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CArbon-14 Source Term

CAST

2nd Annual progress report on WP4 – 2015 – (D4.3)

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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.

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

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

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

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Executive Summary

The second year of the fourth work package (WP4) concerning the study of speciation, source term, leaching, and gaseous release of ^{14}C from spent ion exchange resins, was mainly dedicated to the development and implementation of analytical techniques and strategies, after the definitions of the sampling campaigns within the framework of each national programs–see D4.1 [Rizzato *et al.*, 2014], and D4.2 [Reiller *et al.*, 2014] for further details.

This deliverable consists of an annual report (Year 2) on the current status of sample delivery, sample characterization, and analytical development at the end of September 2015.

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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 situations 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]. Nevertheless, the possible complexation of some radionuclides by unidentified radiolytic product(s) was clearly shown [HUMMEL AND VAN LOON, 1999; VAN LOON AND HUMMEL, 1999a; VAN LOON AND HUMMEL, 1999b].

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.

2. Partners Activity

2.1. *CEA-EDF*

2.1.1. Objectives

The work of CEA within WP4 is involving two laboratories. The Laboratory of Radiochemical and Chemical Analyses (LARC) in CEA Cadarache will proceed to the determination of the inventory of ^{14}C in SIERs from nuclear power plants provided by Électricité De France (EDF– PWR reactors). The reason of the choice and sampling strategy are presented in REILLER *et al.* [2014]. The objective of this study is to determine the total activity of ^{14}C and the distribution among mineral and organic forms.

The Laboratory of Radiolysis and Organic Matter (LRMO) in CEA Saclay is more focussed on the speciation within the organic form of ^{14}C on the same samples.

2.1.2. Description of the works

This second period was devoted to:

- the reception of samples in compliance with the French regulations (LARC);
- analytical developments for the measurement of the total activity and the distribution of ^{14}C (LARC);
- first measurements on SIERs (LARC);
- test the desalination of Na^+,K^+ loaded solution (LRMO);
- test of Fourier transformed infrared on active samples (LRMO);
- test of ion chromatography for the detection and quantification of small soluble organic molecules (LRMO).

2.1.3. Reception of samples

All the samples coming from EDF power plants were received (last sample in June 2015).

Table 1. Sample of spent ion exchange resins

Name of the sample	Power reactor unit (MWe)	Type of fuel	Received	Mass (g)	Dose rate (mass) at reception
EDF-A	1450	UOX	06/2014	10	15 µSv/h (10 g)
EDF-B	1300	UOX	02/2015	4×10	300 µSv/h (10 g)
EDF-C	900	MOX	06/2015	4×10	950 µSv/h (10 g)
EDF-D	900	MOX	02/2015	1.7	530 µSv/h (1 g)
EDF-E	1300	UOX	05/2015	4×10	900 µSv/h (10 g)

Samples of SIERs were taken during the “Mercure” process, which is the conditioning process of SIERs used in France by EDF. These SIERs come from various purification system including primary circuit, secondary circuit and effluent treatment, which require high quality nuclear grade resins to retain the dissolved species, some of which may be radioactive. The huge heterogeneity of dose rates is due to the fact that the SIERs come from different circuits and were sampled after different storage delays—radioactive decay of short life radionuclides.

2.1.4. Development of methodology for ^{14}C analyses

2.1.4.1. Methodology for total ^{14}C

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

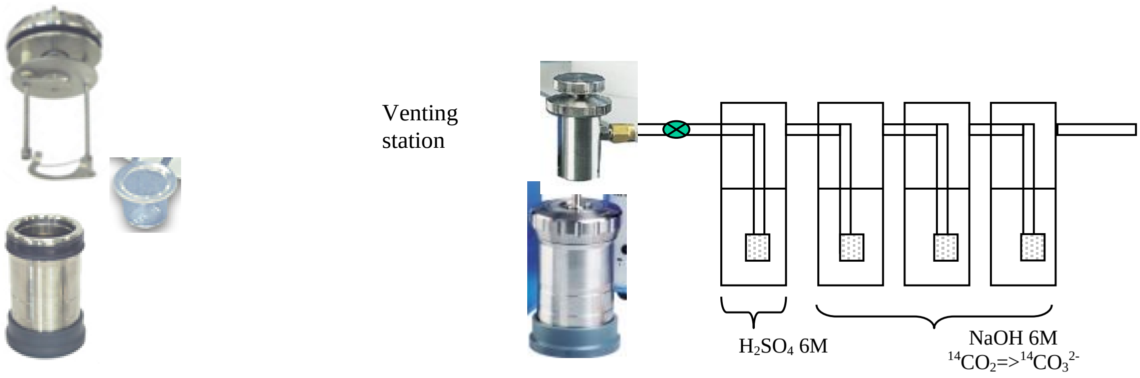

Figure 1. System for total carbon 14 measurement using mineralization under O_2 in closed system

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

Table 2 : Parameters for total dissolution of spent ion exchange resins and ^{14}C total measurement

Parameters	Optimum	Maximum
mass of resin (g)	0,3 g	0,4 g
mass of the carbon carrier (g)	0,2 g	0,2 g
trapping solution	NaOH 2M 10 ml	NaOH 2M 10 mL
trapping gas	Yes	Yes

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

2.1.4.2. Speciation of ^{14}C

The study of inorganic and organic forms distribution was carried out by acidic dissolution of the ion exchange resin (Figure 2). A first step consists in introducing the sample in a glass reactor and mixing it with acidic solutions to provide the degassing of CO_2 and to catch CO_2 into bubblers with sodium hydroxide solution (mineral form). During a second step, a total oxidation of the ion exchange resin and the organic forms of the carbon 14 was performed by a hot acidic dissolution with oxidant reagent. Some experiments on virgin

IERs spiked with ^{14}C as carbonate or glucose forms, or both, were operated to optimize parameters of the dissolution to achieve the total recovery of ^{14}C and a good selectivity between mineral and organic forms.

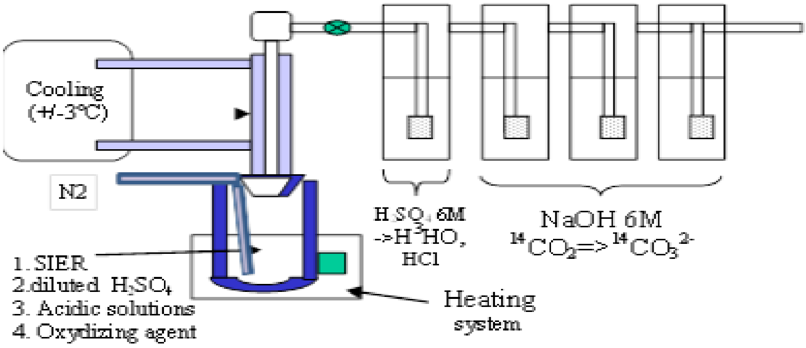

Figure 2. Schematic representation of dissolution process.

All the parameters were optimized (Table 3) and the results show that the yield of recovery of ^{14}C was above 95% for mineral form and above 90% for organic without cross-contamination (Table 4).

Table 3. Parameters for total dissolution of spent ion exchange resins and 14C speciation measurement

Mass of resin (g)	^{14}C	Solution	Heating	Degassing
0,25 to 0,5	Mineral	5 mL H_2SO_4 9 M	No	Yes (1 h)
	Organic	22.5 mL H_2SO_4 (18 M) / 7.5 mL HNO_3 14 M + 5 mL H_2O_2	Yes (3 h)	Yes (3 h)

Table 4. Carbon 14 recovery and selectivity

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

2.1.4.3. First measurement

The methodology developed was applied on a wet irradiated ion exchange resin sample (Sample EDF-A). The results show that the two methodologies give the same results for total ^{14}C, around 5700 Bq/g of carbon were measured. 77 % of the total ^{14}C is under mineral form and the complement on organic form (23%).

Table 5 : Results on wet irradiated sample EDF-A

Sample EDF-A	**^{14}C Bq/g**	**Mineral form**	**Organic form**
Wet sample N°1	5700±270	79±6%	21±2%
Wet sample N°2	5520±226	74±4%	26±2%
Mean	**5610±430**	**77%**	**23%**

The same experiments were performed on the same sample after drying. The results obtained by the two methods are different. These results, presented in detail during the WP4 meeting in June 2015, show that the methodology for measuring the speciation of ^{14}C is not adapted for dry resin; a loss of ^{14}C, mainly the mineral form, was observed.

These results will be published in a specific technical report with all the analytic developments and results during the next period of CAST project.

2.1.5. Organic carbon speciation

2.1.5.1. Analytical Strategy

To perform organic carbon speciation in CEA-LRMO, an analytical strategy has been established in D4.2 [REILLER *et al.*, 2014]. The different objectives and analytical techniques are summarized in Table 6.

Table 6. Analytical techniques and associated aims

	AIM	ANALYTICAL TECHNIQUES
CARBON MASS BALANCE	Organic and inorganic total carbon	Total carbon analyser
SAMPLE PREPARATION	Desalination	Filtration
ORGANIC SPECIATION	Qualitative analysis for determination of chemical families	Fourier transform infrared (FTIR)
	Quantification of low mass carboxylic acids (C1-C5)	Ion chromatography (IC)
	Detection of low mass molecule	Gas chromatography coupled with mass spectrometry (GC-MS)
	Detection of molecules with higher molecular weight	Electrospray-mass spectrometry analysis (ESI-MS)

All the points of this analytical strategy are detailed below with progress realized in 2015

2.1.5.2. Carbon mass balance

The analysis of total organic (TOC) and total inorganic (TIC) carbon is realized on TC analyzer (in a glove box). The first calibration has been realized showing a detection limit around 1 mg_C/L in TOC and TIC (without sample dilution). The quantification limit is determined by the lowest measure for which the signal to noise ratio is obtained above 5, knowing that the injection volume is around 500 µL and that it is better to realize several repetitions. The available volume of sample and the background noise of the device are the limiting factors.

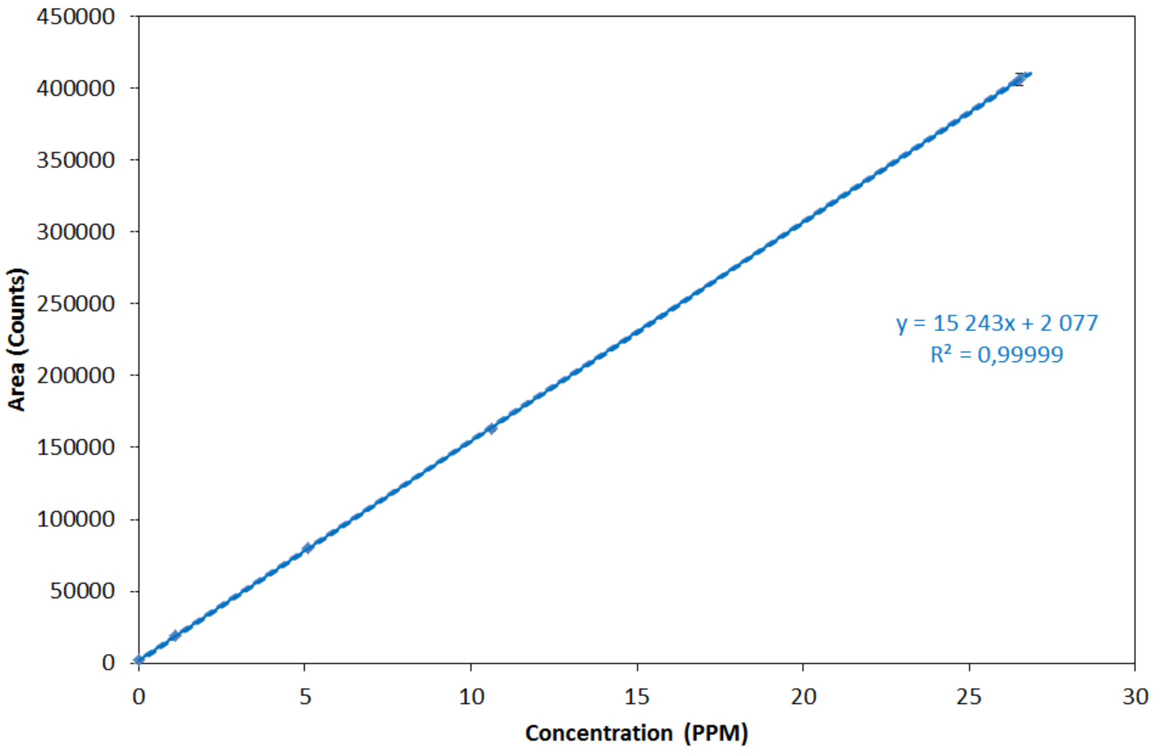

Figure 3. Calibration of the TOC analyses in CEA-LRMO

2.1.5.3. Desalination

In order to increase the detection of organic molecules in alkaline media, a step of sample preparation is required. A desalination of the sample using ion exchange resin to replace alkaline ions with H^+ is used.

In 2015, first tests were realized. A solution of organic molecules (mix of acids and diacids) in alkaline buffer representative of cementitious type water—0.16 mol/L KOH and 0.07 mol/L NaOH defined in BOURBON [2009]—is analyzed by TOC and ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry) before and after treatment with ion exchange resin (Chromafix PS-H+). TOC is used to control that no organic matter is released from the resin, and ICP-OES is used for potassium and sodium quantification to control the efficiency of the sample purification.

The initial concentration of total organic carbon is 414 mg_C/L. The results presented in Table 7 show:

1. an efficient removal of salts present in solution;
2. a slight decrease in TOC;
3. a high concentration in TIC observed before filtration probably due to carbonation of the alkaline solution.

Table 7. First results of desalination

ION EXCHANGE	TIC (mg_C/L)	TOC (mg_C/L)	K (mol/L)	Na (mol/L)
no	555	451 ± 1	0.148	0.063
yes	7	419 ± 1	0.0004	0.0018

A high concentration in TIC is observed before filtration probably due to carbonation of solution. The first results are good because salts are effectively removed but other tests must demonstrate if this decrease in TOC is significant.

2.1.5.4. Fourier transformed infrared

The use of FTIR aims to identify functional groups of organic compounds present in solution, *i.e.* carboxylic acids, aromatic compounds, ketones, *etc*. The use of "Omni-Cell' universal cell" is considered (Figure 4) to analyse radioactive liquid samples. This removable system with CaF_2 sealed windows is waterproofed to allow analysis of aqueous solutions.

Figure 4. Omni-Cell universal cell

This idea remains to be studied because two major difficulties are noted:

- sample activity of analyzed sample have to be compatible with lab bench handling;
- handling and cleaning of CaF_2 sealed windows without contamination.

This system will be better studied if other analytical techniques give no satisfactory results.

2.1.5.5. Ion chromatography

Ion chromatography is used to quantify small carboxylic acids. For that, the method has already been developed in the laboratory for the detection of carboxylic acids from C_1 to C_5 in high NaOH concentrations. This device is equipped with a conductimetric detector, which allows the detection of carboxylic acids but doesn’t give information on the ^{14}C content. The possibility to add a scintillator counter at the end of the ion chromatography was envisaged to identify molecules labelled with ^{14}C. The first tests realized with the conductimetric detector show a detection limit around 1 mg/L according to the interference between the sample and the matrix.

The purchase of scintillator is not considered anymore because the device is too large to be introduced in the glove box. The GC-MS could be an alternative technique to realize ^{14}C speciation on the identified molecules.

2.1.5.6. Electrospray-mass spectrometry analysis

To detect molecules with molecular weight higher than 100 g/mol, electrospray is a soft ionization technique, which allows the detection of intact polar molecules in complex mixtures. For molecular weights lower than 1000 g/mol, the resolution of mass spectrum may be sufficient to determine $^{12}C/^{13}C/^{14}C$ ratio. The detection of molecules labelled with ^{14}C can so be realized if the concentration of ^{14}C is high enough. To appreciate the detection limit, tests must be performed using standard ^{14}C-labeled molecules.

Palmitic acid ($C_{15}H_{31}COOH$, M = 256.4228 g/mol), a standard carboxylic (fatty) acid is chosen with different ^{14}C-labellings:

- Palmitic acid without ^{14}C;

- [1-^{14}C]- palmitic acid with one ^{14}C on the carboxylic group;
- [^{14}C(U)] palmitic acid with all carbon labelled with ^{14}C.

The purchase of standards is ongoing and their analyses are planned. Analytical parameters need to be optimized with the aim to obtain the best isotopic resolution with a good detection limit.

2.1.6. Conclusions

The two methodologies developed (total ^{14}C and speciation) were tested with success on wet irradiated ion exchange sample. The others samples will be measured during the next period of the project. However, the use of two methods for ^{14}C determination has permitted to identify an analytical difficulty for the measurement on dry resin sample. During the next period, we try to solve the analytical bias for the ^{14}C speciation measurement on dry sample.

Organic sample speciation has been confronted with difficulties related to impossible adaptation to nuclear facilities—LSC adaptation to ion chromatography set-up. Analytical strategy is evolving towards ESI-MS analysis.

2.2. *ENEA*

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

2.2.1. Task 4.2 – ^{14}C Inventory and speciation in SIERs

2.2.1.1. Resins Procurement

The workload for the request of the authorization, the packaging and the delivery of the spent resins samples has been finalized.

Nine wet samples (3.5-10.0 g for each sample) have been received by ENEA on July 25th 2015, coming from the Trino Vercellese NPP. These amounts of resins are the remaining material available from SOGIN as most of the SIERs have been already stored. The samples came from three different demineralizer vessels, and for each vessel three samples have been taken: on the top, in the middle and at the bottom of the filling—sample code A, B, C.

The scheduling of the delivery was longer than planned as both counterparts experienced logistical and administrative difficulties in managing the delivery. The samples are now at ENEA premises in Roma and they will be analysed for their ^{14}C content in both ENEA laboratories, in Roma and Bologna, after the proper conditioning for the transportation and the acceptance procedures. There was no previous information about the original ^{14}C content in the resins so ENEA will eventually explore the possibilities to make estimation on it by calculation. The water content and the volume of the resins are shown in Figure 5 and Figure 6—for some samples not all the information has been retrieved.

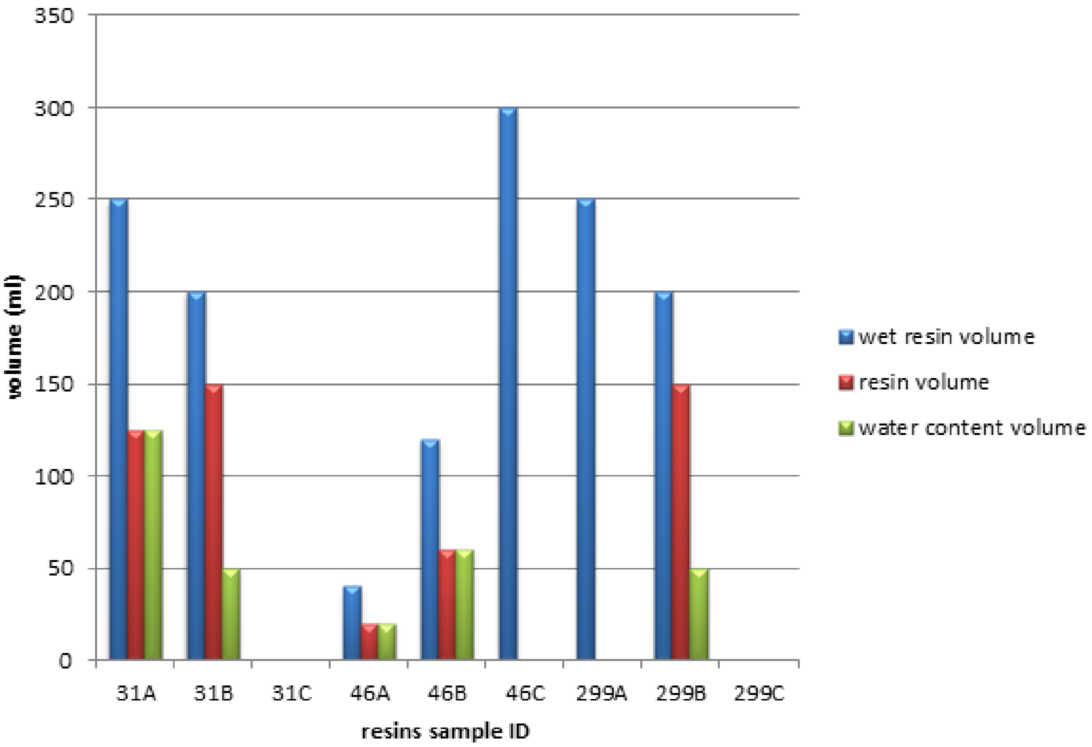

Figure 5. Volume of resins provided by SOGIN and their water content

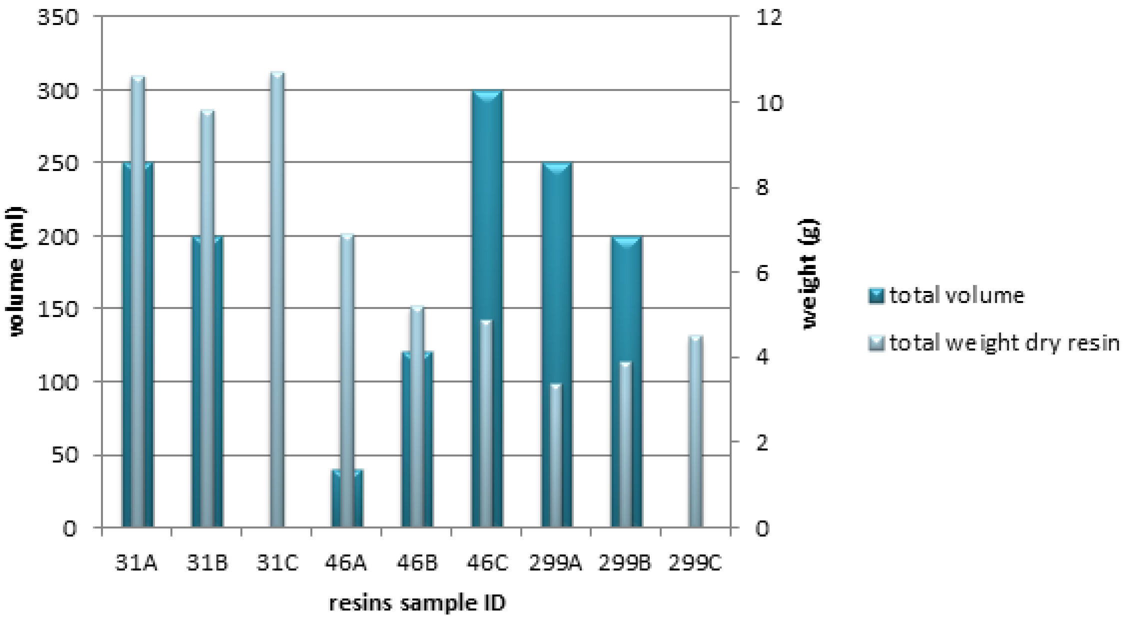

Figure 6. Total volume and weight of resins samples.

2.2.1.2. Speciation experiment

As regards the speciation, a major issue in the implementation of the activities planned for the second year has been encountered, as the ENEA ^{14}C laboratory has been closed in October 2014 for safety reason (infrastructure weakness). After a technical evaluation, ENEA decided to move the entire laboratory—including equipment and personnel—in a new location at the main headquarters in Bologna, so the laboratory was definitely closed in November 2014—all experimental activities have been stopped—, and the construction works for the new location, after the acceptance of the engineering and architectural plan, has been initiated in January 2015. In April 2015 the new facility in Bologna was ready and we were authorized to start the packing of the equipment and of the materials of the ^{14}C laboratory.

Up to now the re-location has been completed and since the beginning of September 2015 we will start to install all the equipment of the lab, including the prototype of the newly designed combustion system—see D4.2 for details [REILLER *et al.*, 2014].

The double chamber combustion cell will be directly set up within the pipeline of the existing combustion system so the possibility to have pyrolysis and/or oxidation—see scheme in the circle of Figure 7—will be completely embedded in the original design of the ENEA combustion system.

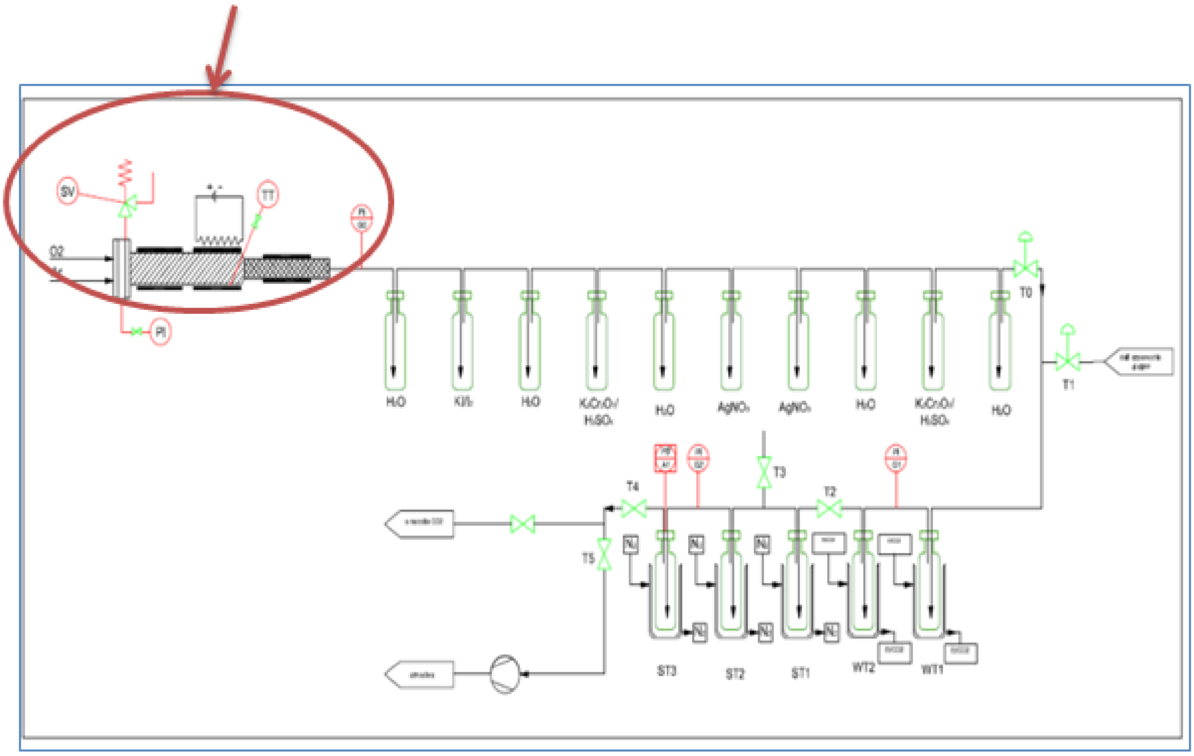

Figure 7. Scheme of the stepped combustion/pyrolysis system designed and implemented by ENEA.

The speciation experiments will proceed as soon as the system will be completely installed, and background and efficiency measurements will be carried out.

During the re-location period the opportunity for improving the instrumentation of the laboratory has been taken by procuring a new equipment for the combustion of the resins and for the elemental analysis with the ultimate scope to add some functionality for the recovery of the C content (CO_2), in order to complement the measurement of the ^{14}C content in the resins. The equipment has been acquired by external funds and will be used as in kind contribution for the CAST objectives.

The equipment runs two main chemical steps (Figure 8):

1) Combustion
    - Sample combusts in furnace at 950°C to 1200°C;
    - Jet injection of oxygen via lance right over/at sample (turbulent flow).
2) Gas Separation
    - Helium carrier gas pushes combustion gases through analyzer.

C, H and S (eventually) combustion gases are trapped in separate columns, then sequentially released (“purge and trap”).

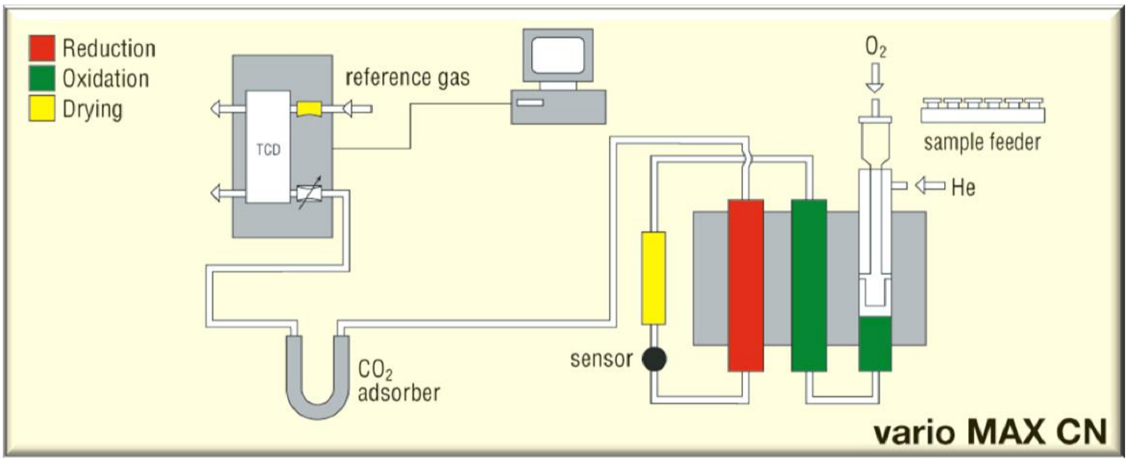

Figure 8. Processing scheme of the elemental combustor acquired by ENEA— Courtesy by Elementar Analysensysteme GmbH.

The combustion/purge step will be used to run oxidation at different temperature and collecting the fraction separately. In order to achieve this objective a tailored connection between the purge system and our home made system for the CO_2 direct absorption (Figure 9) will be set up. The CO_2 collected in the second column (red dots column) will be pumped in the recovery system and absorbed in carboxyl amine or alkaline medium for the determination of the ^{14}C content by Liquid Scintillation Counting. This so called “spilling system” will be built and tested in order to try separating different fraction of carbon molecules in the resins.

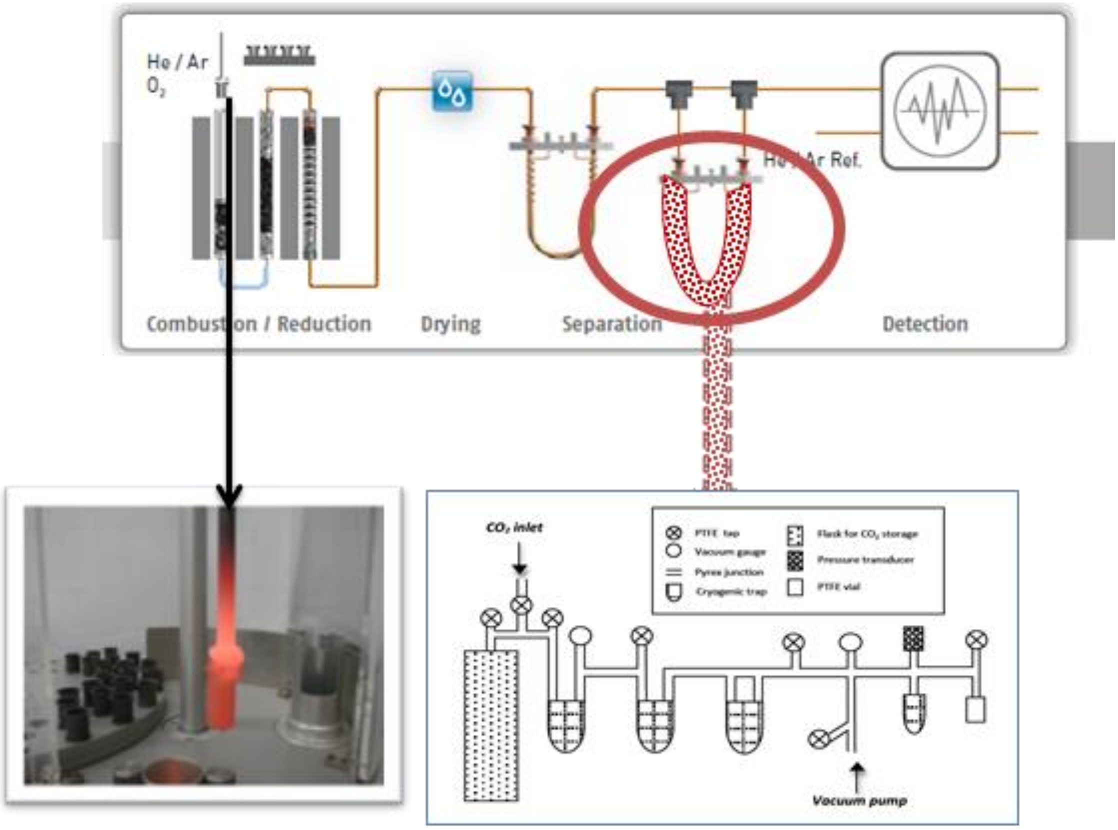

Figure 9. Separation and recovery of the CO_2 for ^{14}C analysis with the new equipment at ENEA.

As regards the innovative outreach activities in which ENEA has been involved since the beginning of the CAST project, the first phase of our internal assessment of the innovative patent pending Cavity Ring Down Laser Spectrometry technique—namely “INO SCAR ^{14}C analyzer”—, developed by the Institute of Optics of the National Research Council (Firenze, Italy), has been finalized (Figure 10). As a follow up of our assessment it has been proposed to the developer to test the performance of this technique by running some ^{14}C analyses on CO_2 fraction from CAST resins with prototype equipment that will be set at ENEA premises by the end of 2015.

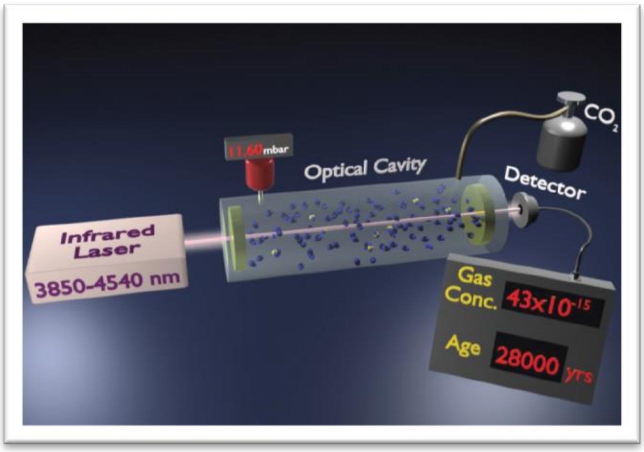

Figure 10. Scheme of the INO SCAR 14C analyser that will be tested by ENEA.

2.3. *FZJ*

2.3.1. Task 4.1

Together with the other partners FZJ contributed to the first WP4 deliverable "Current status review of ^{14}C and its release from SIERs" [RIZZATO *et al.*, 2014]. FZJ is also involved in other relevant R&D activities to establish and deepen the understanding of ^{14}C forms and leaching behaviour. In the following, a short summary is reported together with the updated list of samples (Table 8) and criteria for the samples choice.

2.3.1.1. Sample choice

FZJ is focusing its research on IERs used in water cleaning circuits of BWRs. 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.

For the sampling of SIERs the following selection criteria were applied:

- Low γ-radiation
- High ^{14}C content
- Different storage time
- Corresponding water and gaseous samples

From the point of view of the ^{14}C content, the resins of major interest are those used in the Condensate Clean-Up System CCU and the Reactor Water Clean-Up System RWCU [RIZZATO *et al.*, 2014]. It was previously demonstrated [MAGNUSSON, 2007] that ^{14}C content is generally higher in SIERs from the CCU system. However, RWCU SIERs have rather high ^{60}Co—up to tens of $MBq \cdot g^{-1}$, depending on the reactor and boundary conditions—, which results in a more difficult and expensive handling, transport and storage. Accordingly, FZJ will consider investigation of CCU SIERs. Examination of mixed SIERs, coming from different cleaning circuits, is not considered. Further distinction is related to fresh and legacy samples: the first ones can be retrieved only in nuclear power plant under current operation, while the second ones can be retrieved independently of the operational status of the nuclear power plant, where an intermediate storage has taken place—see CAST D-4.1 for further details [RIZZATO *et al.*, 2014]—. In some cases the intermediate storage requested a (pre-)conditioning method (FZJ-B), as *e.g.* dewatering, partial drying, *etc*. In other cases, no intermediate storage took place and the SIERs were directly conditioned—cemented or even bituminized.

The selected SIERs samples received by FZJ are summarized in Table 8. Samples FZJ-C and FZJ-E were not delivered after internal decision at the Nuclear Power Plants.

Table 8. Summary of the different samples received by FZJ.

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

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

2.3.1.2. Analytical techniques

FZJ is focused on analysis of speciation of released ^{14}C, both in solution and in the gas phase. In particular, the following approaches can be adopted:

1. Direct measurement and speciation
2. Implication of ultra-sensitive techniques

3. Concentration techniques

Whenever possible, the total ^{14}C released in the liquid and gas phases must be quantified and linked to the operational/storage conditions, *e.g.* temperature, dry or wet storage, pH, *etc*. In case of a detectable amount with radio-analytical methods (LSC), approach 1 can be applied and a direct speciation of ^{14}C in the gas phase could be determined by R-GC/R-GC-MS. Correspondingly, LSC, HPLC, HPLC-MS, HPLC-LSC are being used for analysis of the liquid phase.

Analytical development to lower the detection limits is going on in FZJ, for the ^{14}C-speciation in solution and in the gas phase. Particular effort is put in the validation of the equipment implied for the gas phase analyses. In detail, the conversion efficiency of organic compounds in the catalyser is being investigated with reference gases (*in primis* CH_4) at different gas flows and temperatures. The washing bottles sequence has been successfully optimized, allowing a lower dilution of the ^{14}C activity and an optimal volume for the ^{3}H and ^{14}C absorption. The experimental setup of the experimental facility to analyse ^{14}C in gaseous samples is reported in Figure 11. The first four washing bottles are absorbing ^{3}H and ^{14}C in form of HTO and $^{14}CO_2$. A catalyser of CuO or CuO-Pt/Al_2O_3 is converting HT to HTO, ^{14}CO to $^{14}CO_2$, and organics to CO_2, with different efficiencies depending on temperature, gas carrier flow, and on the amount of catalyser. The washing bottles, positioned after the catalyser, are absorbing the new-formed HTO and $^{14}CO_2$. Once the conversion efficiencies of the catalyser are evaluated for different organics, a two-step oxidation would allow separating CO and the organics in the gas phase, similarly to the apparatus used in AMEC studies for RWM that were reviewed in WP5. However, gaseous releases from SIERs are expected to be more complex and variegated as the ones from i-graphite. Accordingly, an improvement of the analytical techniques and a parallelism of different analyses are necessary to obtain an efficient and optimised quantification and qualification of ^{14}C in the gas phase.

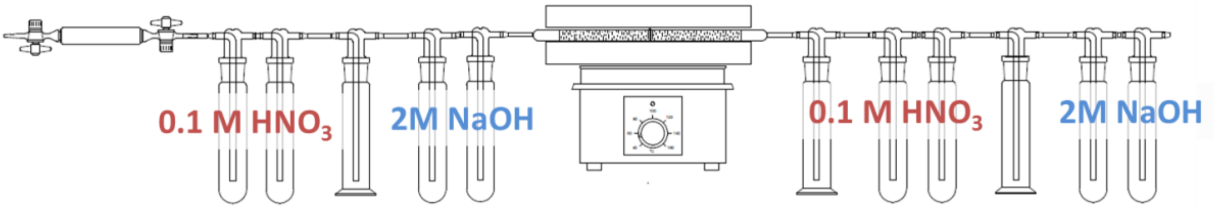

Figure 11: Experimental setup for the analysis of ^{14}C, with a catalyser to convert HT to HTO, CO to CO_2, and organics to CO_2.

When ^{14}C activity will be below the detection limit (approach 2) and the species determination is not possible, at least with a direct method, more sensitive mass spectrometric or vibrational techniques (like AMS, ICOGS and CRD) could be an alternative solution for ^{14}C speciation.

Option 3 consists in applying/developing concentration techniques, based *e.g.* upon distillation, molecular sieves and pressure/temperature swing adsorption (PSA/TSA). It is anticipated that methods CE-MS, IC, SS-NMR, ^{1}H-NMR and ^{13}C-NMR will be applied for investigation of model SIERs in order to simulate radiation induced effects altering speciation of ^{14}C (see § 2.3.3).

Morphological investigations of (S)IERs are performed with Scanning Electron Microscopy (SEM) (see § 2.3.2).

2.3.2. Task 4.2 – Determination of the total and organic/inorganic ^{14}C fraction

In FZJ, analyses aimed at the determination of the total and organic/inorganic ^{14}C fraction have begun.

2.3.2.1. Separation of mixed-bed resins

The presence of ^{14}C in the cation exchange resins—in mixed bed SIERs—has been hypothesized [MOIR *et al.*, 1994]. No detailed information about the actual amount or speciation is reported. Following this line of thought, experiments on the separation of the cation from anion exchange fraction have been conducted in FZJ with fresh IERs. Taking advantage on the different density of the resins in different ionic forms, a successful separation of the two fractions has been achieved, with efficiencies up to 90-95 %, depending on the sample amount (Figure 12).

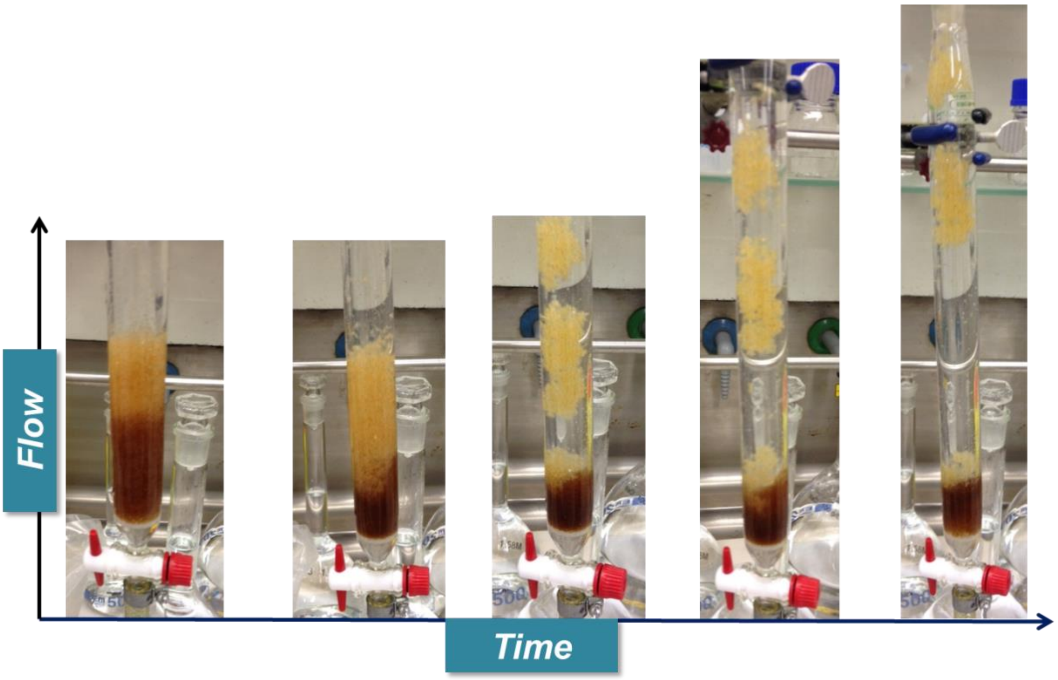

Figure 12. Separation of mixed bed resins in bead form.

The separation process aims to investigate only the organic ^{14}C, since a stripping (or regeneration) of the resins is necessary. Another technique of separation, consisted on the application of a sucrose solution, which not seemed to remove any ^{14}C [Moir *et al.*, 1994]. However, the process is functioning properly only for resins in bead form due to the broad particle size distribution of the powder resins that is hindering an efficient separation. Consequently, a separation of SIERs powder will not be performed.

2.3.2.2. Morphology of powder resins

The morphology of SIERs could highlight degradation of different nature, which could be significant for what concerns the releases of ^{14}C. SEM investigations on the morphology of resins in powder form have been performed using reference material, i.e. flocculation media (Figure 12) and fresh IERs (Figure 13). The inert material, used in the past to flocculate the powder resins in-situ, shows a characteristic fiber-like shape.

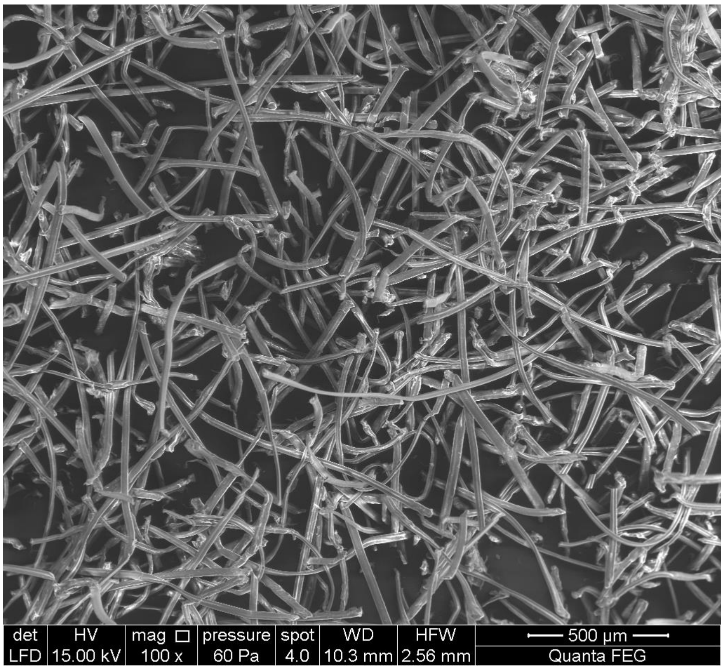

Figure 13. Inert material (Acrysorb) implied in the past in BWRs to allow the flocculation of powder IERs

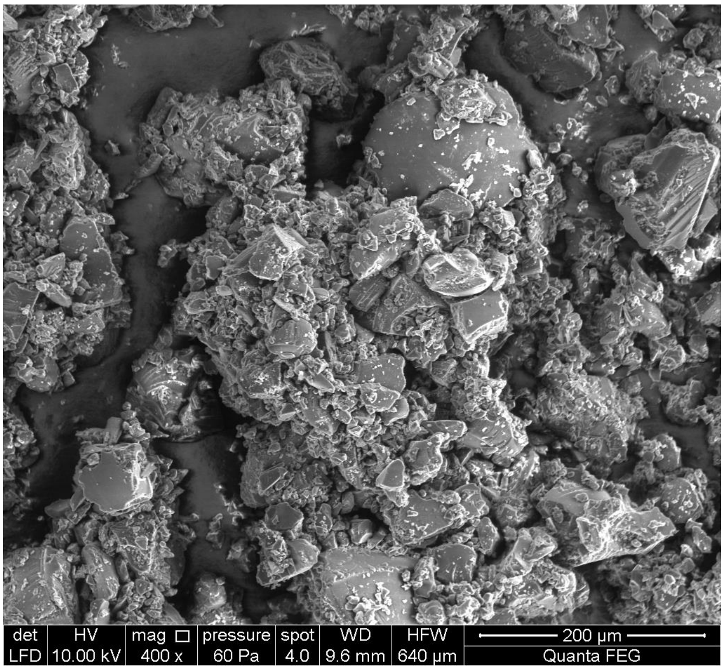

Figure 14. Powder SIERs used in BWRs (pre-flocculated)

The size distribution of the powder resins seems quite broad (Figure 14), with particles ranging from few to some hundreds of micrometre. A comparison of the morphology with SIERs is planned.

2.3.3. Task 3 – Generation of gases and degradation of SIERs

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

1. Experiments on the SIERs: leaching experiments in different conditions and evaluation of organic and inorganic ^{14}C fraction have started. All available SIERs samples have been delivered to FZJ.
2. ^{14}C speciation on SIERs will be simulated by $^{13}C^{-}$-loaded IERs exposed to gamma-radiation: a dedicated preliminary gamma-irradiation campaign has been performed and the corresponding equipment has been developed—vials and sampling of the gas phase. Resin samples, loaded with carbonate and formate, have been exposed to gamma radiation in aerobic conditions—see Figure 15 and Table 9. First, analyses on the gas and liquid phase of irradiated samples have been completed and evaluation of the results, together with the planning of the next irradiation campaign, is in progress. The results obtained from these preliminary tests, together with the results reported earlier [VAN LOON AND HUMMEL, 1999a; YIM AND CARON, 2006; BAIDAK AND LAVERNE, 2010; TRABOULSI *et al.*, 2013], are being considered for optimization of a larger campaign, including the development and test of the equipment for gas sampling, analytical techniques and concentration methods.

Table 9. List of samples used in the preliminary γ-irradiation campaign (FZK)

Sample ID	Sample type	Dose [MGy]
U1	IER-H	0.1
U2	IER-H	0.5
U3	IER-OH	0.1
U4	IER-OH	0.5
U5	IER-OH	1.0
B1	$NaHCO_3$/Water	0.1
B2	$NaHCO_3$/Water	0.5
B3	CH_2O_2/Water	0.1
B4	CH_2O_2/Water	0.5
L1	IER-OH/ $NaHCO_3$/Water	0.1
L2	IER-OH /CH_2O_2/Water	0.5
L3	IER-OH/ $NaHCO_3$/Water	0.5
L4	IER-OH /CH_2O_2/Water	0.1

Figure 15. Sample vials filled with anion exchange resins and water, before (left) and after irradiation campaign (right) (FZK).

2.4. *INR*

2.4.1. CANDU SIERs characteristics

CANDU SIERs sample was shipped from Cernavoda NPP to Institute for Nuclear Research (RATEN ICN) to be used in the experiments performed under CAST WP4. The SIERs were sampled from a container with SIERs originating from purification system of moderator (MOD) and Primary Heat Transport System (PHTS) of Cernavoda NPP Unit 1. These SIERs were collected from the two purification systems during maintenance procedures.

Since these systems contain heavy water, the SIERs beads were collected and stored together with small amount of heavy water that contains after almost 19 years of Unit 1 operation a high ^{3}H activity. To decrease the tritium activity and also to get a D_2O content less than 10%, a volume of distilled water were added over the 100 g of SIERs and the container was put in a gas tight vessel and transported to ICN Pitesti.

For this SIERs sample, tritium content in water and its dose in the air above the water were measured. Also the activity of beta-gamma emitters was measured. These data are reported in Table 10.

Table 10. CANDU SIERs characteristics

Type of analysis		Result
D_2O in water [%]		8
^{3}H activity in water [Bq/kg]		2.39 10^{10}
^{3}H dose in air above the water [μSv/h]		17
Activity for β-γ radionuclides [Bq/kg]	^{54}Mn	(6.19 ± 0.63) 10^{3}
	^{60}Co	(1.24 ± 0.03) 10^{5}
	^{134}Cs	(6.22 ± 0.16) 10^{4}
	^{137}Cs	(1.88 ± 0.07) 10^{6}

2.4.2. Preliminary tests for total ^{14}C measurement in SIERs using combustion method

To measure the total ^{14}C activity in CANDU SIERs, non-catalytic combustion by flame oxidation method will be used. By this method, the SIERs sample is combusted in an oxygen-enriched atmosphere with a continuous flow of oxygen using Sample Oxidizer, Model 307 PerkinElmer® and any hydrogen present is oxidized to water while any carbon is oxidized to carbon dioxide.

If tritium is present then the combustion product will be $^{3}H_2O$ and if ^{14}C is present then the combustion product will be $^{14}CO_2$. The water is condensed in a cooled coil and then washed into a vial where it is mixed with an appropriate LSC cocktail while the CO_2 is trapped by vapour-phase reaction with an amine and the resulting product is mixed with an appropriate LSC cocktail. At the end of the combustion cycle, two separate samples—a ^{3}H sample and a ^{14}C sample—are trapped at ambient temperature, thus minimizing cross contamination. Carbo-Sorb® E is used to trap the released $^{14}CO_2$ in form of carbamate that is furthermore flushed into the ^{14}C counting vial using the Perma-fluor® E+ scintillator as a rinsing media. The ^{14}C activity is measured by liquid scintillation method using a Tri-Carb®3110TR. This analyser allows for ultra-low level counting mode with typical count rate in the range of 1-20 CPM above background.

Preliminary combustion tests were carried out using the same type of resin that is used at Cernavoda for moderator purification system: Amberlite IRN-150 - a 1:1 (eq) mixture of IRN 77 - strong acid cation-exchange resins and IRN 78 - strong base anion-exchange resin. The IRN 150 resin was labeled with known ^{14}C activity to measure the ^{14}C recovery but also the memory of this method. A SPEC-CHEC solution with ^{14}C activity of 1.46 10^4 Bq/ml was used to measure the recovery and memory of the combustion method following the procedure reccomended by the PerkinElmer in the user manual of the Sample Oxidizer.[*] To achieve the complete combustion the resin sample was mixed with different percent of cellulose. An average combustion recovery of 100.08% and a memory of 0.04% were obtained using this protocol.

Figure 16. The combusto-cones prepared for the resin combustion (left) and the combustion system (right).

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[*] Model 307 PerkinElmer Sample Oxidizer, Operation Manual, PerkinElmer, Inc., 2003

For the tests with IRN 150 resin (~0.2 g) labeled with a SPEC-CHEC solution with ^{14}C activity of 55.93 Bq/ml an average C-14 recovery of ~ 97.5% was achieved—with a minimum of 93.8% and maximum of 99.9%.

Since the real SIERs samples contain beside ^{14}C other β-emitters such as ^{137}Cs and ^{60}Co, radionuclide that have the potential to be collected after the combustion process in the ^{14}C or ^{3}H counting vials, further tests will be performed using IRN 150 resin labeled not only with ^{14}C but also with these two radionuclides to check the potential interferences.

2.4.3. Preliminary tests for inorganic ^{14}C measurement using acid stripping method

Preliminary tests to assess the recovery and the memory of the acid stripping method were carried out using the experimental set-up presented in Figure 17. It consists in a reaction vessel (three-neck-flask), a separatory funnel, a nitrogen supply and four gas washing bottles: one bottle contains an acid solution (5% H_2SO_4) to trap the released tritium and other potential interfering radionuclides and the others with alkaline solution (2 M NaOH) for CO_2 absorption [Magnusson *et al.*, 2008]. The reaction vessel (containing the SIER sample) is placed on a magnetic stirrer.

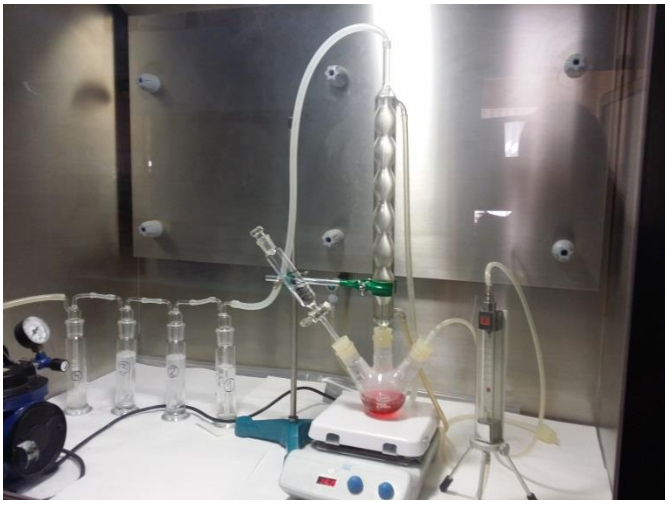

Figure 17. The experimental set-up for acid stripping in INR

The stock ^{14}C solution used to label the resin sample was obtained by stripping the ^{14}C content of a barium carbonate standard with activity of 1 mCi. By this approach a solution containing C-14 (in form of carbonates/bicarbonates) with activity of 37 10^3 Bq/ml was obtained.

A sample of IRN-150 resin (1 g) was contacted with 10 ml of ^{14}C stock solution. After 24 hours the solution was removed and the resin marked with ^{14}C activity was used to measure the recovery and memory of acid stripping method. In the reaction vessel 100 mg of $NaHCO_3$ carrier, some drops of methyl orange as indicator and 25 ml of NaOH 2 M were added before the resin sample. After a low vacuum (0.2 bar below the atmospheric pressure) was achieved, the nitrogen gas was introduced in the system. The nitrogen flow rate was controlled by a flow meter, and flow rates between 40 ml/min and 200 ml/min were used to select the optimum flow rate for which the ^{14}C recovery is maximum. Between 15 ml and 20 ml of H_2SO_4 6 M was added to the reaction vessel through the separatory funnel to release the ^{14}C under the form of $^{14}CO_2$. To ensure the complete CO_2 adsorption in the gas washing bottles, nitrogen was purged between 30 minutes and 1 hour.

The ^{14}C content in all four gas washing bottles was measured using liquid scintillation analyzer model Model 3110 TR. For the acid solution UltimaGold XR scintillation cocktail was used while for the alkaline solution Hionic Fluor scintillation cocktail was used. Using repeated tests, the ^{14}C recovery was around 80% and we concluded that during acid stripping some $^{14}CO_2$ remained on the reaction vessel walls and its necks and the three-neck-flask used as reaction vessel was replaced by a 300 ml Erlenmayer flask with a three-holes rubber stopper for gas and separatory funnel inlets and gas outlet. Also the refrigerator was replaced by a tap-water cooling loop, made of copper tubing that fit the outer side of the Erlenmeyer flask (Figure 18).

Figure 18. The modified experimental set-up for ^{14}C acid stripping in INR

In this new experimental set-up, the ^{14}C recovery was between 90.8% and 94.3%. The average recovery was 92% with a standard deviation of 1.5%. From the recovered ^{14}C activity around 99% was found in the gas washing bottle N° 2, around 0.2% in the acid gas washing bottle and around 0.8 % in the third gas washing bottle. No ^{14}C was found in the fourth gas washing bottle. An average memory effect of less than 1% was observed. No washing step was performed between the recovery step and the memory one. The experiments will continue to achieve a higher ^{14}C recovery by testing the Carbo-Sorb® E solution in the alkaline gas washing bottles.

Also, since the SIERs from MOD purification system could contain other β-emitters—especially ^{129}I that could be trapped together with ^{14}C in the alkaline bottles—, before measuring the SIERs samples further experiments will be carried out using IRN-150 resin labelled not only with ^{14}C but also with ^{3}H, ^{137}Cs, ^{60}Co and ^{129}I.

The catalytic furnace necessary to oxidise the ^{14}C compounds to CO_2 in the wet oxidation step was ordered and it will complete the experimental set-up described above for the measurement of the organic fraction of ^{14}C.

2.5. *SKB*

Since the first annual report—see D4.2 [Reiller *et al.*, 2014]—, SKB has further analysed the available data from the Swedish ^{14}C sampling and analysis program. This is done in an attempt to find the reactor operating factors that influences the uptake of ^{14}C on the IERs.

The reactors in Sweden have been in operation for about 30-40 years. During these years the operation parameters such as (S)IERs operation times, mass of mounted resin on the filters, reactor cooling water flow and condensate water flow have varied. These parameters might have an impact on the uptake of ^{14}C on the IERs. Currently SKB is investigating a number of factors that could influence the uptake of ^{14}C in an attempt to attribute each reactor a historical uptake, which might be variable for specific operational parameters of the reactor. SKB is currently investigating which operational parameters, at the nuclear power plants, influence the uptake of ^{14}C on the SIERs. This can be used in the future to change the uptake factors when operational parameters changes.

2.6. *ÚJV*

Experimental plan for ÚJV laboratory work in 2015 was mainly focused of studies on inorganic form of carbon, using hydrogeno-carbonate. First, non-active experiments were performed and the methodology of titration was verified for non-active experiments. Obtained results will be used in following experimental studies with ^{14}C tracers. For basic studies background ^{14}C activity analyses of resins used in experiments were also performed.

In a first phase, non-active sorption/interaction experiments using anion-exchange resins were performed. This type of experiment will be used as a background and for comparison to active experiments. Non-active $NaHCO_3$ was used as a tracer in experiments. In the following, ^{14}C also as a hydrogeno-carbonate will be used. For evaluation of amounts/concentrations of the non-active tracer in the experiments, the titration method was chosen. Titration is a simple, easy and available method, which can be used in every laboratory. The measuring procedure is based on the Czech technical norm [ČSN-ISO-9963-1]. Titration procedure of HCO_3^- was performed on TitraLab TIM800 device. For verification the measuring methodology and evaluation of detection limits of this method following set-up was used:

- testing solution - $NaHCO_3$ stock solution;
- titration agent - 0.02M and 0.1M hydrochloric acid solution;
- common pH electrode calibrated by buffers at pH 4 and 7;

- titration under N_2 atmosphere;
- for titration method verification 0.1M and 0.01M $NaHCO_3$ solutions were used and for limit of detection tests and determination the 0.00001M solution of $NaHCO_3$ was used.

By the titration method the acid neutralisation capacity of the sample is evaluated. In our case the acid neutralisation capacity is equal to the concentration of $NaHCO_3$. The concentration of tracer specie is calculated by following equation, where c_t is the concentration of titration agent; V_t – volume of the titration agent; V_S – volume of sample; f – correction factor. Because hydrogeno-carbonate ion and hydrochloric acid are both monovalent, no other factors or coefficients are needed for evaluation.

$$c = \frac{c_t \cdot V_t}{V_S} \cdot f$$

Results variation of standard test was evaluated < 5 % at method verification experiments and this value was also obtained in sorption/interaction tests.

For sorption/interaction experiments, following set-up was used:

- tracer - pure $NaHCO_3$ (from 0.1M to 0.00001M prepared from stock solution),
- liquid phase - degassed distilled water,
- solid phase - Amberlite resin (Cl^- form),
- solid/liquid ratios - 1 g/10 ml or 5 g/40 ml,
- samples stored under N_2 atmosphere,
- continuous shaking,
- short-term interaction - 7 days.

In first set of replicated experiments, sorption test of HCO_3^- on anex form of Amberlite resin were performed. It was shown, that 10^{-4} M HCO_3^- is fully sorbed on the resin after 3 days of contact, so the 7 days are enough to reach the steady state. In following experiments with 10^{-3} M HCO_3^- tracer it was shown, that 7 days of the contact are not enough to reach the steady state at sorption test for both used solid/ liquid phases ratios (**Figure 19**).

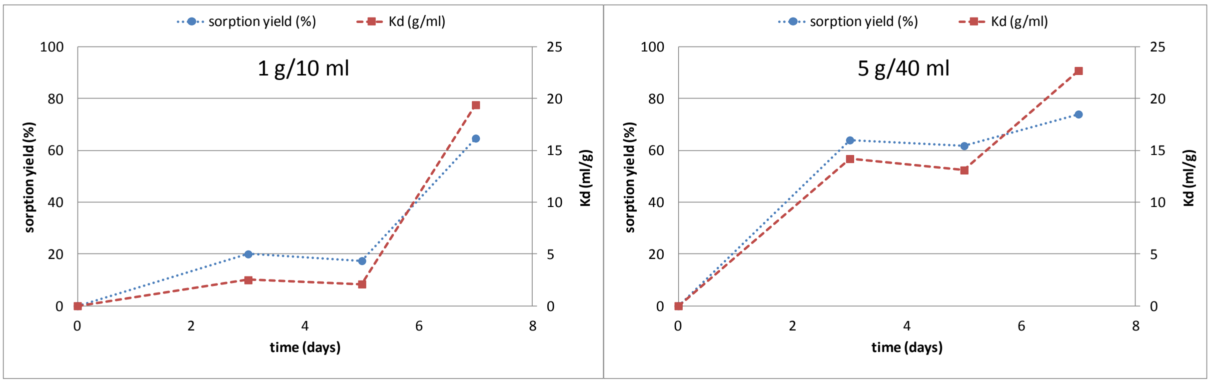

Figure 19. Sorption of 10^{-3} M HCO_3^- tracer on Amberlite resin at different solid/liquid ratios during 7 days tests.

Studies of ^{14}C background activities in resins used in experiments were performed to obtain the information about the presence of ^{14}C in resins matrix. These values are necessary for next analyses of samples with active tracers.

These analyses were performed by Central Analytical Laboratory, Chemistry of Fuel Cycle & Waste Management division, ÚJV Řež, a. s. on Hidex 300SL device by Liquid Scintillation Counting (LSC) method.

Table 11. Background activities of ^{14}C in different resins matrix.

Sample	Activity
Amberlite anex (Cl^- form)	< 3.90 Bq/g
Amberlite catex (Na^+ form)	< 4.40 Bq/g
unknown mix-bed sample	< 4.02 Bq/g

2.6.1. Results

Titration method is appropriate for 10^{-4} M or higher concentrations of hydrogeno-carbonate ions and is not suitable for 10^{-5} M or lower HCO_3^- concentrations.

7 days sorption/interaction experiments are enough for using 10^{-4} M HCO_3^- tracer, but this time range is not enough to reach the equilibrium for 10^{-3} M HCO_3^- because the values of distribution coefficient (K_d) and sorption yield are still increasing.
Background activities of ^{14}C in matrix of different resins are approximately 4 Bq/g.

2.6.2. Ongoing work and plans to the end of 2015

There were prepared sets of samples for long-term experiments (30 days) to reach the steady state of the sorption/interaction in all types of experiments - different tracer concentrations and solid/liquid ratios. These long-term sorption/interaction experiments are ongoing.

After the finishing of sorption experiments, desorption and leaching experiments will follow, same as the fixation of saturated resins into the cement matrix and subsequent leaching test of prepared samples.

By fixation resins into cement matrix the cubic samples (4×4×4 cm) will be prepared. Leaching test based on the leaching methodology [ANSI/ANS, 1986] will be performed. The leaching medium will be the distilled and/or synthetic granitic water (SGW) prepared for the laboratory tests to be as close as possible to realistic conditions *in situ*. Laboratory prepared synthetic granitic water SGW [HAVLOVÁ *et al.*, 2010] is based on a statistical evaluation of Czech granitic massif groundwaters for depths 20-200 meters.

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Glossary

AMS	Accelerator Mass Spectrometry	20
BWR	Boiling Water Reactor	1, 17
CRD	Cavity Ring-Down Spectroscopy	20
ESI-MS	Electrospray-Mass Spectrometry analysis	7, 10
FTIR	Fourier Tranformed Infra Red Spectroscopy	7, 9
GC-MS	Gas-Chromatography Mass Spectrometry	7
HPLC	High Performance Liquid Chromatography	19
IC	Ion Chromatography	7, 10
ICOGS	Intracavity Opto-Galvanic Spectroscopy	20
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry	8
LSC	Liquid Scintillation Counting	11, 19, 32
PWR	Pressurized Water Reactor	1