Most of the information is related to the partition between inorganic (carbonate) and organic fractions. Available results seem to show that the majority of the ^{14}C activity comes from the inorganic part. In particular, for CANDU reactors, the major part is retained in anionic exchange resins in an inorganic form. A minor fraction of ^{14}C-containing species were found in cation-exchange resins, after their separation from a mixed bed, and were probably in the form of metal carbonates. However, results on the partition of inorganic and organic molecules are contrasting. For SIERs from PWRs, around 20% was in the form of organic molecules but only an average of 5% for SIERs from CANDU reactors was found. More recently, the inorganic *vs.* organic partition in two actual cemented SIERs from RMBK graphite-moderated BWRs has been measured. An almost equal partition (48/52) of inorganic *vs.* organic 14C was found for the first sample and slightly more inorganic than organic (59/41) 14C was found in the second sample. These data may not be directly compared with other BWRs.

At present no determination of organic molecules in leachates from SIERs has been published. It has been hypothesized that acetate and formate are the possible organic forms of ^{14}C since they are expected in the reactor coolant of PWRs and BWRs. However, no direct measurements have been reported. In addition, the conditions of the coolant water going through the resins, e.g. 300°C and 72 bar for BWRs, are different from near-ambient conditions and lead to different redox potentials and, accordingly, potentially different speciation. Finally, the storage conditions for the SIERs are expected to affect the amount of ^{14}C released and its speciation depending on, for example, pH, temperature, microbial activity and radiolysis.

No published investigations on the release of gaseous ^{14}C from SIERs have been found. In general, inorganic releases in the gas phase are expected to be in form of $^{14}CO_2$. When a factor affecting the bicarbonate-loaded resin or the acid-base equilibria in the solution occurs bicarbonate will be released leading to the formation of $^{14}CO_{2(g)}$. However, ^{14}CO cannot be excluded at present and $^{14}CH_{4(g)}$ and, more generally, volatile organic ^{14}C-species could be released. In the gas phase one could expect to measure organic radiocarbon, coming directly from the degradation (of different nature) of the resin or from secondary reactions due to the concomitant presence of H_2 and other gases.

In general, a disturbance of the acid-base equilibrium of the solution in contact with the resins will result, directly or indirectly, in a release of ^{14}C present in the form of a carbonate. This could also arise through the ingress of foreign anions with selectivity on the resin higher than HCO_3^-, e.g. as chloride, nitrate, or hydrogenosulphate anions. Other less known effects leading to ^{14}C release from SIERs are the effects of service/storage temperatures and strong oxidants (thermal and chemical degradation), that could affect resin equilibrium and capacity. Microbial growth, which could convert some inorganic ^{14}C into an organic form or produce anions that may displace the ^{14}C from the resins; however, highly alkaline media ($pH > 12$) are not favourable for microbial activity.

Radiolysis could represent an important variable affecting the release and possibly the speciation of the released radionuclides. IERs are in most of the cases DVB-based resins, *i.e.*, they are particularly sensitive to radiation damage during and even after operation, compared to other materials like inorganic IERs or cement. Effects on the speciation of radionuclides due to the degradation of mixed bed IERs have been reported with releases of trimethylamine (TMA), H_2(g) and CO_2(g) from anion exchange resins (SBA type I) due to γ-irradiation. A distinction between anaerobic and aerobic conditions was made with CO_2(g) detected only in the presence of oxygen. Studies on radiolytic and chemical degradation of strong acidic IERs underlined the formation of mainly sulphate and dissolved organic carbon in solution. Among these, only oxalate was identified, constituting 10-20% of the organic fraction. Other degradation products were CO_2 and H_2.

Releases in the gas phase could be investigated following three approaches:

i. direct measurement and speciation;

ii. application of ultra-sensitive techniques;

iii. concentration techniques.

The total ^{14}C released in the gas phase should be quantified in relation to specific conditions, e.g. temperature, dry/wet storage, pH. In the case of a detectable amount by radiometric methods (scintillation counter), approach (i) can be applied and a direct speciation of ^{14}C in the gas phase could be performed through radio-gas chromatography (R-GC) coupled with mass spectrometry (R-GC-MS). In cases where the ^{14}C activity is below the detection limit, species determination is not possible, at least with a direct method. In these cases, ultra-sensitive mass spectrometric and/or vibrational spectroscopic techniques, e.g. accelerator mass-spectrometry (AMS), intracavity optogalvanic spectroscopy (ICOGS) and cavity ring down spectroscopy (CRDS) could represent a solution i.e. approach (ii). The last option, approach (iii) consists of developing and applying concentration techniques based, for example, on distillation, molecular sieves and pressure/temperature swing adsorption (PSA/TSA).

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Glossary

AMS

Accelerator Mass Spectrometry 24, 30, 31, 32, 38, 39, 40, 42, 55

BWR

Boiling Water Reactor 1, 11, 14, 15, 18, 22, 24, 25, 28, 57, 59

CANDU

Canadian Deuterium Uranium Pressurized Heavy Water Reactor 9, 28, 57, 58

CCU

Condensate Clean-Up system 20, 24

CRD

Cavity Ring Down 39, 40, 42, 60

DMA

Dimethylamine 62

ESI-MS

Electrospray Ionization Mass Spectrometry 53

FID

Flame Ionization Detector 53

FTIR

Fourrier Transformed Infrared Spectroscopy 55, 56

GC/MS

Gas-Chromatography coupled with Mass Spectrometry 52, 53

HPLC

High-Performance Liquid Chromtography 54, 55, 59

HWC

Hydrogen Water Chemistry 24