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# CArbon-14 Source Term

# CAST

## $3^{rd}$ Annual progress report on WP4 – 2016 – (D4.4)

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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 $^{14}$C, geological disposal research, safety case development and experimental work on gas generation. The consortium consists of national waste management organisations, research institutes, universities and commercial organisations.

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

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

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## Executive Summary

The third 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], D4.2 [REILLER *et al.*, 2014], and D4.3 [BUCUR *et al.*, 2015] for further details.

This deliverable consists of an annual report (Year 3) on the current status of sample delivery, sample characterization, and analytical development at the end of September 2016.

When measured, the differences in inorganic/organic repartition of $^{14}$C seem to be confirmed between Pressurized Water Reactors (PWR), and Boiling Water Reactors (BWR) [RIZZATO *et al.*, 2014, and references therein]. For instance the EDF-A sample (UOx-1450) the total $^{14}$C activities determined in wet and dry states seem to be in agreement, and the repartition of 23/77 for organic to inorganic forms is found. For BWR, the FZJ samples evidenced almost only inorganic $^{14}$C

The change in morphology of IERs after long term storage has been evidenced on IERs from SOGIN. It seems that anionic resins are more prone to ageing than cationic ones.

The desorption test evidenced the need of using a strong basic solution – 1 M LiOH, i.e. pH *approx.* 13.8 – directly in contact with Spent ion exchange resins (SIERs) to obtain a strong release of $^{14}$C from EDF SIERs, when neither pure water nor a $10^{-3}$ M LiOH solution, i.e. pH *approx.* 11, permit to obtain a significant release. The total released activity seem to be lower than the total activity determined in combustion suggesting a loss of $^{14}$C in gaseous

phase. The majority of the desorbed $^{14}C$ is under the inorganic form, but the proportion of organic $^{14}C$ seems to be slightly more important than in the total samples – 55/45 for EDF-A and 54-46 for EDF-B. Nevertheless, it seems from leaching experiments on SIERs from PWR (ÚJV samples), fixed into a cement matrix, that no measurable leaching can be observed during a preliminary 10 days experiments.

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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 contributors 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 inorganic and organic forms, up to the more detailed speciation and content of organic acids, carbonate, etc. 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*

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

This period was devoted to:

- measurements on real samples (SIERs) by all the analytical processes developed (total activity, mineral and organic forms distribution);
- desorption tests.

The sample characteristics, activities, and reception were described in BUCUR *et al.* [2015].

### 2.1.1. Development of methods

All the SIERS samples was stored in the dark. All desorption solution were stored at 3 °C and in the dark.

All $^{14}C$ activity counting were done using a Quantulus (Perkin Elmer) liquid scintillation apparatus, with 3600 s counting time. The relative limit of detection is of 3 %.

#### 2.1.1.1. Methodology for total $^{14}C$

The objective is to optimize the mineralization process with a total recovery of $^{14}C$. Developments were led on virgin ion exchange resins. About 0.2-0.5 g of wet ion exchange resins was introduced into a quartz vessel mixed with a “stable carbon” carrier. Mineralization was carried out under $O_2$ pressure (25 bars) in a closed system (“Parr bomb”, IKA AOD 1). The combustion of the ion exchange resins produced $CO_2$, which is trapped in sodium hydroxide solution as carbonate. To achieve the $^{14}C$ recovery, the mineralization system was degassed under a venting station and the gases were flushed into sodium hydroxide bubblers (Figure 1).

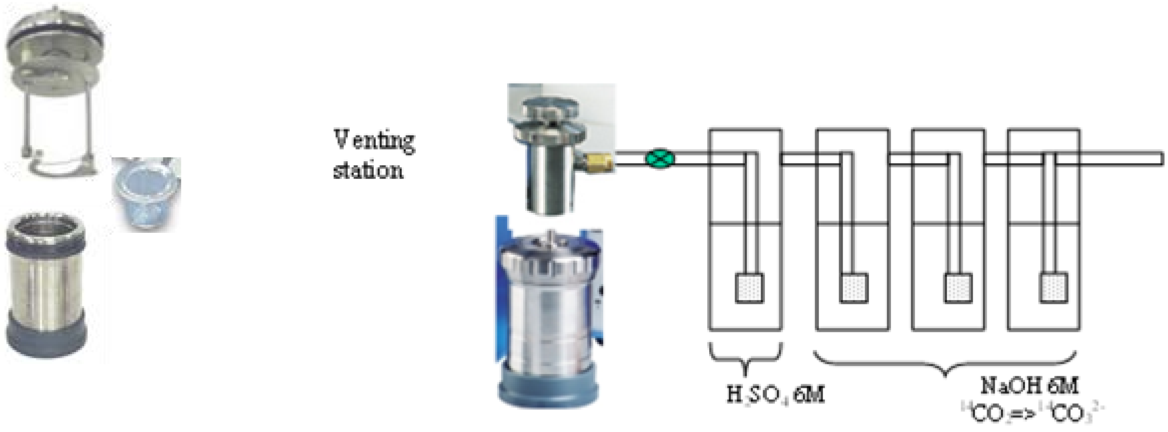

**Figure 1. System for total $^{14}C$ measurement using mineralization under $O_2$ in closed system at CEA.**

Tests on virgin IERs spiked with $^{14}C$ (as $^{14}C$-carbonate or $^{14}C$-glucose or both) were used to optimize the 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.

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

**Table 1. Parameters for total dissolution of SIERs and $^{14}$C total measurement**

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

### 2.1.2. Speciation of $^{14}$C

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

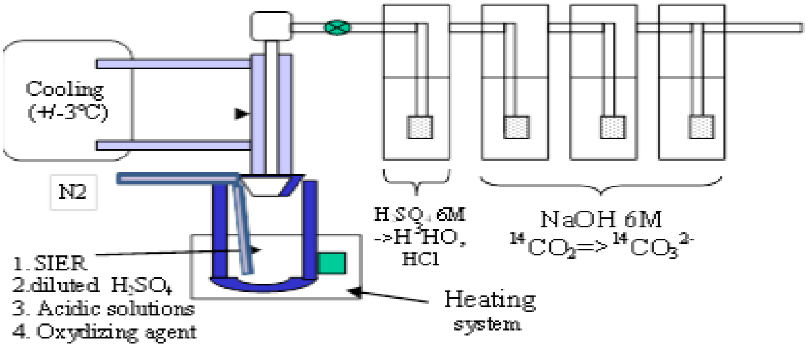

**Figure 2. Schematic representation of the dissolution process.**

All the parameters were optimized (Table 2) and the results show that the recovery yield of $^{14}$C was above 95% for the mineral form and above 90% for the organic form without cross-contamination (Table 3).

**Table 2. Parameters for total dissolution of SIERs and $^{14}C$ speciation measurement.**

| Mass of resin (g) | $^{14}C$ | Solution | Carrier | Heating | Degassing |
|---|---|---|---|---|---|
| 0.25<br>to<br>0.5 | Mineral | 5 mL $H_2SO_4$ | Yes | NO | 1 h |
| | Organic | 30 mL $H_2SO_4/HNO_3 + H_2O_2$ | No | 3 h | 3 h |

**Table 3. $^{14}C$ recovery and selectivity**

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

### 2.1.3. Measurement on SIERS

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

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

#### 2.1.3.1. Total $^{14}C$

The results obtained on dry and wet samples in $Bq.g^{-1}$ are indicated in Table 4.

**Table 4. $^{14}C$ total determination in SIERs**

| Origin | Ref | State | Wet sample N°1 $Bq.g^{-1}$ | Wet sample N°2 $Bq.g^{-1}$ | Mean $Bq.g^{-1}$ |
|---|---|---|---|---|---|
| UOx-1450 | EDF-A | Wet | 5500 ± 290 | 5630 ± 325 | 5565± 436 |
| UOx-1450 | EDF-A | Dry | 10745 ± 680<br>($H_2O$ = 40%) | 10930 ± 760<br>($H_2O$=57%) | Not calculable<br>(≠ $H_2O$ content) |
| UOx-1300 | EDF-B | Wet | 2130 ± 135 | 2120 ± 145 | 2125 ± 200 |

#### 2.1.3.2. $^{14}C$ repartition between mineral and organic forms

The results obtained in $Bq.g^{-1}$ on dry and wet same samples are presented in Table 5

**Table 5. $^{14}$C determination for the repartition between mineral and organic forms in SIERs**

| Origin | ref | State | $^{14}$C | N°1 Bq.g$^{-1}$ | N°2 Bq.g$^{-1}$ | N°3 Bq.g$^{-1}$ | Average |
|---|---|---|---|---|---|---|---|
| UOx-1450 | EDF–A | Wet sample | Mineral form | 4480 ± 260 | 4110 ± 210 | / | 4300 ± 620 |
| | | | Organic form | 1220 ± 70 | 1410 ± 80 | / | 1315 ± 290 |
| | | | Total | 5700 ± 270 | 5520 ± 226 | / | 5610 ± 430 |
| UOx-1450 | EDF–A | Dry sample | Water content | *$H_2O$ = 19.6%* | *$H_2O$ = 47%* | *$H_2O$ = 58%* | Not calculable (≠ $H_2O$ content) |
| | | | Mineral form | 2450 ± 150 | 1280 ± 80 | 610 ± 40 | |
| | | | Organic form | 1610 ± 90 | 3580 ± 200 | 1945 ± 115 | |
| | | | Total | 4060 ± 170 | 4860 ± 215 | 2550 ± 120 | |
| UOx-1300 | EDF–B | Wet sample | Mineral form | *48 ± 4* | *44 ± 4* | / | *46 ± 8* |
| | | | Organic form | 1560 ± 94 | 1570 ± 120 | / | 1565 ± 150 |
| | | | Total | 1610 ± 94 | 1615 ± 120 | / | 1612 ± 150 |

### 2.1.4. Interpretations

#### 2.1.4.1. Results on wet samples

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

**Table 6. Comparison of methodologies**

| Sample | Type | Total $^{14}$C Combustion with oxygen Bq.g$^{-1}$ | Total $^{14}$C Acidic dissolution Bq.g$^{-1}$ | Difference Bq.g$^{-1}$ |
|---|---|---|---|---|
| UOx-1450 EDF-A | Wet sample | 5630 ± 325 | 5610 ± 430 | 20 (0.3%) |
| UOx-1300 EDF-B | Wet sample | 2125 ± 200 | 1612 ± 150 | 513 (24%) |

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

#### 2.1.4.2. Effect of drying

The entire tests were performed on EDF-A sample (Table 7). The water content in the resin samples varies according to the tests from 40% up to 58%. This variation is probably due to the individual drying of each sub-sample before analyses. It seems difficult to have reproducible drying with such small samples. One experiment gave a very low content of about 20%.

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

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

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

**Table 7. Comparison of the method for the effect of drying for total $^{14}C$ determination. Experiment on EDF-A sample**

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

### 2.1.5. Conclusions on analytical developments and measurements at CEA

Developments of two methods were made and validated using $^{14}C$ in organic (glucose) and mineral (carbonate) forms. The application of this analytical method on real samples was also performed on dry and wet real IERs. An analytical problem for the $^{14}C$ measurement by acidic dissolution was identified in the case of dried samples (EDF-A) and maybe also in the case of one wet sample (EDF-B). This problem has been identified by using two methodologies for $^{14}C$ measurement inventory in SIERs. Table 8 gives the main results for the EDF-A sample.

**Table 8. Main results for EDF-A samples.**

| Origin | Sample | State | |
|---|---|---|---|
| UOx-1450 | EDF-A | WET | |
| **Method** | | **Activity $^{14}C$ (Bq $g^{-1}$)** | **Repartition** |
| Combustion with oxygen | Total | 5630 ± 325 | |
| Acidic dissolution | Mineral form | 4300 ± 620 | ~77% |
| | Organic form | 1315 ± 290 | ~23% |
| | Total (sum) | 5610 ± 430 | |
| Difference between the two methods (balance) | | 20 Bq | |

Table 9 shows the main results for the EDF-B sample. In this case, as specified above, a difference in total $^{14}C$ is found between the methods and does not allow calculation of the distribution of $^{14}C$ under mineral and organic form.

**Table 9. Main results for EDF-B samples.**

| Method | | Activity $^{14}C$ (Bq $g^{-1}$) | Repartition |
|---|---|---|---|
| Combustion with oxygen | Total | 2125 ± 200 | |
| Acidic dissolution | Mineral form | *46 ± 8* | *Not precisely calculable* |
| | Organic form | 1565 ± 150 | *Not precisely calculable* |
| | Total (sum) | 1612 ± 150 | |
| Difference between the two methods (balance) | | 513 Bq | |

The total activities are not the same for the samples tested: 5600 and 2125 Bq.$g^{-1}$ for EDF-A and EDF-B, respectively. These results question the representativeness of the sampling. To illustrate this point, Figure 3 shows the differences in the aspects of the samples (color of grain).

Non active resins Sample EDF - A Sample EDF - B

**Figure 3. Photographs of the EDF-A and EDF-B SIERs samples compared to the non-active IER sample.**

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

### 2.1.6. Desorption test

#### 2.1.6.1. Experimental procedure

Experiments of desorption of $^{14}C$ from SIERs were performed to identify the organic molecules and check the analytical methodology for $^{14}C$ speciation by acidic mineralization.

The following analytical parameters were chosen:

- around 1 g of wet resin was contacted with 10 mL of desorption solution for 30 min at room temperature;
- two experiments – with a blank and 2 virgin resins – were performed to appreciate the reproducibility.

The EDF-B sample is used, the organic $^{14}C$ activity of which is the highest (around 1600 $Bq.g^{-1}$). No preliminary test has been carried out before. The initially chosen desorption solution was a $10^{-3}$ $mol.L^{-1}$ LiOH, i.e., pH *approx.* 11, solution for several reasons:

- Li was the ionic ion shipped on cationic resin and was maybe present on the real sample,
- Solution with pH > 8.2 to avoid $CO_2$ release into the gas phase,
- Solution with pH < 11 to avoid precipitation of metallic hydroxides that may cause the clogging of SIERs porosity.

The radiochemical analyses of the desorption solution showed that no $^{14}C$ was desorbed from the SIERs. The quantification limit in the $10^{-3}$ M LiOH solution is 3 Bq in the 10 mL sampling sequence. In water the quantification limit in 10 mL sampling sequence is 1 Bq. The concentration of the LiOH solution was increased up to 1 M, i.e. pH *approx.* 13.7, to increase the ionic exchange, which resulted in the detection of both mineral and organic forms of $^{14}C$ in solution. It is worthy to notice that increasing pH favours chemical degradation of resins [VAN LOON AND HUMMEL, 1995]. Six desorption sequences were performed and the experiment were completed by two washings with water. These additional washes were performed to solubilize the hydroxides present in the pores of the resins.

#### 2.1.6.2. Results

The behaviours of the mineral and organic $^{14}$C forms are shown in Figure 4 and Table 10. To allow comparison of the results the activities are normalized to 1 g of wet SIERs. Both experiments give the same results. Most of the $^{14}$C is released during the first sequence in LiOH 1 M. The concentration decreases with successive washings. No activity is detected in the water washing solution. The quantification limit is < 1 Bq in the sampling sequence with water. Final analysis of the ion exchange resin after desorption indicate that the remaining $^{14}$C activity is quite low (around 10 % or less of the initial activity) and mainly as organic carbon form.

The results on blanks and virgin resins will be performed by LRMO.

**Table 10. Determination of the speciation $^{14}$C remaining in SIERs after desorption from sample EDF-B.**

| **Experiment** | | **$^{14}$C Bq.g$^{-1}$ After experiment** | **Mineral Form (Bq.g$^{-1}$)** | **Organic Form (Bq.g$^{-1}$)** |
|---|---|---|---|---|
| 1 | Sub sample1 | 209 ± 12 | <5 | 209 ± 12 |
| | Sub sample2 | 153 ± 8 | <5 | 153 ± 8 |
| | *Mean* | *180 ± 80* | *<5* | *180± 80* |
| 2 | Sub sample1 | 175 ±12 | <5 | 175 ±12 |
| | Sub sample2 | 150 ± 8 | <5 | 150 ± 8 |
| | *Mean* | *162 ± 38* | *<5* | *162 ± 38* |

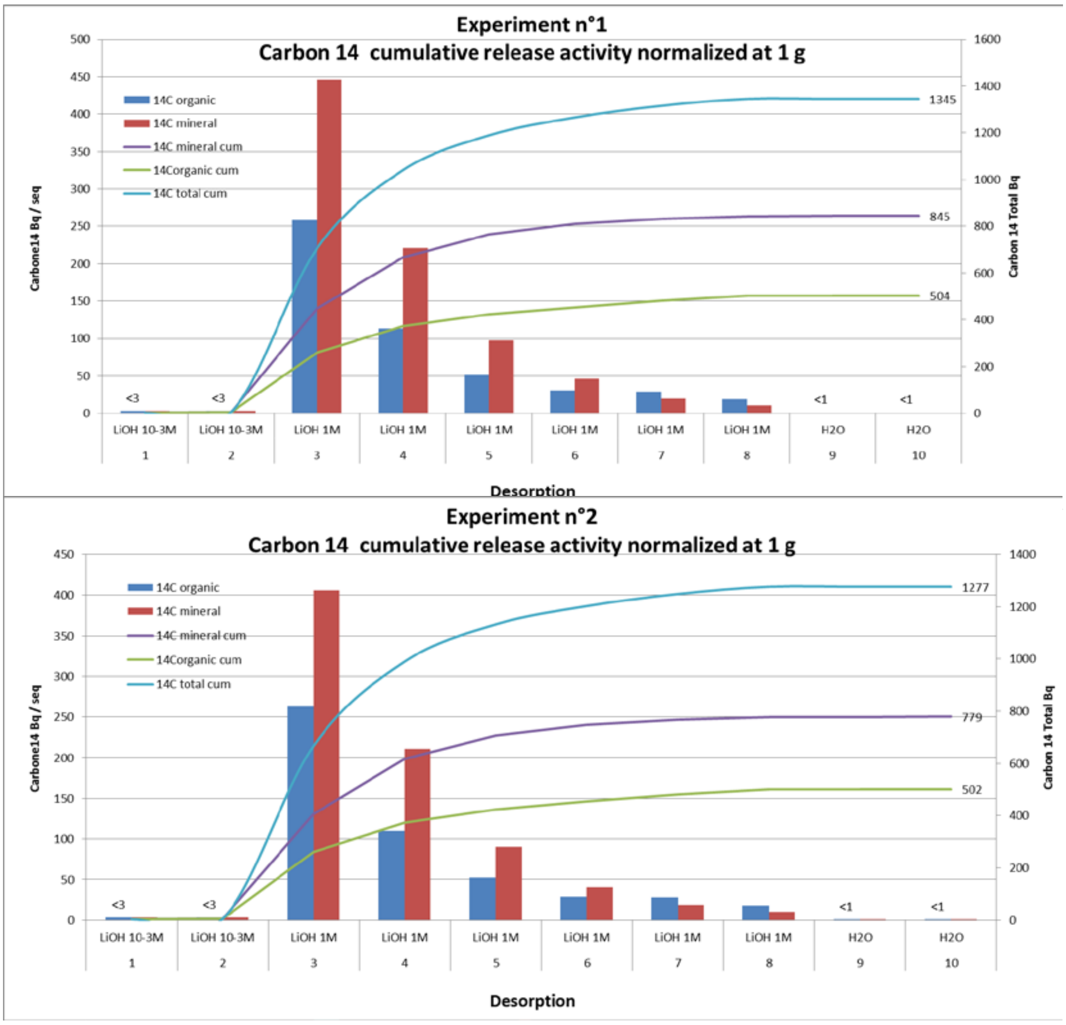

**Figure 4. Release and cumulative release of $^{14}$C (total, mineral, and organic forms) during desorption experiments for sample EDF-B.**

#### 2.1.6.3. Interpretations

These experiments show the good reproducibility of the desorption protocol: the results obtained are equivalent for the two tests. The influence of the concentration of the LiOH desorbing solution is also clear. A 1 M LiOH solution is needed in order to achieve $^{14}$C desorption. The distribution between organic and mineral forms and total activity are shown in Table 11.

**Table 11. $^{14}$C desorption assessment of the experiment with wet EDB-B SIER.**

| Experiment Sample EDF-B | $^{14}$Carbon | Total (Bq.g$^{-1}$) | Mineral Form (Bq.g$^{-1}$) | Organic form (Bq.g$^{-1}$) |
|---|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| 1 | Total desorbed fraction | 1345±120 | 845±160 (63%) | 505±100 (37%) |
| | Final activity | 180 ± 80 | <5 Bq | 180 ± 80 (100%) |
| | **Estimated initial activity** | **1525 ± 200** | **845±160 (55%)** | **680 ± 180 (45%)** |
| 2 | Total desorbed fraction | 1280±100 | 780±130 (61%) | 500±90 (39%) |
| | Final activity | 160 ± 40 | <5 Bq | 160 ± 40 (100%) |
| | **Estimated initial activity** | **1440 ± 140** | **780±130 (54%)** | **660 ± 130 (46%)** |

The comparison between total $^{14}$C activity achieved through desorption experiments (around 1500 Bq.g$^{-1}$) and total $^{14}$C activity achieved with the combustion method (2125 Bq.g$^{-1}$ see Table 8), evidence a loss of $^{14}$C during desorption experiments. A difference about 30% is measured. The organic fraction determined by the summation of the desorbed fraction and that remaining in the SIERs represents around 45% of the total activity

#### 2.1.6.4. Conclusion on desorption experiment

Desorption tests allow obtaining solutions with organic $^{14}$C from SIERs, which are being transferred to CEA LRMO laboratory in CEA Saclay Centre, which is specialized in organic compounds determination, and is in charge to measure the speciation of organic molecules.

Nevertheless these first experiments do not permit to confirm the initial distribution between organic and mineral forms. The experimental process must be reviewed including:

- the choice of a new desorption solution to minimize the possible degradation of organic molecules;
- the account of the possible volatilization of organic or mineral forms of $^{14}$C during the experiments – chemical reaction of the solution on minerals or organics compounds.

### 2.1.7. Interim conclusion of the 3rd year of CEA program

During this third year:

- two analytical procedures for the measurement of the total $^{14}C$, and the distribution between organic and mineral form on real samples, dry or wet, were tested;
- the desorption of the $^{14}C$ from SIERs for further determination of the speciation of organic molecules was done.

The use of two methods for $^{14}C$ has permitted identifying an analytical difficulty for the measurement on dry resin (samples EDF-A), or maybe for the mineral form of the $^{14}C$ (sample EDF-B). This analytical problem has been evidenced for the acidic dissolution method used for the assessment of the speciation of $^{14}C$. An apparent loss of $^{14}C$ is observed. These results are not yet understood. Furthermore, the distribution or total activity is not the same in the two samples tested.

Desorption tests were performed with $10^{-3}$ and 1 M LiOH aqueous solutions. A 1 M LiOH solution is needed to achieve a nearly complete desorption of $^{14}C$. In that case, an apparent loss of $^{14}C$ is evidenced. The solutions are being transferred for analyses by LRMO to have a first identification of the nature of the organic molecules.

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

All these elements show that further studies must be done, outside of the framework of CAST, including:

- a better knowledge of the sample;
- further development of the analytical methods;
- development of new desorption tests;
- characterization of other samples.

## 2.2. *ENEA*

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

### 2.2.1. $^{14}$C Inventory and speciation in SIERs

ENEA has received nine wet samples (3.5-10.0 g for each sample) from Italian WMO (SOGIN) (Figure 5). They have been used in the Trino Vercellese NPP (PWR) and have been stored in closed vessels (wet conditions) in a warehouse for more than 10 years. Some samples were taken and processed with traditional wet oxidation (addition of $HNO_3$ 65% + $H_2O_2$ 35% and digestion in microwave at 200°C) for the measurement of $^{14}$C content, but phenomena of flocculation and partial digestion were observed. This phenomena has also been observed in the old virgin IERs, also provided by SOGIN (Figure 6). The partial digestion jeopardised the accurate measurement of $^{14}$C content, so further investigation has been planned in order to completely dissolve the ionic resin matrix. The used procedure was the same as other partners applied to their samples so we are studying what type of ageing effect could have affected the solubility of the resins.

**Figure 5. Spent ionic resins received by the Italian WMO SOGIN.**

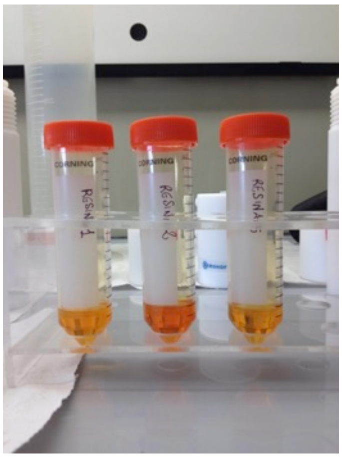

**Figure 6. Residual solutions after wet oxidation of the aged ionic exchange resins**

### 2.2.2. Speciation experiment

As regard the speciation, the re-location of the radiocarbon laboratory has been completed and the prototype of the newly designed combustion system [BUCUR *et al.*, 2015] has been installed. A double chamber combustion cell is now directly connected within the pipeline of the existing combustion system so it is possible to run a stepped pyrolysis and/or complete oxidation directly in the combustion system – Figure 7, see scheme in the circle.

A further post combustion furnace – highlighted in green in Figure 7 – has been added to the original design in order to have a complete oxidation of the sample and to replace the chemical oxidation traps containing bichromate solution – red star in Figure 7.

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

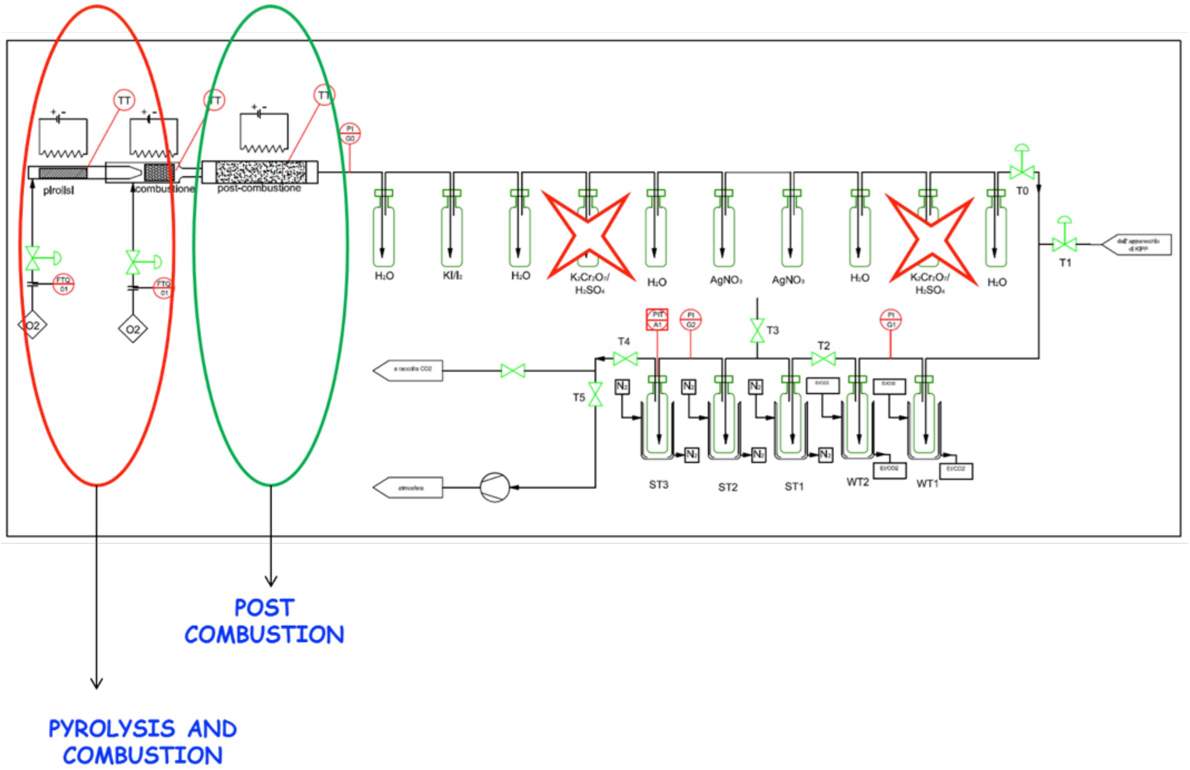

**Figure 7. Scheme of the stepped combustion/pyrolysis system integrated with post combustion chamber, designed and implemented by ENEA.**

### 2.2.3. Ageing effect

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

Two type of resins were selected:

- LEWATIT ® MonoPlus S200KR, which is a monodisperse, strong acidic gel type cation exchange resin, nuclear grade designed. The functional group for $H^+$ exchange is sulphonic on cross-linked type polystyrene beads. The bead size is specified at (0.60 ± 0.05) mm. Formerly known named as LEWATIT® S100 KR-H (Cl frei) as denoted in Figure 9 and Table 12;

- LEWATIT ® MonoPlus M500KR, which is a monodisperse, strongly basic, gelular anion exchange resin, nuclear grade. The functional group of $OH^-$ exchange is a quaternary amine, on cross type polystyrene beads. The bead size is specified at (0.64 ± 0.05) mm.

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

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

The choice to use “old” fresh IERS and “new” fresh IERS could lead to some consideration about the degradation of the physical structure and the chemical transformation of the resins due to storage conditions.

### 2.2.4. Total carbon content

The total carbon content of the resins was measured for both the freshly produced resins and the aged ones. Drying processes were avoided because it may insert some variables in the analysis, so the resins are both wet and their storage conditions are similar. The water content was not measured.

The resins were combusted at 900 °C – see Figure 8 – in a mixture of oxygen/helium by an elemental combustor system, recently acquired [BUCUR *et al.*, 2015] and the produced $CO_2$(g) was trapped in an activated charcoal trap and subsequently released for the measure by a thermal conductivity detector (TCD, see Figure 8).

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

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

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

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

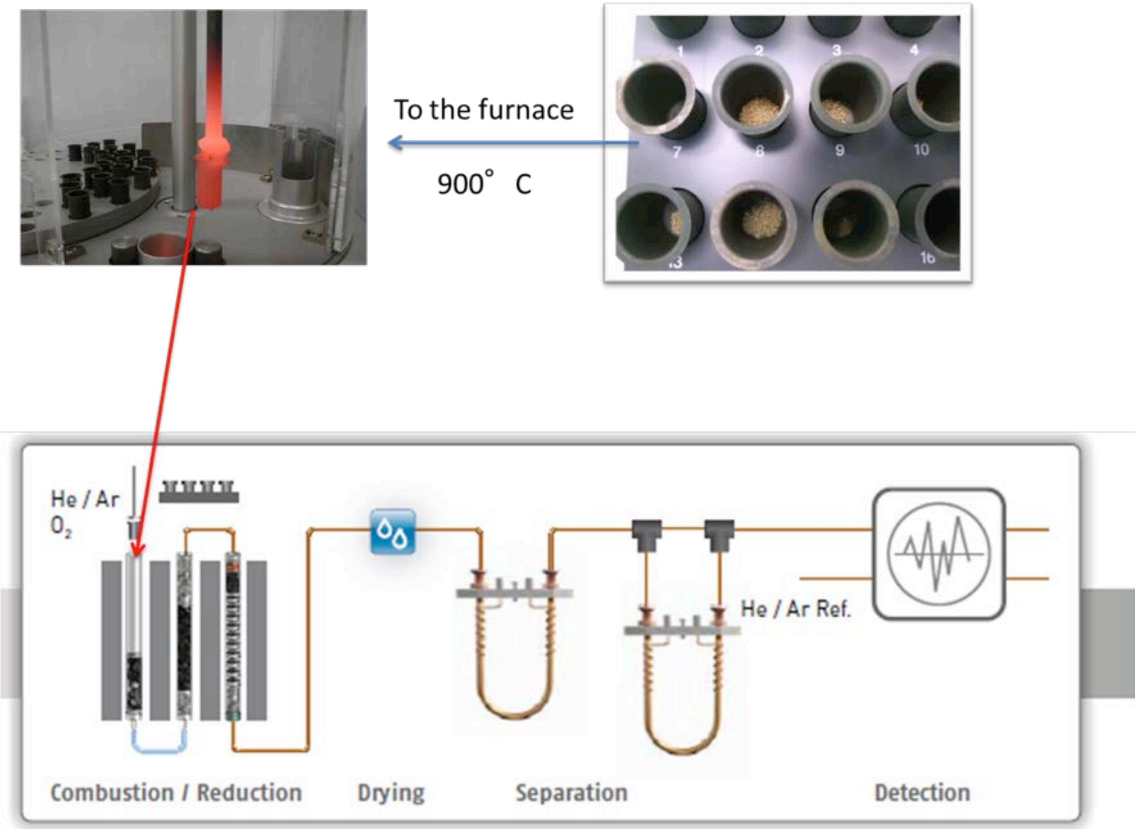

**Figure 8. Combustion and separation systems for the total carbon content – samples in the figure are inactive resins.**

**Table 12. Total carbon and nitrogen obtained after combustion of the different samples.**

| Sample | %C | dev. %C | %N | dev. %N |
|---|---|---|---|---|
| **M500 aged** | 41.226 | ± 0.076 | 3.338 | ± 0.030 |
| **M500 new** | 33.809 | ± 0.224 | 2.552 | ± 0.025 |
| **S100 aged** | 25.358 | ± 0.064 | 0.018 | ± 0.003 |
| **S100 new** | 28.115 | ± 0.223 | 0.0018 | ± 0.003 |

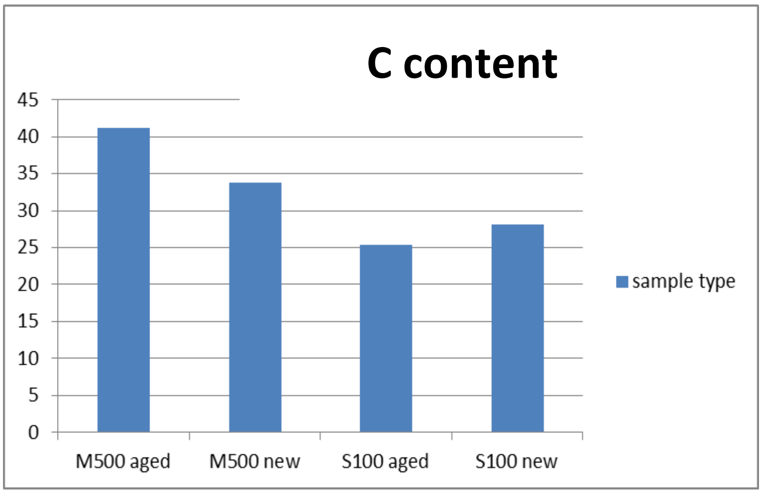

**Figure 9. Carbon content of new and aged resins.**

### 2.2.5. Ageing effect on the morphology of the IERs

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

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

One of the key parameters for the efficiency assessment of ion exchange resins, especially as far as the $^{14}C$ containment is concerned, is the preservation of their spherical shape in time. The preservation of the spherical symmetry implies that the original structure of the resins (backbone and functional groups) stays fixed during the storage. The loss of symmetry is related to the loss of materials and consequently to the decomposition of terminal groups, production of debris, corrosion of the external layers. Isotopic exchanges of $^{14}C$ between original carbon content in the resins and carbon content of surrounding materials could be enhanced during these degradation processes. “Sphericity” is defined as the measure of the amount of ion exchange resin beads that are unbroken. The assessment of the sphericity reservation along time is a purely qualitative index, but could give some understanding of the general behaviour.

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

The Figure 10 shows the typical appearance of an anionic beads specimen. Large scale images such as the one depicted have been used for the diameters assessment.

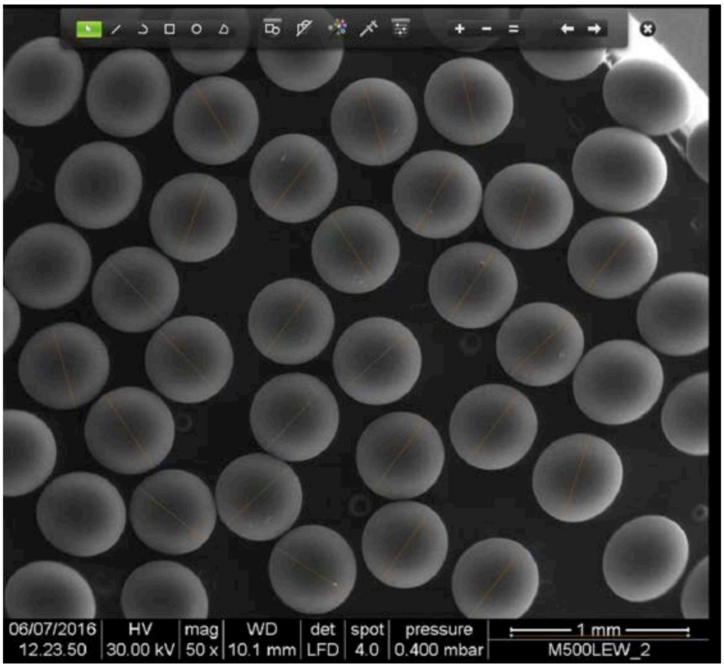

**Figure 10. 1mm scale SEM image of anionic resin beads (M500KR).**

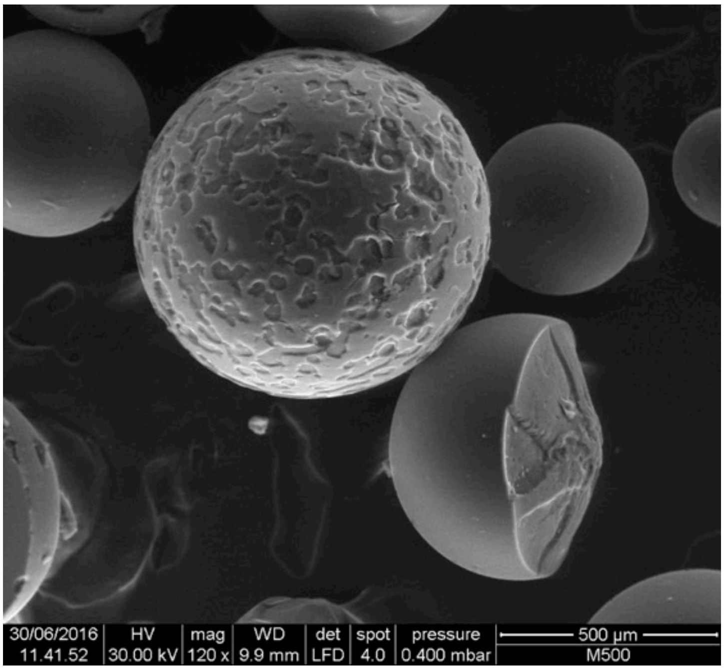

**Figure 11. 500 µm scale SEM micrography of anionic resin.**

Figure 11 represents an aged specimen of the same anionic resin, appearing heavily damaged. In Figure 11 the three degrees of sphericity degradation are apparent: some spheres are still intact, the foreground one is still spherical but with a clear surface corrosion, the right one shows a large material loss, ending in a shape loss. The aged samples appear, macroscopically, as full of random dimensions debris, hardly contained by storage filters, designed for the original beads diameters.

Figure 12 shows an aged sample of the cationic resin, which appears less damaged when compared to the anionic one.

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

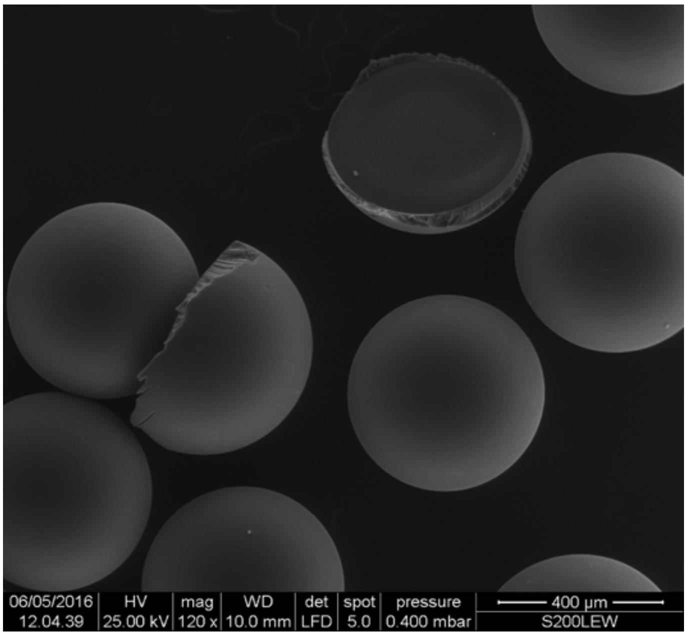

**Figure 12. Aged cationic beads.**

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

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

We associated a colour code to each definition (Figure 13).

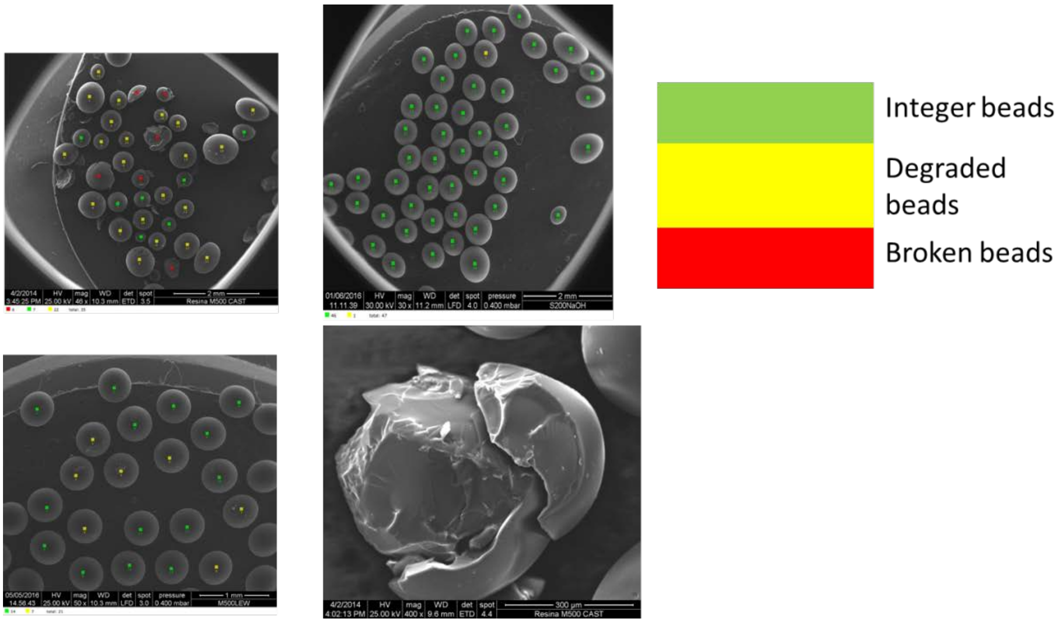

Figure 13. Colour table classification of the beads according to their morphology

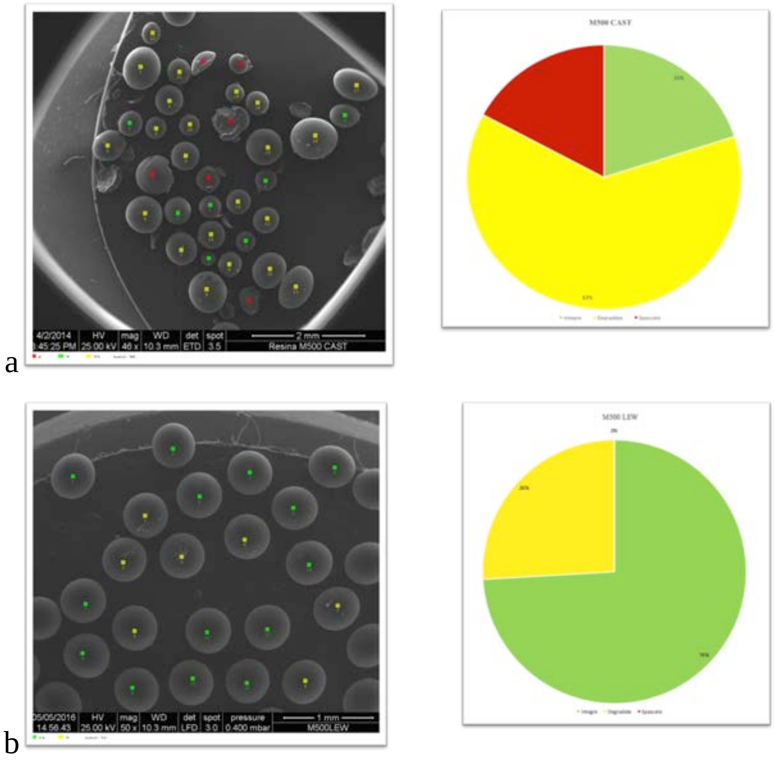

Figure 14. Classification of anionic aged (a) and new (b) resins M500. Color code on Figure 13.

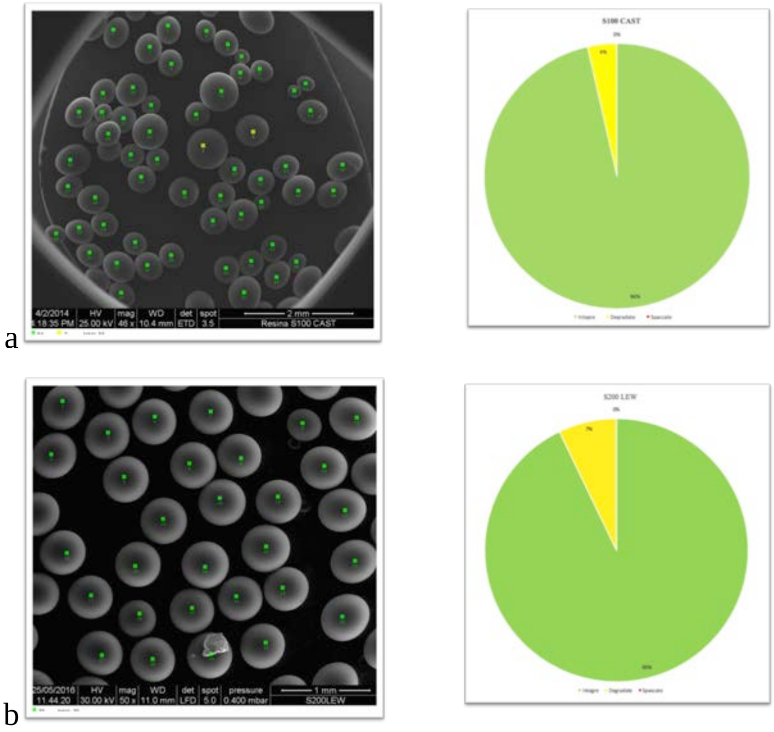

**Figure 15. Classification of cationic aged (a) and new (b) resins S200. Color code on Figure 13.**

Figure 16 summarizes the diameters evolution in time of the two resins. The sheets' specified diameters are confirmed, with small variations from sample to sample: diameters are globally preserved in time, with small variations.

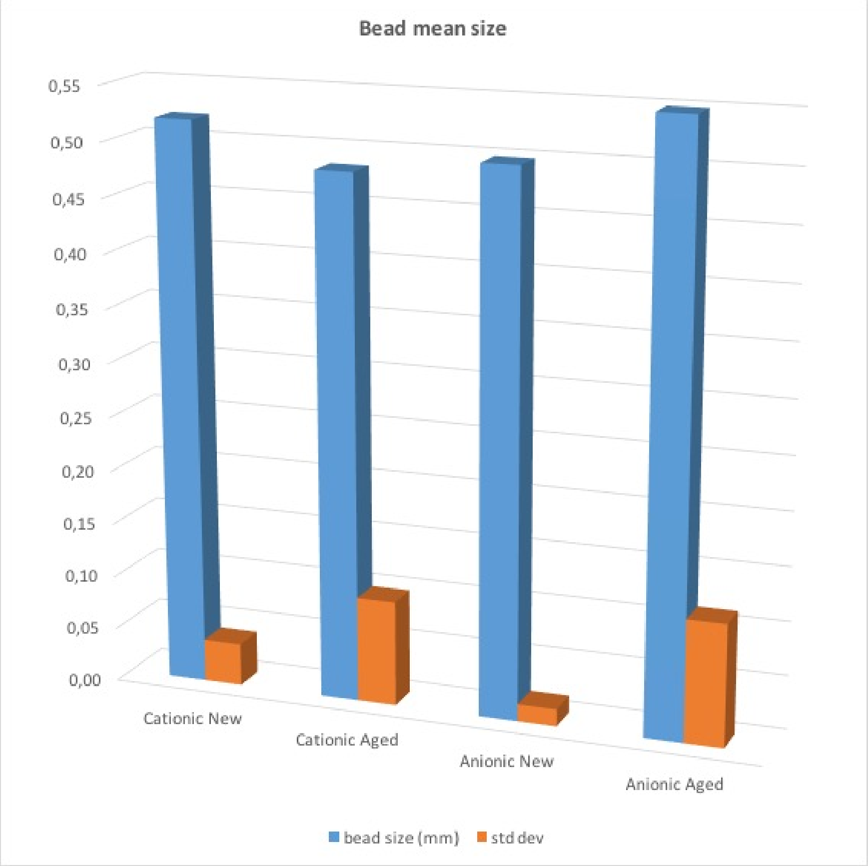

**Figure 16. Comparison of bead mean diameters for new and aged resins**

Analysing the full set of images, it shows up that the “new” – unused – cationic resin shows a better resistance to ageing. The amount of damaged beads reaches the 21% of the total in the anionic, whilst only the 8% in the cationic one.

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

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

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

## 2.3. *FZJ*

Forschungszentrum Juelich (FZJ) is involved in all tasks of WP4, in particular on $^{14}C$ on SIERs and in the fractions released from (S)IERs used in BWR. Quantitative evaluations of the total, organic and inorganic $^{14}C$ on and released by the resins are going to be performed for the BWR SIERs, similarly to earlier works [MAGNUSSON *et al.*, 2008]. The effect of different conditions, *e.g.* pH, radiolysis, degradation, rehydration, on $^{14}C$ speciation is to be studied. In a first step, the state of the art is drawn from the reported data, which is anticipated to constitute the basis for optimization of further investigations on $^{14}C$ release. This is considered to be a necessary input for the safe assessment of a repository, going beyond the total activity and partitioning of $^{14}C$.

It has to be noted that the work at FZJ, related to WP4, is part of an on-going PhD thesis, which is scheduled to be defended in the beginning of 2017. Authorisation by the PhD candidate is necessary prior to publication or quotation of any results.

### 2.3.1. Progress in Task 4.1

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

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

#### 2.3.1.1. Sample choice

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

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

**Table 13: Summary of the different BWR samples received by FZJ.**

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

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

#### 2.3.1.2. Analytical techniques

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

Analytical development to lower the detection limits for the $^{14}C$-speciation/quantification in solution and in the gas phase has been performed in FZJ. Particular effort was put in the validation of the equipment implied for the gas phase analyses. In detail, the conversion efficiency of organic compounds in the catalyser has been investigated with reference gases

(CO, $H_2$, $CH_4$) at different gas flows. The experimental set-up is reported in Figure 17. A sample of calibration gases (extra pure and certified) has been loaded in a gas mouse at a well-defined pressure. After the background stabilization of the quadrupole mass-spectrometer under argon, a by-pass allows the flowing of the sample through the catalyser. The resulting gas composition was analysed by MS and the conversion efficiency has been calculated. The experiments have been performed with the catalyser at room temperature and at 750°C, in order to have a reliable comparison of the results. The catalyser was regenerated after each experiment.

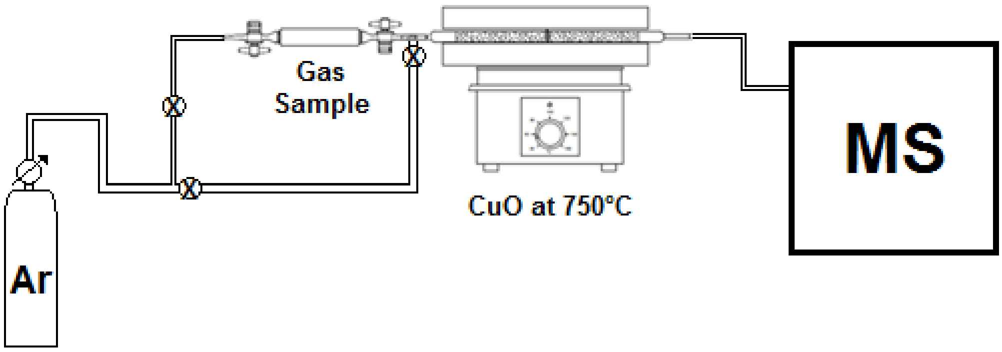

**Figure 17: Experimental set-up for testing the conversion efficiency of the CuO catalyser.**

Pressures of 50, 100, 200, and 350 mbar have been employed for the gas sample preparation in the gas mouse. A flow-rate of about 6 ml/min with 50 g of catalyser resulted in a successful conversion of all the gases. This value has been chosen accordingly to the average flow-rate of the developed washing bottles – see CAST D.4.3 [BUCUR *et al.*, 2015]. In all cases, a total conversion of $H_2$ to $H_2O$ has taken place. The conversion efficiency for CO to $CO_2$ was higher than 99% and the conversion of methane to $CO_2$ was higher than 99% as well. In conclusion, the chosen parameters (*i.e.* temperature of the catalyser, gas flow, amount of catalyser) showed an efficient conversion of the gases at different partial pressures (concentrations).

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

The employment of CuO-Pt/$Al_2O_3$, initially considered, has been abandoned due to the activity retention (memory effect) experienced during leaching tests on graphite. Only CuO has been employed for the catalyser. The washing bottles, positioned after the catalyser, are absorbing the new-formed HTO and $^{14}CO_2$. However, gaseous releases from SIERs could be more complex and variegated than the ones from i-graphite. Therefore, GC-MS has been used for the measurement of the compounds in the gas phase.

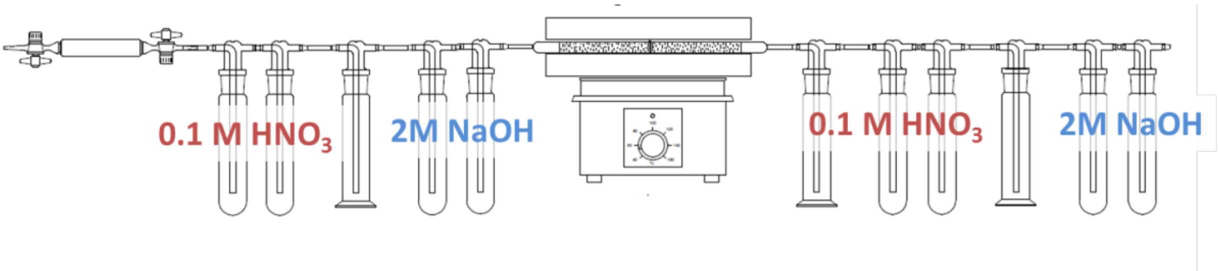

**Figure 18. Experimental setup for the analysis of $^{14}C$ in FZJ, with a catalyser to convert HT to HTO, CO to $CO_2$ and organics to $CO_2$.**

Morphological investigations of (S)IERs are performed with Scanning Electron Microscopy (SEM) and the activity distribution is analysed with Autoradiography (see § 2.3.2, page 30).

It is anticipated that methods like IC, SS-NMR, $^{1}H$-NMR and $^{13}C$-NMR will be applied for the investigation of model SIERs that simulate radiation-induced effects that may alter the speciation of $^{14}C$ (see § 2.3.3, page 35).

### 2.3.2. Progress in Task 4.2

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

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

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

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

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

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

indistinguishably both materials; a separation of the two materials is rather challenging and requires additional efforts and experimental development.

#### 2.3.2.1. Separation of mixed-bed resins

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

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

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

The separation of mixed-bed ion-exchange resins was performed following the ASTM standard method 2187. Mixed-bed resins are put in a column and backwashed with 100 g/L NaCl solution. The anion-exchange resins are separated from the cation-exchange resins. The method is efficient only for resins in bead form.

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

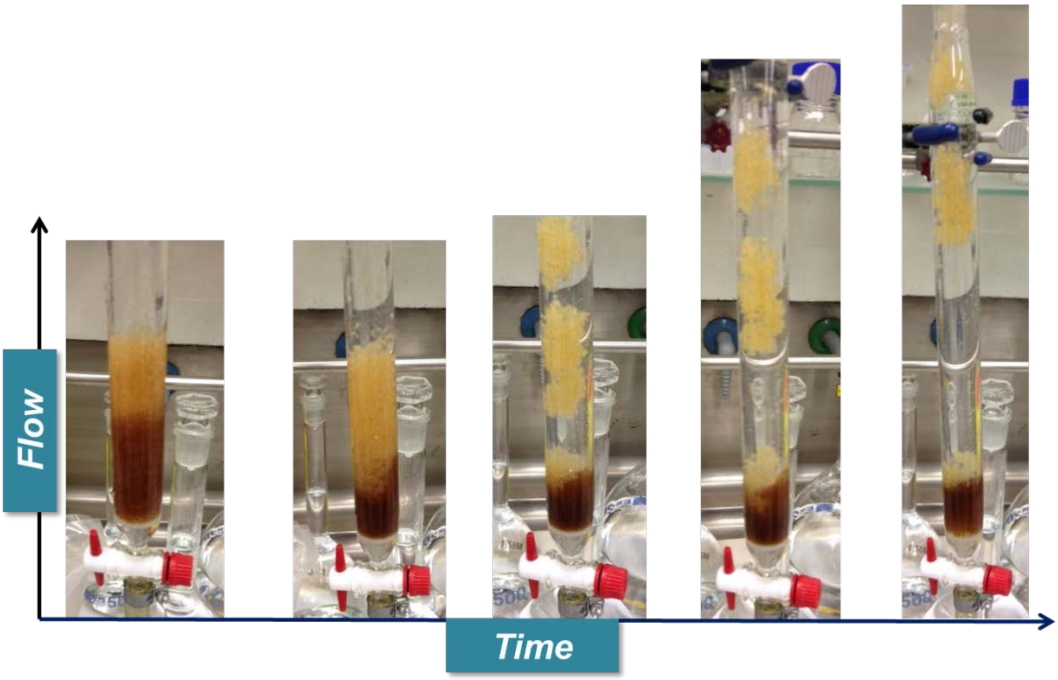

**Figure 19. Separation of mixed bed resins in bead form**

#### 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 and fresh IERs – see CAST D.4.3 [BUCUR *et al.*, 2015].

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

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

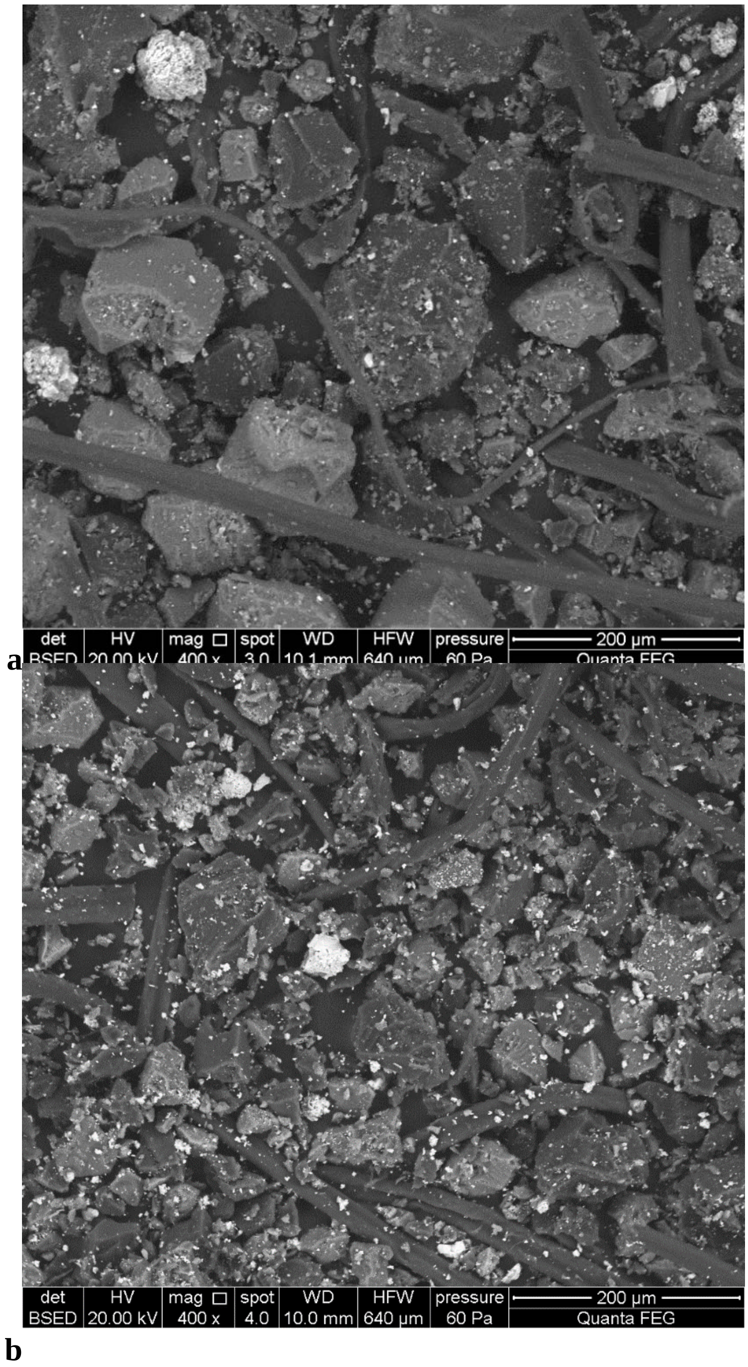

**Figure 20. Powder SIERs from FZJ-A (a) and FZJ-B (b) (with particulate matter and acrylic fibers)**

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

### 2.3.3. Progress in Task 4.3

#### 2.3.3.1. Generation of gases and degradation of SIERs

The generation of gases during the storage and degradation of SIERs from BWR in different waste forms has been investigated by FZJ following different approaches:

- Experiments on the SIERs

  Leaching/storage experiments in different conditions and evaluation of organic and inorganic $^{14}$C fraction have been performed. The experimental work for this task focused on the samples FZJ-A and FZJ-B. Evaluation of the results is in progress. At the present state, a release of mainly – if not exclusively – inorganic $^{14}$C has been measured, in relation to the sample age, storage temperature and storage atmosphere. The results have been obtained by means of LSC (with optimized washing bottles) and GC-MS.

- $^{14}$C speciation on and released by SIERs has been simulated by loaded IERs exposed to γ-radiation

  A dedicated γ-irradiation campaign has been performed and the corresponding equipment has been developed (vials and sampling of the gas phase). Resin samples, fresh or loaded with carbonates, have been exposed to γ-radiation in aerobic conditions (see Figure 21). First analyses on the gas and liquid phase of irradiated samples have been completed and evaluation of the results has been performed. It is confirmed that organic compounds of different nature are released, depending on the dose, presence of water and ionic form of the resins, both in solution and in the gas phase. Techniques like IC, $^{1}$H-NMR, $^{13}$C-NMR have been employed for the analyses of the solution. GC-MS has been used for the analyses of the gas phase and the solid phase has been investigated by $^{13}$C-SS-NMR. Additionally, morphological analyses and the determination of the residual exchange groups have been performed. The results obtained from these 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 the understanding of the γ-induced degradation processes. The characterization of the γ-irradiated could allow for a link between the simulated and the real waste (SIERs). Additionally, molecular dynamic simulations could clarify some primary degradation processes, induced by γ-radiation.

**Figure 21. Sample vials filled with anion exchange resins and water, before (left) and after irradiation (right).**

The results reported here, together with their interpretation, are part of a doctoral thesis that will be published in the beginning of 2017. The manuscript will be made available on the CAST website.

## 2.4. *RATEN ICN*

During this period, RATEN ICN purchased the catalytic furnace needed to complete the experimental set-up used to measure the inorganic and organic $^{14}C$ in CANDU SIERs and liquids sampled from the desorption tests. Once the experimental set-up was completed, preliminary tests to evaluate the $^{14}C$ decontamination from interfering radionuclides and to assess the efficiency of catalytic furnace were carried out. Also, desorption tests on CANDU SIERs in alkaline solution (NaOH 0.1 M, i.e. pH *approx.* 12.9) were initiated.

Under CAST WP4 RATEN ICN proposed to measure the $^{14}C$ content in CANDU SIERs and its partition between inorganic and organic species and to measure the $^{14}C$ release in liquid phase under disposal conditions. No detailed $^{14}C$ speciation will be performed only the partition between inorganic and organic species.

For the third year of the project, RATEN ICN proposed to work on real CANDU SIERs received from Cernavoda NPP and characterized last year.

The method to be used in measuring the $^{14}C$ partition between inorganic and organic species consists of an acid stripping process combined with wet oxidation. To complete the experimental set-up tested for acid stripping method and start carry out experiments on real resins, a Nabertherm tubular furnace was purchased – at beginning of September 2016 – and tested to evaluate the efficiency of the catalyser used for converting CO and organic carbon to $CO_2$.

After the tests on catalytic furnace efficiency are completed, leaching/desorption tests will be performed to evaluate the $^{14}C$ released in liquid phase during the SERs storage and disposal. Also its partition between inorganic and organic species will be assessed.

Until the catalytic furnace was available, the experimental set-up used to measure the inorganic $^{14}C$ by acid stripping method, and described in the CAST D4.3 [BUCUR *et al.*, 2015], were tested using an IER (IRN-150) labelled with inorganic $^{14}C$ but also other potential interfering radionuclides such as $^{129}I$, $^{3}H$ and $^{137}Cs$.

To evaluate the effect of resin degradation on $^{14}C$ release, sorption and desorption tests on fresh resin and on resin dried at 50 and 80°C, to simulate thermal effect, are ongoing.

### 2.4.1. Preliminary tests to evaluate the $^{14}C$ decontamination from interfering radionuclides

CANDU SIERs contain beside $^{14}C$ other radionuclides that interfere when $^{14}C$ is analysed by LSC, especially $^{129}I$ that would be trapped in NaOH solution together with $^{14}C$ but also $^{137}Cs$. Experimental tests were performed using IRN 150 IER labelled with inorganic $^{14}C$ ($NaHCO_3$), $^{129}I$ (NaI), $^{3}H$ (HTO) and $^{137}Cs$ (CsCl) to evaluate the efficiency of gas washing line in $^{14}C$ decontamination from these interfering radionuclides.

The experimental set-up used in these experiments was described in CAST D4.3 [Bucur *et al.*, 2015], but the gas washing line was completed with one more gas washing bottle. The gas washing line used in these tests consists in 5 glass washing bottles with glass frit:

- bottle #1 is a tritium trap and contains 50 mL of 5% $H_2SO_4$;
- bottle #2 is a iodine trap and contains 50 ml of 0.1 M $AgNO_3$;
- bottles #3 and #4 are $^{14}C$ traps and contain 50 ml of 2 M NaOH each;
- bottle #5 is filled with 100 ml of 2 M NaOH and used as a safety bottles.

The labeled IER sample (0.5 g wet resin) was introduced in the reaction vessel (a 250 ml Erlenmeyer flask with a three-hole rubber stopper for gas and separatory funnel inlets and gas outlet) together with 30 ml of NaOH 2M. Both for $^{14}C$ and $^{129}I$, carriers (100 mg) in form of $NaHCO_3$ and NaI respectively, were added together with IER in the reaction vessel. After a vacuum of - 0.2 bar was reached and the carrier gas ($N_2$) was introduced in the system, 25 ml of $H_2SO_4$ 6 M was added to the reaction vessel through the separatory funnel. To ensure the complete absorption of the released gases, the nitrogen was flushed for 2 hours at flow rate of *approx.* 100 ml/min.

At the end of the test, parallel samples were collected from each gas washing bottles and also from the reaction vessel to quantify the activity of the radionuclides used to label the IER sample. For $^{14}C$ and tritium measurement by LSC Hionic Fluor scintillation cocktail and respectively UltimaGold AB respectively were used.

The result showed good radionuclide separation. Neither $^{137}Cs$ nor $^{129}I$ were identified in the washing bottles used to collect the released $^{14}C$. A subsample of the washing bottle solution was analysed by γ-spectrometry using a GeHp detector to check for the presence of $^{137}Cs$. A few milliters of $AgNO_3$ solution were added to a subsample of the washing bottle solution in order to precipitate any iodide. No precipitate were observed in these solutions, even after the samples were centrifuged at 4000 rpm for 1 hour.

### 2.4.2. Experiments to assess the efficiency of catalytic furnace

The $^{14}C$ partition between inorganic and organic species in CANDU SIERs, but also in the solutions collected from the leaching tests, will be measured by acid stripping/wet oxidation method. To complete the experimental set-up previously described and tested for the acid stripping step, a catalytic furnace has to be used. It consists in a tubular furnace (Nabertherm) with a quartz tube with the catalyser used to oxidise the organic carbon – and eventually tritium and iodine –, at 750°C (Figure 1). A mixture of CuO and $Pt/Al_2O_3$ is used to convert CO(g) and organic carbon to $CO_2$(g), HT to HTO, and also organic iodine. Organic iodine is converted to $I_2$(g), which is trapped in an iodine trap ($NaHSO_3$-$AgNO_3$).[*] Up to now no precipitation of AgI(cr)[†] has been observed for the Cernavoda samples.

**Figure 22. The experimental set-up to assess the efficiency of catalytic furnace at INR**

Before using this catalytic furnace in acid stripping/wet oxidation tests on CANDU SIERs, it was tested to evaluate its efficiency in converting organic carbon species to inorganic ones. Since the tubular furnace purchased has a long heating tube also the quartz tube is also quite long (*approx.* 90 cm) and it was filled only on *approx.* 15 cm with catalyser (70% CuO and 30 % $Pt/Al_2O_3$ by weight), which was placed between two quartz wool inserts.

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[*] Reduction of dissolved $I_2$ by $S_2O_3^{2-}$ and precipitation by AgI.

[†] Solubility of *approx.* $10^{-8}$ mol/L.

The $^{14}C$ used in this first set of tests was in form of sodium acetate ($CH_3{}^{14}COONa$). To have a better control of the $^{14}C$ quantity introduced in the reaction vessel, the tests were carried out using a solution of $CH_3{}^{14}COONa$ in reaction vessel not an IER sample labelled with $^{14}C$, but in the next tests a labelled IER will be used.

Since in these tests only the organic $^{14}C$ was introduced in the reaction vessel, the gas washing line used to collect the inorganic $^{14}C$ released in the acid stripping step (placed before the catalytic furnace) was bypassed and only three gas washing bottles placed after the catalytic furnace were used. These were filled with 100 ml of 2 N NaOH solution.

10 ml of $^{14}C$ solution were introduced in the reaction vessel together with 100 mg of carrier (inactive sodium acetate) and 30 ml of 2N NaOH solution. When the system was ready to start the experiments (the vacuum of -0.2 bar, $N_2$ flow and the tubular furnace had reached the desired temperature), 25 ml of $H_2SO_4$ were added through the separating funnel. After 20 minutes, the reaction vessel was heated at 90°C and 40 ml of 5% $K_2S_2O_8$ and 4 ml of 4% $AgNO_3$ were added through the separating funnel. The oxidation process was repeated after one hour and the gas was flushed through the system for two more hours.

A few similar tests were performed and in all tests the $^{14}C$ recovery was between 88% and 92% (with an average of 89%). From the recovered $^{14}C$, 82.25 % was found in the gas washing bottles #1, 16.17 % in washing bottles #2, and 1.57 % in washing bottles #3. Around 0.11 % of $^{14}C$ remained was found in the reaction vessel.

Further tests will be carried out to optimize this process. Once the conversion efficiencies of the catalyser will be improved, the experimental set-up will be used first on a resin sample labelled with the main radionuclides found in CANDU SIERs to measure their recovery and after that tests will be performed on the real SIERs.

## 2.5. *SKB*

Since the last annual report SKB has further analysed the available data from the Swedish $^{14}C$ sampling and analysis program. This is done in an attempt to find the reactor operating factors that influences the uptake of $^{14}C$ on the SIERs. The reactors in Sweden have been in operation for about 30-40 years. During these years the operation parameters such as SIERs operation times, anion equivalents used, reactor cooling water flow and condensate water flow has varied. The work has now been finalized and summarised in two reports. The first report summarises the results sampling campaign that has been ongoing 2008-2015. A model is derived which can be used to calculate historical and future $^{14}C$ accumulation in the waste. The second report uses the derived model to calculate historical $^{14}C$ content in the waste for each reactor up to and including 2014. The model is also applied to calculate future amounts of $^{14}C$. The $^{14}C$ content is divided into organic and inorganic form, which is essential for the safety assessments performed by SKB. The primary uptake of $^{14}C$ on the SIERs depends on the anion equivalents used in the IERs as well as the water flow through the IERs. Downstream processing such as wet storage and stirring techniques (air bubbling) influences the final amount of $^{14}C$ in waste packages. Downstream processing depends on the design of each reactor waste treatment facility hence it is reactor specific. The two reports will be uploaded on the public CAST website by the end of January 2017 depending on the authorisation from the NPPs.

## 2.6. *ÚJV*

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

### 2.6.1. Resins from nuclear reactor operation

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

#### 2.6.1.1. EDU SIER

Spent ion exchange resins from Dukovany PWR Nuclear Power Plant (EDU) operation were sampled in 1998. Unfortunately there is no detailed information about the sample – date, place, procedure of sampling, conditions… The sample was stored sample was wet and contained impurities, sediments and mud (see Figure 23). Therefore it was necessary to separate resins beads from impurities and mud by rinsing and decantation. Separated resins were then used for desorption/leaching experiments.

The rinsing distilled water was analysed to evaluate if any $^{14}$C was released during the rinsing and decanting. It was found, that no $^{14}$C species were released from EDU spent resin into the water during this process. EDU resin was analysed to obtain activities of $^{14}$C in total and as organic and inorganic species and also of other major radionuclides (see Table 14). Other major radionuclides $^{60}$Co and $^{137}$Cs were observed.

**Figure 23. SIER from Dukovany Nuclear Power Plant operation**

**Table 14. $^{14}$C and other major radionuclides activity in EDU SIER. The mass of IER is referring to dry resin**

| Nuclide | Activity (Bq/g) |
|---|---|
| $^{14}$C (total) | 48 ± 6 |
| $^{14}$C (inorg.) | 14 ± 2 |
| $^{14}$C (org.) | 34 ± 5 |
| $^{60}$Co | 140 ± 8 |
| $^{137}$Cs | 22 ± 3 |

#### 2.6.1.2. ETE SIER

SIERs from Temelín PWR Nuclear Power Plant (ETE) operation were sampled in 2013. Unfortunately there is no detailed information about the sample (date, place, procedure of sampling, conditions etc.). Stored sample was stored wet and contained some impurities (see Figure 24) that were removed before using resin in experiments.

ETE resin was analysed to obtain activities of $^{14}$C in total and as organic and inorganic species and also of other major radionuclides (see Table 15). Other major radionuclides $^{125}$Sb, $^{137}$Cs, $^{125}$I, $^{134}$Cs, $^{51}$Cr, $^{40}$K and $^{60}$Co were observed.

**Figure 24. SIER from Temelín Nuclear Power Plant operation**

**Table 15. $^{14}$C and other major radionuclides activity in ETE SIER (dry resin)**

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

#### 2.6.1.3. ÚJV SIER

A sample of spent ion exchange resins from research reactor of ÚJV Group (UJV) which is located in Řež was available. There is no detailed information about sampling of this SIER:

date, place, procedure of sampling, conditions etc. The stored sample was wet and without impurities (see Figure 25).

**Figure 25. SIER from ÚJV Group research reactor operation**

The ÚJV resin was analysed to obtain activities of $^{14}C$ in total and as organic and inorganic species and also of other major radionuclides (see Table 16). Other major radionuclides $^{60}Co$ and $^{108m}Ag$ were observed.

**Table 16. $^{14}C$ and other major radionuclides activity in ÚJV SIER (dry resin)**

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

### 2.6.2. Desorption experiments

For desorption experiments of real resins samples two resins with different total $^{14}C$ activity were chosen, the ÚJV SIER and EDU SIER. Spent ion exchange resins from ETE had comparable $^{14}C$ activity to EDU SIER (43 vs. 48 Bq/g), so that only one SIER from NPP reactor operation was used. Activity of $^{14}C$ in second sample for desorption experiments, ÚJV SIER, is order of magnitude higher (2000 Bq/g).

In desorption experiments two types of liquid media were used, synthetic granitic water (SGW) and sodium hydroxide solution. Laboratory prepared SGW [HAVLOVÁ *et al.*, 2010] is based on a statistical evaluation of Czech granitic massif groundwaters for depths 20-200 meters, NaOH solution represent the alkaline solution simulating the leachate from cement/concrete environment of repository or fixation matrix. Concentration of sodium hydroxide solution was 0.02 M with pH 12.7 and chemical composition of SGW is given in Table 17 – amount of salt used in Table 18: theoretical pH of 8.11.

**Table 17. Synthetic granitic water (SGW, pH approx. 7.8-8.1) chemical composition**

| **SGW compound** | **$Na^+$** | **$K^+$** | **$Ca^{2+}$** | **$Mg^{2+}$** | **$Cl^-$** | **$SO_4^{2-}$** | **$NO_3^-$** | **$HCO_3^-$** | **$F^-$** |
|---|---|---|---|---|---|---|---|---|---|
| concentration (mg/L) | 10.6 | 1.8 | 27.0 | 6.4 | 42.4 | 27.7 | 6.3 | 30.4 | 0.2 |

**Table 18. Salts for SGW preparation**

| Salt | mg/L |
|---|---|
| $NaHCO_3$ | 38.0 |
| $KHCO_3$ | 4.61 |
| NaF | 0.44 |
| $CaCl_2$(anh.) | 66.37 |
| $CaSO_4:2H_2O$ | 13.03 |
| $MgSO_4:7H_2O$ | 52.43 |
| $Mg(NO_3)_2:6H_2O$ | 13.02 |

In desorption experiments solid/ liquid ratio S/L = 1/20 was used, that means using 10 ml of liquid phase and 0.5 g of dry resin. Because stored resins were wet, moisture content was determined. For all types of resins samples moisture content was 66% in average. For experiments wet resins were weighed, so 0.5g of dry resin = 1.5g of wet resin. Interaction of solid and liquid phase in desorption experiments were performed for the period of one month. Experiments were performed in duplicate. After desorption the activity of $^{14}C$ in solution was determined by liquid scintillation counting (LSC).

#### 2.6.2.1. EDU SIER desorption experiments

As can be seen in Figure 26 desorption experiments of EDU SIER shows almost constant release of $^{14}C$, which was measured by LSC. Desorption experiments were performed in duplicates. The activity of the $^{14}C$ in leachate is approximately 2-3 times higher than activity of blank/background (*approx.* 80-140 cpm) in all sampling intervals. Results showed, that EDU spent resins evinced some instant release fraction of $^{14}C$ species, which was released in one day and was constant throughout month experiment in both desorption liquid media, NaOH solution and SGW.

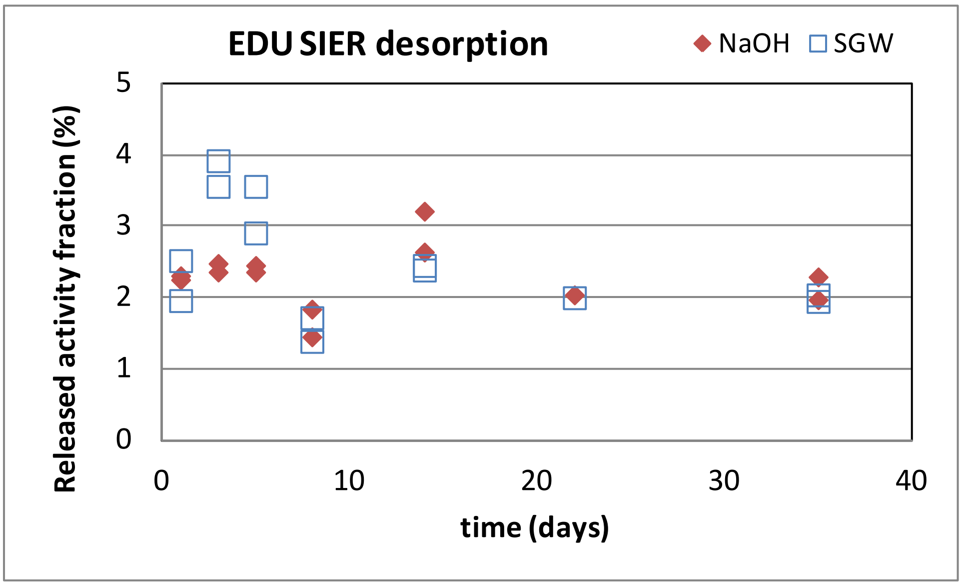

**Figure 26. Desorption experiments of EDU spent resins in NaOH or SGW solutions**

#### 2.6.2.2. ÚJV SIER desorption experiments

Experiments studied desorption of $^{14}C$ were also performed on ÚJV spent resins. The activity of $^{14}C$ released during desorption experiments is shown in Figure 27. In the first week of interaction with liquid phases, the released amount of $^{14}C$ increased, and after one month of interaction, activity of $^{14}C$ in liquid phases was stabilised at *approx.* 100 cpm, which is approximately 2 times higher than activity of blank/background (*approx.* 45 cpm).

Results showed, that ÚJV SIERs evinced some instant release fraction of $^{14}$C species, which was released during the first week of the experiments and that after this time the concentration in solution stayed constant during the one month experiment in both desorption media, NaOH solution and SGW.

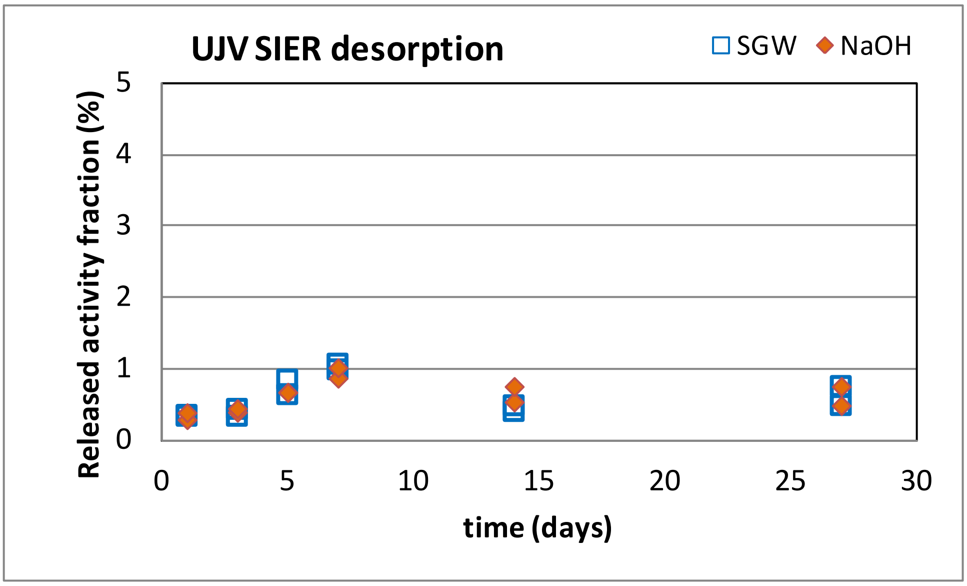

**Figure 27. Desorption experiments of ÚJV spent resins in NaOH or SGW solutions**

#### 2.6.2.3. Results

Both spent ion exchange resins (EDU, ÚJV) used in desorption experiments shows some instant release fraction of $^{14}$C. Even though there is difference in total $^{14}$C activity in EDU and ÚJV SIERs – *approx.* 40 times higher in ÚJV SIER –, the released $^{14}$C activity during all desorption experiments is similar and it is independent of the total $^{14}$C activity in SIER (see Figure 28). In comparison of released fractions of $^{14}$C from SIERs (Figure 26 and Figure 27) it can be seen that the ratio of released activity is lower for ÚJV SIER, because of higher activity of total $^{14}$C in this spent resin.

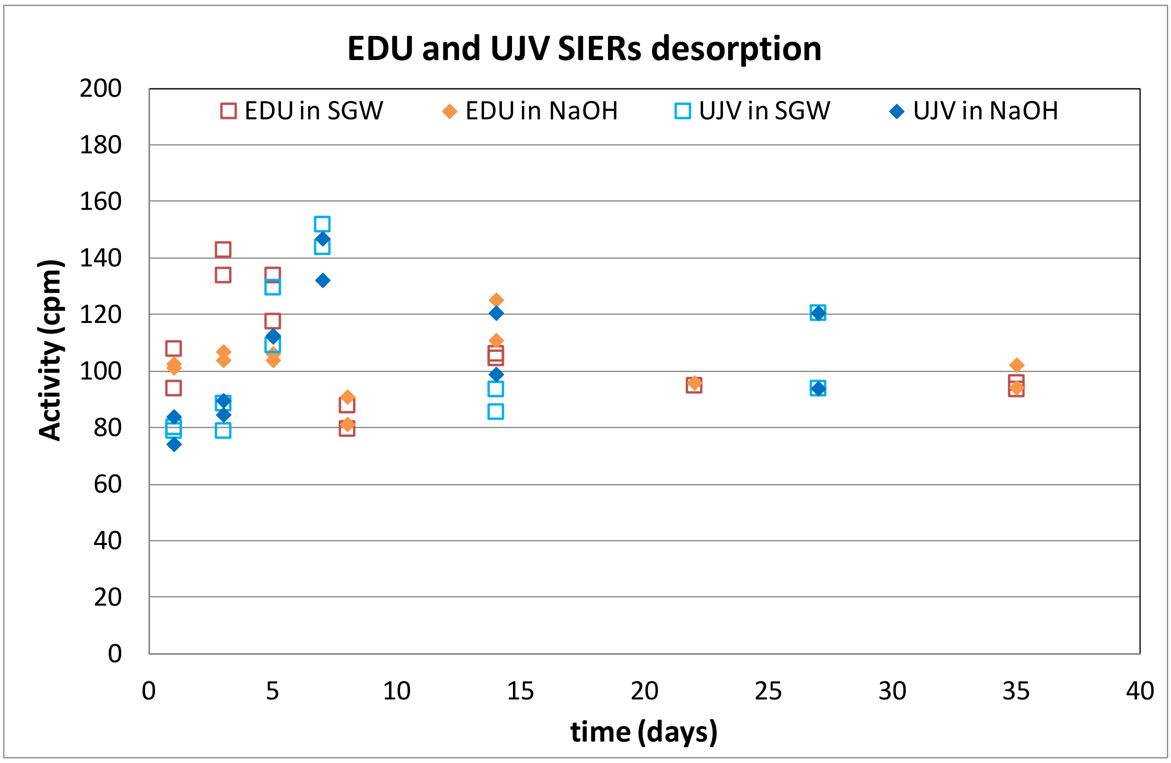

**Figure 28.** $^{14}C$ **activity in leachate in desorption experiments of EDU and ÚJV spent resins in NaOH or SGW solutions**

### 2.6.3. Fixation into cement matrix

One of the goals of the experimental work was to test the possibility of SIERs fixation into the cement matrix. For these tests laboratory prepared samples of ion exchange resins with sorbed $^{14}C$ in form of hydrogenocarbonate were used. In laboratory $H^{14}CO_3$ was sorbed on Amberlite resin in OH form. The adsorbed activity of $^{14}C$ was 6500 Bq/g of dry resin. Cement CEM II/A-S 42,5 R (Lafarge Cement a.s. - Čížkovice, Czech Republic) was used as the fixation matrix. Cylindrical samples (diameter: 26mm; height: 55mm) were prepared from cement/resin mixture (cement/resin ratio = 10/1; water/cement ratio = 0.6). Prepared cylindrical testing samples were let hardened for 28 days in 100% relative air humidity. After the hardening cylindrical testing samples were Samples were visually checked, if they are solid, homogeneous with smooth surface and without cracks.

During the fixation of SIERs into the cement matrix, there is a risk of structural failure of prepared solidified specimens, mainly by shrinkage/swelling of resins beads and by the chemical interactions of resins and cement. By choosing of correct cement type and limiting the amount of fixed resins the risk of damage of prepared samples can be eliminated.

Prepared testing samples of solidified SIERs in the cement matrix showed very good structural integrity, no prepared testing sample showed evidence of damages or was destroyed. Thus, fixation of ion exchange resin into the cement matrix was successfully tested and cement CEM II/A-S 42,5 R was verified as suitable matrix for fixation of testing Amberlite resin at 1:10 loading of resin:cement.

### 2.6.4. Leaching experiments

Leaching experiments were performed based on ANSI/ANS-16.1 method [ANSI/ANS, 2003]. Solidified spent ion exchange resins fixed in cement matrix are leached by liquid media in defined solid sample surface/volume of liquid phase ratio. For quantification of the leaching characteristics of solidified wastes leachability index and effective diffusivity can be calculated. Effective diffusivity ($D$) can be evaluated by equation (1):

$$D = \pi \left[ \frac{\alpha_n / A_0}{(\Delta t)_n} \right]^2 \left[ \frac{V}{S} \right]^2 T \tag{1}$$

where $V$ is a volume of specimen, $S$ is the surface area of specimen, $T$ is the leaching time, $\alpha_n$ is the quantity of a radionuclide released from the specimen during leaching interval $n$, $(\Delta t)_n$ is the cumulative leaching time, $A_0$ is the tracer amount after 30 s rinsing.

In performed first testing experiment cylindrical testing sample, prepared as described in previous text, was leached in distilled water. The ratio was: liquid volume ($cm^3$)/sample surface ($cm^2$) = 10 (cm). After each time interval (0.5; 3; 4; 5; 6; 7; 14; 30; 60 and 90 days) total amount of liquid phase was replaced by fresh one and in the total $^{14}C$ activity was determined in the leachate. As it is shown in Figure 28 activity of $^{14}C$ in leachate is at the same level as blank measurement (orange line). Due to no release of $^{14}C$ to the liquid phase it is not possible to evaluate the leachability or diffusion coefficient.

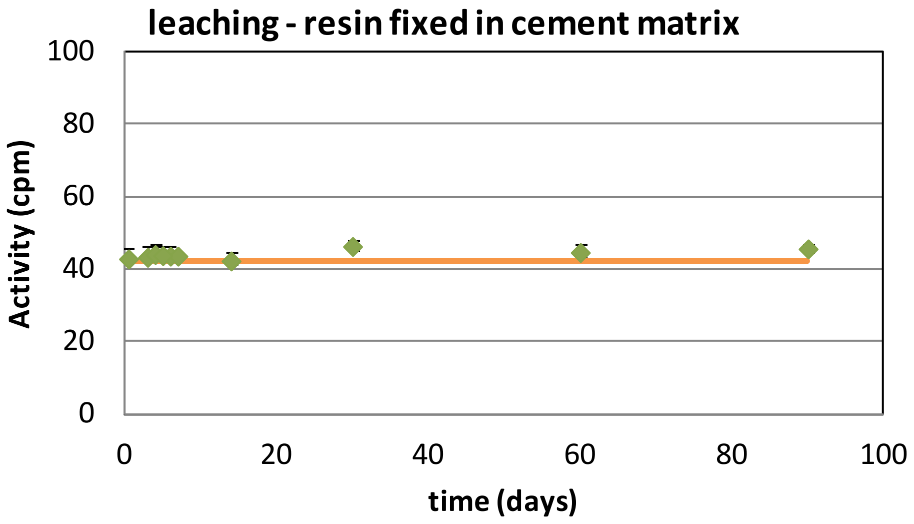

**Figure 29. $^{14}$C activity in the leachate, first leaching test with distilled water**

In second type of leaching experiments three different liquid phases were used: distilled water, SGW and 0.02M NaOH. Because of very low leaching of $^{14}$C in the first testing experiment, the ratio of liquid volume/sample surface was decreased to 5. The design of this set of leaching test was to increase the concentration of leached radionuclide by decreasing of liquid phase volume. All experiments were performed in triplicates. In every leachate collected during the tests values of pH and conductivity in liquid phase were measured. Data obtained for activity measurements in leachate in experiment with distilled water, SGW and 0.02M NaOH solution are shown in Figure 29, Figure 31, and Figure 33. Orange line in graphs represent the value of blank activity. The behaviour of conductivity and pH values in the leachate during the tests is shown in Figure 30, Figure 32 and Figure 34. Values of blank activity, conductivity and pH for distilled water, SGW and 0.02M sodium hydroxide solution are shown in Table 18.

**Table 19. Blank activity, conductivity and pH values for experimental liquid phases**

| liquid phase | activity (cpm) | conductivity (µS/cm) | pH |
|---|---|---|---|
| distilled water | 47 | 19.5 | 5.5 |
| SGW | 41 | 370 | 8.1 |
| 0.02M NaOH | 46 | 5200 | 11.7 |

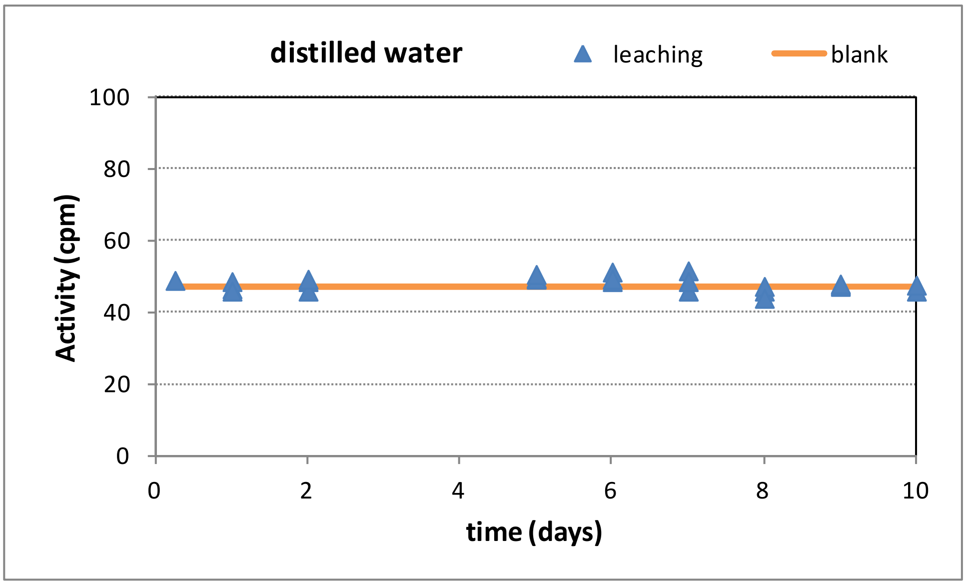

**Figure 30. Activity of $^{14}$C in the leachate; test with distilled water.**

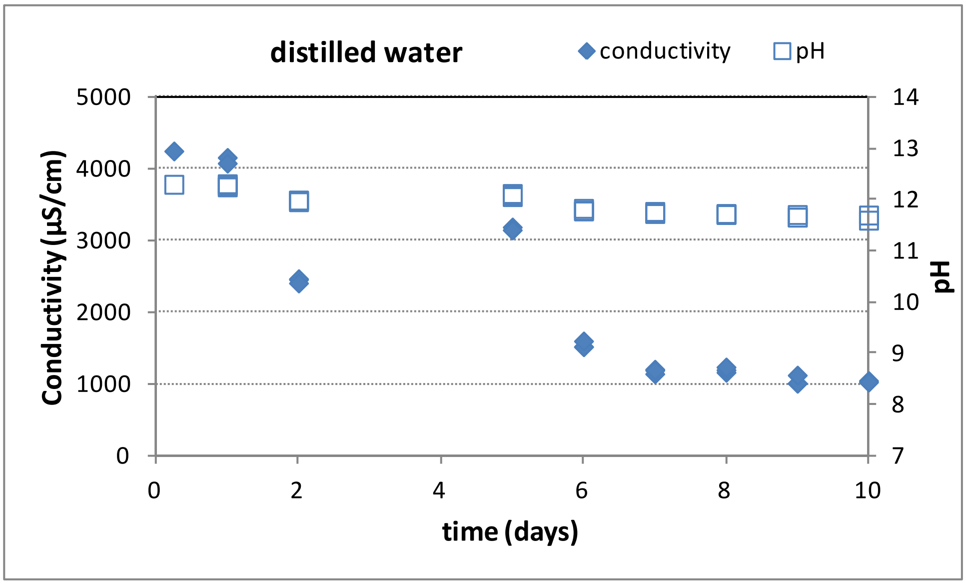

**Figure 31. Conductivity and pH values in the leachate; test with distilled water.**

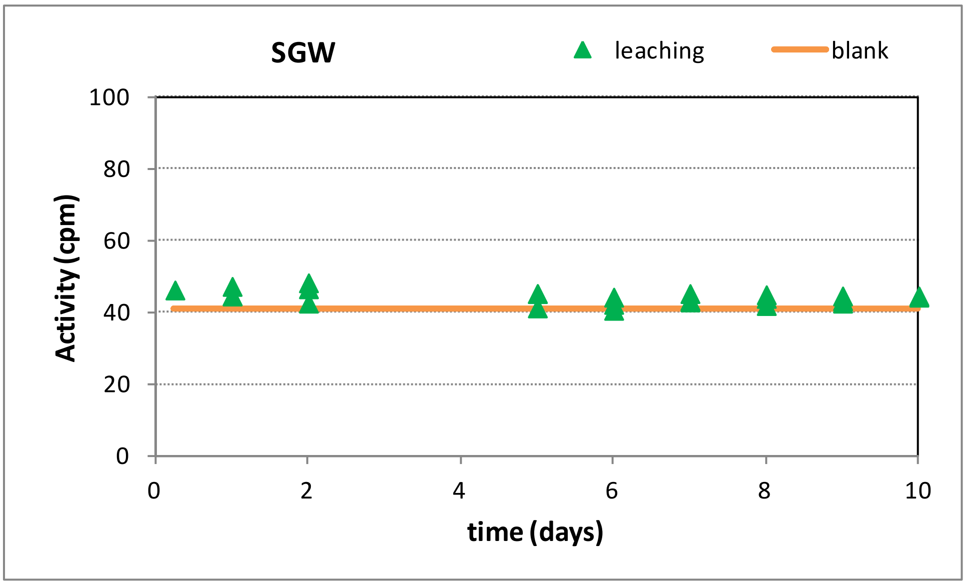

**Figure 32. Activity of $^{14}$C in the leachate; test with synthetic granitic water.**

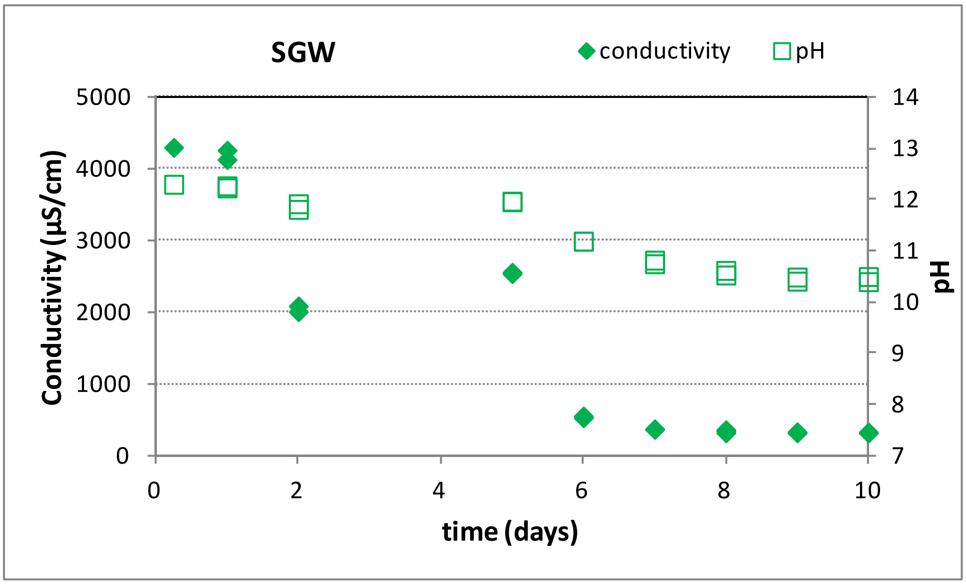

**Figure 33. Conductivity and pH values in the leachate; test with synthetic granitic water.**

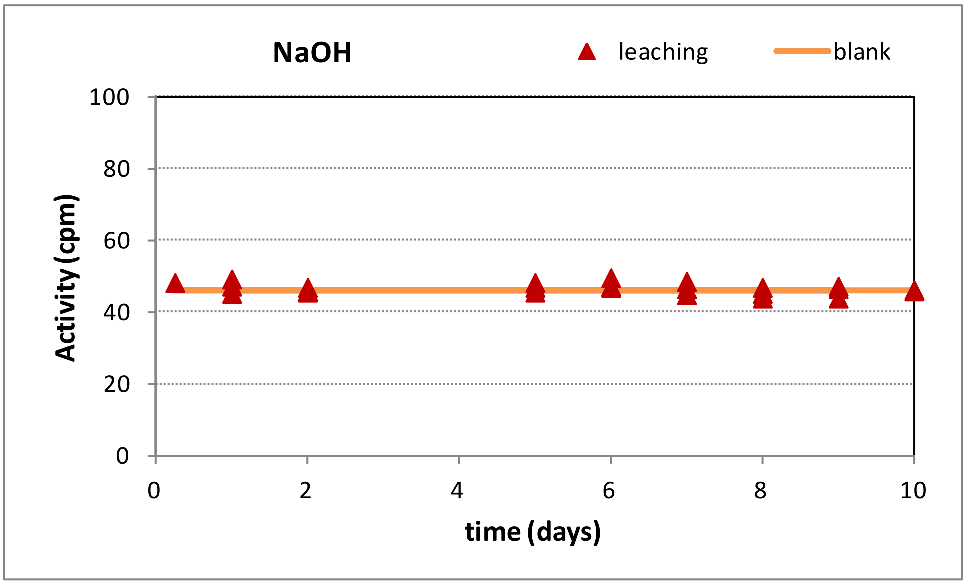

**Figure 34. Activity of $^{14}C$ in the leachate; test with 0.02M NaOH solution.**

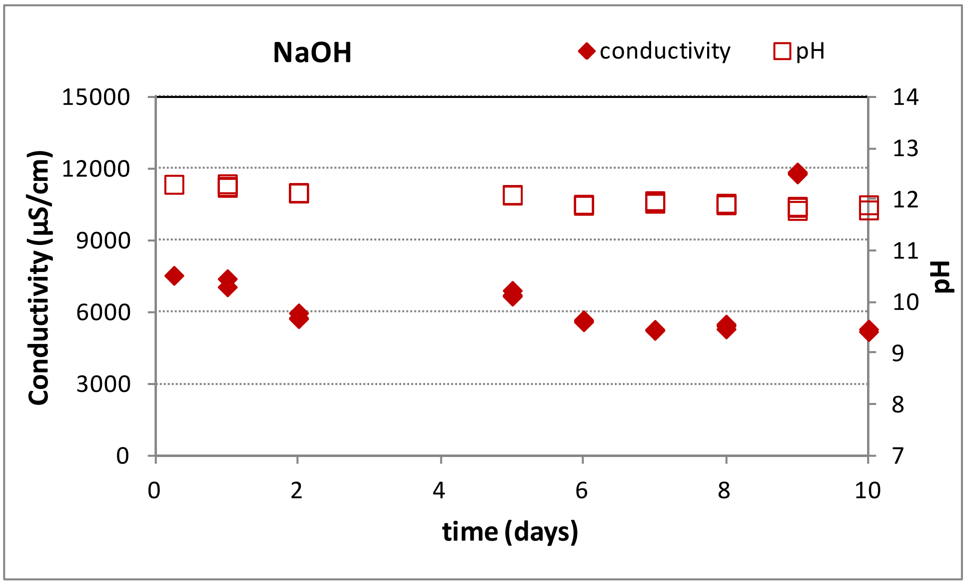

**Figure 35. Conductivity and pH values in the leachate; test with 0.02M NaOH solution.**

In leaching experiments using all three types of liquid phases it was not observed measurable activity of $^{14}C$ released into the leachate during the tests. The interaction between testing sample and liquid phase can be seen as changes in conductivity and pH values in the leachate. For distilled water used as liquid phase values of conductivity in leachate decrease from 4100 µS/cm after first day of leaching to approx. 1000 µS/cm after one week, since that time the conductivity values are stable in 10 days experiment. Values of pH slightly decrease from 12.3 to 11.7 during the 10 days of experiment with distilled water as a liquid phase due to cement phases alteration – mainly $Ca(OH)_2$ dissolution. Values of conductivity in leachate decrease from 4200 µS/cm after first day of leaching to *approx*. 330 µS/cm after one week, since that time the conductivity values are stable in 10 days experiment, in experiments with SGW as a liquid phase. For this case values of pH decrease from 12.3 to 10.5 during the 10 days of experiment due to cement phases alteration. In the last set of experiments the pH values are slightly decreasing from 12.3 to 11.8, when sodium hydroxide is used as a liquid phase. Also conductivity of the leachate slightly decrease from 7400 to 5200 µS/cm in experiments with NaOH solution.

#### 2.6.4.1. Results

There is no measurable release of $^{14}C$ observed during the leaching test of fixed resin into the cement matrix. Due to this it is not possible to evaluate the leachability or diffusivity of fixed $^{14}C$. Therefore it could be said, that $^{14}C$-carbonate adsorbed on ion exchange resin (Amberlite), which fixed in the cement matrix (CEM II/A-S 42,5 R), is stabilised and protected from the release to the environment of repository, which was simulated by three types of liquid media.

## 2.7. *Interim conclusions*

When measured, the differences in inorganic/organic repartition of $^{14}C$ seem to be confirmed between Pressurized Water Reactors (PWR), and Boiling Water Reactors (BWR) [Reiller *et al.*, 2014, and references therein]. For instance the EDF-A sample (UOx-1450) the total $^{14}C$ activities determined in wet and dry states seem to be in agreement, and the repartition of 23/77 for organic to inorganic forms is found. For BWR, the FZJ sample evidenced almost only inorganic $^{14}C$

The change in morphology of IERs after long term storage has been evidenced on IERs from SOGIN. It seems that anionic resins are more prone to ageing than cationic ones.

The desorption test evidenced the need of using a strong basic solution – 1 M LiOH, i.e. pH *approx.* 13.8 – directly in contact with SIERs to obtain a strong release of $^{14}C$ from EDF SIERs, when neither pure water nor a $10^{-3}$ M LiOH solution, i.e. pH *approx.* 11, permit to obtain a significant release. The total released activity seem to be lower than the total activity determined in combustion suggesting a loss of $^{14}C$ in gaseous phase. The majority of the desorbed $^{14}C$ is under the inorganic form, but the proportion of organic $^{14}C$ seems to be slightly more important than in the total samples – 55/45 for EDF-A and 54-46 for EDF-B. Nevertheless, it seems from leaching experiments on SIERs from PWR (ÚJV samples), fixed into a cement matrix, that no measurable leaching can be observed during a preliminary 10 days experiments.

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# Glossary

- BWR
  - Boiling Water Reactor .......... 1, 27
- CEA
  - LARC .......... 2
  - LRMO .......... 2
- EDF .......... 2
- FZJ
  - Forschungszentrum Juelich .......... 27
- GC-MS
  - Gas Chromatography coupled with Mass Spectrometry .......... 28
- HPLC
  - High Performance Liquid Chromatography .......... 28
- IERs
  - Ion Exchange Resins .......... 1, 3, 4, 8, 15, 20, 27, 28, 30, 32, 33, 34, 36, 42, 56
- LSC
  - Liquid Scintillation Counting .......... 3, 28, 36, 48
- PWR
  - Pressurized Water Reactor .......... 1, 2, 15, 43, 44, 56, 57
- R-GC
  - Radio-Gas Chromatography .......... 28
- SIERs
  - Spent Ion Exchange Resinsv, 1, 2, 4, 5, 6, 7, 8, 9, 10, 11, 13, 14, 15, 27, 28, 30, 32, 33, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 48, 49, 50, 51, 56, 57
- SKB .......... 42, 58