CArbon-14 Source Term

CAST

FINAL REPORT ON LEACHING AND DESORPTION EXPERIMENTS OF ^{14}C FROM SPENT ION EXCHANGE RESINS (D4.6)

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CAST – Project Overview

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

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

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

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

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Final Report on Leaching and Desorption Experiments of ^{14}C from Spent Ion Exchange Resins

Executive Summary

This deliverable is one of the final reports summarizing the results obtained in WP4 from the CAST project. It is focused on desorption and leaching tests using spent ion exchange resins (SIERs). The report contains the contributions from CEA (France), FZJ (Germany), RATEN-ICN (Romania), and ÚJV (Czech Republic).

Each participant performed their experiments using the local samples available for testing and in operating conditions related mainly to each national context of nuclear waste management [REILLER *et al.*, 2014; RIZZATO *et al.*, 2014]. No standard sample for inter laboratory testing was used.

In experimental works performed by FZJ, samples from boiling water reactors (BWRs) were used. Following the requests from the nuclear power plant operators, the samples have been anonymized. In static leaching experiments the examination of the suspension water and SIERs showed a very small or undetectable ^{14}C activity in the gas and liquid phase. A speciation of the releases in solution by means of HPLC revealed the presence of small amounts of formic acid for FZJ-A SIERs, no formic acid was detected in the leachates from FZJ-B SIERs. The releases of gases from SIERs in alkaline solution were observed and are caused by a transient/permanent decrease in the pH value.

CEA experiments were performed on anonymized EDF samples already characterized in previous deliverables [REILLER *et al.*, 2014; RIZZATO *et al.*, 2014]. Desorption experiments have shown that SIERs from PWR contain ^{14}C in organic form (38% of the total ^{14}C). The observed carbon mass balance is around 50 $mg_C \cdot L^{-1}$. Around 12% of carbon mass balance is identified. The only organic identified compound in resin desorption solutions, *i.e.* glycolate (hydroxyacetate), is identified in very low concentration, around 1% of Total Organic

carbon. No amine derivative is detected and ammonium is quantified in very low concentration by ionic chromatography. So these observations can confirm that no, or very little, chemical degradation, coming from either resin polymer structure or functional groups, occurs under these conditions. However, an organic contamination in concentrated LiOH at 1 M (solution used for resins desorption) makes the characterization of organic molecules coming only from SIERs desorption difficult.

Leaching experiments in alkaline solution carried out by RATEN-ICN on SIERs from CANDU reactors indicate that around 79% from the total ^{14}C content in the SIER samples is released as dissolved species. The ^{14}C release is fast, the most part of it as dissolved species occurred within the first 2 days. The ^{14}C measured in liquid phase in the first days of desorption test was found to be in inorganic form — more than 99% — and only an insignificant amount in organic form. After 24 days of desorption, it seems that the organic ^{14}C is released (~8% from the total ^{14}C measured in solution). The ^{14}C measurement in the SIER sample after 174 days of desorption indicates that the residual ^{14}C content represents only around 8% of the initial activity. Around 7% of the initial ^{14}C content in SIER sample was measured as inorganic ^{14}C released in gas phase. The difference of *ca.* 6% that was not found either as dissolved species and inorganic gas species, or as residual after the desorption test, could represent the ^{14}C released in gas phase as organic species. But, since no organic ^{14}C in gas phase was measured this is only a hypothesis and further experiments need to be carried out to arrive at a firm conclusion on organic ^{14}C release in gas phase.

For ÚJV, leaching experiments were performed on real SIERs from VVER (Water-Water Power Reactor) and on laboratory samples spiked with ^{14}C. Different leaching media were used: a synthetic granitic water (SGW), and a 0.02 M NaOH solution. SGW was chosen as representative liquid for granitic water present in a deep geological repository placed in a granitic massif, and NaOH solution as a representative of alkaline liquid leached from altered cemented wastes. During the experiments it was shown that no or negligible amount of ^{14}C was leached in any type of leaching/desorption test of SIERs. In leaching tests of laboratory-prepared cemented resins, the release of organic (acetate) or inorganic forms (ions from the carbonate system) were not observed; the former should be limited by adsorption and the latter by the solubility of calcite ($CaCO_3$).

Some general comment can nevertheless be proposed:

- The release of ^{14}C from SIERs can only occurs in highly basic media;
- The immobilization in cement seems to prevent the release of ^{14}C from SIERs.

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1 Introduction and Context

The aim of WP4 is to obtain a better understanding of the ^{14}C source term from spent ion exchange resins (SIERs) from different origins — Boiling Water Reactors (BWR) or Pressurized Water Reactors (PWR) — and under different storage strategies. This report summarizes and presents experiments and results of desorption and leaching experiments on SIERs samples obtained within the WP4 CAST project. Each chapter of the report is divided into project participant parts, in which the partners' contributions are presented.

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

1.1 *CEA*

The French strategy for long term SIERs management is surface storage of SIERs embedded into a non-leachable matrix. As leaching experiments on embedded SIERs were not possible, CEA carried out direct desorption tests on SIERs (not conditioned) in order to determine ^{14}C speciation. For desorption studies, experiments were conducted on two sub-samples of one SIERS associated to a blank of reagent and two experiments on virgin resin.

Experimental desorption tests were performed to release the organic and mineral forms of ^{14}C, the objective of which is to obtain aqueous solutions for the determination of the hydro-soluble organic compounds at the Laboratory for Radiochemical and Chemical Analyses in CEA Cadarache (LARC). Desorption tests have been realized with virgin ion exchange resins (IERs) and SIERs. Desorbed ^{14}C activities in organic or mineral forms have been measured. The solutions were transferred to the analytical laboratory in charge of organic compound measurement — LRMO (Laboratory for the study of Radiolysis of Organic Matter), CEA Saclay.

An analytical approach has been developed in CEA-LRMO to identify the organic compound speciation from resins desorption solution coming from CEA-LARC. The partition between organic/inorganic total carbon, the carboxylic acids and amines quantification (Ionic chromatography) and the detection of organic molecules with low or higher molecular mass (Gas chromatography or mass spectrometry) are presented.

1.2 *FZJ*

FZJ has focused its research on IERs used in water cleaning circuits of BWRs from German and other European BWR operators. Following the requests of the operators, the samples have been anonymized to use them for experimental works within the CAST project. FZJ-A samples were delivered in wet conditions with water in suspension. During the intermediate storage in the nuclear power plant (NPP), FZJ-A SIERs experienced most probably a leaching process in contact with air and water.

Leaching of FZJ SIERs were performed in static batch and dynamic tests. Gas and pH evolution were studied with the aim of these experiments to describe the kinetics of ^{14}C release from SIERs in cementitious conditions. ^{14}C activity in the leachates was determined by LSC method. High Performance Liquid Chromatography (HPLC) has been adopted for the speciation of carbonaceous species released by the SIERs into the solution during the tests.

1.3 *RATEN-ICN*

CANDU SIERs transferred from Cernavoda NPP were used in the experimental programme carried out by RATEN-ICN. The total ^{14}C content and its partition between inorganic and organic species — as well as inventories of ^{3}H, ^{137}Cs, ^{134}Cs, ^{60}Co, and ^{54}Mn — were determined in resins, as part of Task 4.2 of WP4. The measured inventories were used to process the experimental data obtained from the desorption tests of ^{14}C from Cernavoda SIER samples under alkaline conditions (NaOH 0.1 M).

Currently, at Cernavoda NPP no decision regarding the option for SIERs treatment and conditioning in view of their disposal was taken. One of the common used methods for SIERs conditioning is their cementation. During the curing period, cementation can generate temperatures up to 100-120°C in the solidification product, and these high temperatures could degrade the resin. For this reason, the effect of thermal degradation on ^{14}C uptake on anionic resin (Amberlite IRN 78) was evaluated for fresh resin and for resin dried for 5 hours at 50°C and 80°C. These tests show that at temperature of 50°C the ^{14}C adsorption percentage slightly decreases compared to fresh resin (from ~99% to ~96%), but temperature of 80°C generates an important decrease of the ^{14}C absorption percentage (to ~63%).

1.4 *ÚJV*

For ÚJV work within the CAST project resins from Czech nuclear reactor operation — Dukovany and Temelín NPP reactors, and ÚJV Group research reactor — and also, in some types of experiments, laboratory prepared samples from virgin Amberlite resins were used. The sampling procedure of resin samples from reactor operation was poorly documented. So there is a lack of information about the samples. Laboratory prepared samples were used due to their known characteristics. In both types of the SIERs, the real ones from reactor operation cycle and artificial prepared in laboratory, the ^{14}C and main radionuclide content were determined.

Desorption/leaching experiments were performed on real and laboratory prepared samples. Different leaching media were used, synthetic granitic water (SGW), and 0.02 M NaOH solution. SGW was chosen as representative liquid for granitic water presented in deep geological repository placed in granitic massif [HAVLOVÁ *et al.*, 2010] and NaOH solution as a representative of alkaline liquid leached from cemented wastes.

A second type of leaching tests was focused on studies of ^{14}C release from resins fixed in cement matrix. For these tests laboratory prepared resins containing defined activity of ^{14}C in form of bicarbonate or acetate were applied. Fixation into the cement matrix is suggested as one of the possible immobilisation procedures for SIERs wastes. For leaching experiments the methodology based on ANSI/ANS-16.1-2003 was applied, three types of leaching liquids were used: distilled water, SGW, and 0.02M NaOH solution.

2 SIERs Samples

For all experiments within the CAST project SIERs samples from nuclear reactor operation (power plant or research) and also artificial SIERs samples prepared in laboratory were used. For various experiment types spent or virgin resins were used. These types of resins were used in desorption/leaching experiments studying release of ^{14}C.

2.1 *Real SIERs samples*

2.1.1 CEA

EDF operates 58 PWR type nuclear reactors in France. IERs are widely used in these nuclear facilities for the purification of water coolant. Important applications include primary circuit, secondary circuit, and effluent treatment, which require high quality nuclear grade IERs to remove the undesired ionic species dissolved in the fluid, such as those which can induce corrosion or radioactive nuclides that affect local dose rates. Generally, purification of the various circuits is ensured by a chain of filters and demineralizers using IERs. A combination of cationic, anionic and/or mixed bed resins are used depending on the physicochemical conditions of the circuits and on their specific needs.

Indeed, the choice of IERs for EDF facilities depends on numerous criteria. Because of the possibly harsh nature of the fluids to be treated (temperature, chemistry, radiation) the IERs need to be of a high grade in order to reduce the degradation and the release of potentially harmful substances into the circuits, and therefore the loss of reactor performance. Based on literature knowledge and on EDF industrial experience it has been specified that all IERs used in EDF nuclear facilities must be of polystyrene divinylbenzene (DVB) copolymer type. Cation exchange resins must be of the strong acid sulphonated type, in hydrogen or lithium form depending on the application. All anion exchange resins must be of the strong base quaternary trimethylamine type, in hydroxide form. Another important property of an IER is the total exchange capacity. Fortunately, this property can be measured practically with a good accuracy and therefore are fully listed in EDF specifications. Type I anion exchange resins are required since they completely dissociate, have a greater selectivity towards the range of ions to be removed and are more resistant to temperature degradation.

Thus, depending on the function of the IER, it can be of different nature. At the end, the SIERs produced in EDF nuclear facilities are a mixture of IERs of different origins and characteristics. Their ionic charge (and activity) depends on the criteria defined to be changed out. The principal criteria are:

- chemical or radiochemical saturation; downstream of the demineralizers, limits are imposed on concentrations of certain substances, the conductivity of the fluid and/or the total γ-radiation measured;
- maximum service lifetime; to avoid degradation products, a maximum lifetime of 7 years has been recommended. This is further reduced to 5 years when the resin is exposed to more aggressive conditions in terms of chemistry or radiochemistry;
- in rare cases, the bed may need to be changed out due to unusual pressure drop behaviour, which is usually an indication of filter or resin degradation;
- along with these criteria, the resin may need to be changed more or less frequently depending on the fluid.

When the criteria are reached in a circuit, the SIERs are discharged and stored under water in storage tanks mixed with others SIERs from the facility. The storage delay lasts some months until the dose rate is low enough thanks to the radioactive decay of the very short-lived radionuclides. Then the SIERs are conditioned on site with the "Mercure" process [RIZZATO *et al.*, 2014] and sent to Andra disposal facility.

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

EDF have provided 5 samples to CEA in the framework of the CAST project as described in Table 1. The sampling was made in the storage tanks without any possibility to know the exact SIERs origin (it is a mixture) and thus their detailed history. These samples have been chosen for their different origins (power reactor units, nature of the fuels). The amount of each sample is defined on site in compliance with the ADR regulation rules [ADR, 2013], and the Chicade facility (CEA Cadarache Centre, France) acceptance criteria. The characteristics of these samples are summarized in Table 1.

Table 1. Characteristics of the EDF samples.

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

As mentioned above, the huge heterogeneity of dose rates is due to the fact that the SIERs come from different circuits and are sampled after different storage delays (radioactive decay of short life radionuclides). All the SIERS samples received at CEA are stored in the dark at room temperature.

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

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

Non active resins Sample EDF-A Sample EDF-B

Figure 1. Photographs of the EDF-A and EDF-B SIERs samples compared to the non-active IER sample.

2.1.2 FZJ

BWR spent ion-exchange resins (SIERs) were used in the experimental programme carried out at FZJ. Two sets of samples were selected for CAST, namely FZJ-A and FZJ-B. The selection criteria for the BWR SIERs are reported in D4.1 [Rizzato *et al.*, 2014]. In addition, a more detailed approach to the sample choice for every selected BWR SIERs is described in D4.4 [Comte *et al.*, 2017].

FZJ-A SIERs were used in a Condensate Clean-Up (CCU) System and then collected in a dedicated vessel (not mixed with spent resins arising from other cleaning circuits). Consequently, samples could be considered as average ones, accounting for the entire lifetime of the nuclear power plant. After water was added to the storage vessel (in January 2013) to keep the resins in wet conditions and to facilitate their removal afterwards, SIERs (powdered resin) were collected and delivered to FZJ.

FZJ-B samples were systematically collected along the lifetime of the reactor. Resins coming from different circuits were dried and stored, in most cases separately, allowing a systematic sample choice. By applying the selection criteria described in D4.1 [RIZZATO *et al.*, 2014], four samples were chosen. Three samples with similar total gamma activities, collected at different times of the reactor lifetime, were chosen to perform an evaluation of the degradation effects on the resins during interim storage. A fourth sample has been considered with a particularly high γ-activity to allow an evaluation of the self-irradiation effects at two different ^{60}Co activities along a storage period in similar conditions.

2.1.3 RATEN-ICN

IERs are used at Cernavoda NPP for fluids purification and also for decontamination of liquid effluents. The SIERs are removed from the purification systems and transferred to the storage vaults in the form of slurry in demineralised water. Currently, at Cernavoda NPP the SIERs are stored in three reinforced concrete vaults, lined with epoxy resin, with capacity of 200 m^3 each. The SIERs are segregated and stored based on their origin as *non-fuel contact resins* — from systems that are not in contact with the fuel, such as moderator purification system, heavy water clean-up system, liquid zone control system, end shield cooling system — and *fuel contact resins* — from purification of primary heat transfer system, spent fuel cooling pool, fuelling machine D_2O supply system. Some spent activated charcoal is also stored together with SIERs. No SIERs sampling from the Cernavoda storage tanks were performed but during maintenance operations.

Some SIERs are collected from the strainers situated on the inlet and outlet of the IERs columns of different purification systems. A sample of mixed spent resins sampled from a drum containing SIERs collected from purification systems of moderator (MOD) and of Primary Heat Transport System (PHTS) from Unit 1 of Cernavoda NPP was transferred to RATEN-ICN in 2015 to be used in the experimental programme carried out under CAST WP4. The systems from where these SIERs were collected contain heavy water that after almost 19 years of operation has a high ^{3}H activity. To decrease the tritium activity and also to get a D_2O content less than 10%, a volume of distilled water was added over the 100 g of SIERs and the container was put in a gas tight vessel and transferred to RATEN-ICN.

Mixed resin type Amberlite IRN-150 is used in MOD and PHTS purification systems. Amberlite IRN-150 is a nominal 1:1 chemical equivalent (same anion and cation exchange capacity) mixture of IRN 77 (strong acid cation-exchange resin) and IRN 78 (strong base anion-exchange resin). For the tests carried out to evaluate the influence of the thermal degradation of the resin on the ^{14}C uptake, fresh IRN 78 resin was used and IRN 78 resin dried for 5 hours at 50°C and at 80°C.

2.1.4 ÚJV

There is relatively low information and data about the composition of SIERs produced in Czech nuclear power plants. In both Temelín and Dukovany NPPs, VVER reactor types (Water-Water Power Reactor) are installed. IERs are used in operation of all of them. Moreover, the trademarks used ion exchangers at the Dukovany NPP changed over time — at least 3 types of cation exchangers and 2 types of anion exchangers. These sorbents showed varied provenance; fundamentally, they were always a strongly acidic cation and strongly basic anion exchangers. Real SIERs are in the form of small spheres/beads with maximum of 10% shape failure and small amount of admixtures. These admixtures could be mainly organic impurities, oils and precipitated borates. Composition of cations and anions is quite variable, spent resins contain mainly sodium, potassium and borate, nitrate ions. In both Czech NPPs the IERs are mainly based on divinylbenzene (catex:anex = approx. 2:1). After usage, SIERs are stored in tanks for radioactive waste without any regeneration. Ion exchange groups are substituted by ions from radioactive wastes.

Specimens of SIER from Czech NPPs Temelín and Dukovany — in experiments labelled as ETE and EDU samples respectively — and experimental reactor operated by ÚJV Group in Řež — in experiments labelled as ÚJV samples — were used for experiments.

EDU SIERs are of unknown origin (probably sampled 12/1998) and were sampled and stored under unknown conditions. EDU SIERs contained impurities, sediments and mud (see Figure 2), therefore the separation of the resin beads was carried out and separated SIER bead were used in experiments. ETE SIERs are also from an unknown origin and were sampled and stored under unknown conditions. ETE SIERs contained some impurities (see Figure 2), but were uses in experiments without modification. ÚJV SIERs were sampled and stored under unknown conditions. ÚJV SIERs did not contain any impurities (see Figure 2).

By laboratory analysis the activity 27 ± 4 $kBq.kg^{-1}$ of organic forms of ^{14}C and 16 ± 2 $kBq.kg^{-1}$ of inorganic forms of ^{14}C were determined in the sample of ETE SIERs, the activity 34 ± 6 $kBq.kg^{-1}$ of organic forms of ^{14}C and 14 ± 2 $kBq.kg^{-1}$ of inorganic forms of ^{14}C were determined in the sample of EDU SIERs and the activity 77 ± 11 $kBq.kg^{-1}$ of organic forms of ^{14}C and 2000 ± 280 $kBq.kg^{-1}$ of inorganic forms of ^{14}C were determined in the sample of ÚJV SIERs. The ^{14}C content and major radionuclide activity in SIERs studies is shown later in this report (Table 21).

Figure 2. EDU, ETE and ÚJV SIERs samples (from left to right hand side respectively).

2.2 *Artificial SIERs samples*

2.2.1 ÚJV

For preparation of laboratory samples, to compare with real SIERs, artificially ^{14}C contaminated Amberlite type resins were used. In laboratory tests Amberlite resins in OH^- and Cl^- forms were used. The sorption behaviour of these types of resins was studied using inorganic and organic form of ^{14}C tracers. For the inorganic form of ^{14}C species sodium bicarbonate ($NaH^{14}CO_3$) was used. For the organic form the sodium acetate ($CH_3{}^{14}COONa$) was used. SIERs were prepared by sorption of these artificial tracers. The activity of ^{14}C in laboratory prepared samples was 6.5 $kBq.g^{-1}$ of dry resin.

2.3 *Solidified resins samples*

2.3.1 ÚJV

Laboratory prepared solidified samples were prepared from artificial SIERs. The ^{14}C activity in resin after saturation was 6500 Bq in 1 g of dry resin. After the saturation, laboratory prepared SIER was solidified into a cement matrix. For solidification cement type CEM II/A-S 42,5 R (produced by Lafarge Cement a.s. - Čížkovice, Czech republic) was applied. The composition of simulated cement-waste mixture was followed: cement/resin = 10/1; water/cement = 0.6. Solidified resins were prepared in the form of cylindrical specimens with diameter 26 mm and height 55 mm. Structural stability of prepared testing specimens was observed by visual control for a testing period of more than 3 months and no cracking, breaking off, damage or some other destruction of prepared specimens were observed.

3 Types of Leaching Experiments

Two types of experiments were performed on leaching/desorption behaviour of SIERs: direct leaching of resins into the liquid media and leaching of solidified resins into the liquid media.

3.1 *Direct leaching of SIERs*

3.1.1 CEA

Experiments of desorption of ^{14}C from SIERs (EDF-B) are performed to identify the organic molecules that are present in SIERs and to 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 and agitated during 30 min at room temperature;
- tests were carried out under air — the protocol does not include trapping or measurements in the gas phase in equilibrium;
- two experiments were performed to appreciate the reproducibility on EDF-B sample; in order to ensure further measurements of the organic molecules, tests on SIERs are completed by a “blank” experiment for the identification of pollutants from reagents and materials and by two tests on virgin IERs for identification of compounds coming from the chemical degradation of resins;
- all desorption solution are stored at 3°C in glass container and in the dark to avoid organic molecules degradation before transfer to LRMO.

The initially chosen desorption solution was a 10^{-3} mol.L^{-1} LiOH solutionn for several reasons:

- Li was the conditioning ion of 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 in the 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. The concentration of the LiOH solution was increased to 1 M, to increase the ionic exchange, which resulted in the detection of both mineral and organic forms of ^{14}C in solution (see part 3). Solutions of LiOH were prepared by dissolution of LiOH salt (grade 98% for analysis, Merck batch K46761291 603).

Six desorption sequences (6 × 10 mL) were performed with LiOH 1M and the experiments were completed by two washings with water. These additional washes were performed to solubilise the hydroxides present in the pores of the resins.

3.1.2 FZJ

For leaching test FZJ-A and FZJ-B samples were used.

Direct measurement

FZJ-A samples were delivered in wet conditions in suspension in water. During the intermediate storage in the NPP, FZJ-A SIERs experienced most probably a leaching process in contact with air and water. Activity measurements of the suspension water were performed by LSC and gamma-spectrometry. Further analyses included high performance liquid chromatography (HPLC).

Batch leaching

Static leaching experiments were established with FZJ-A samples of about 1.5 grams placed in small glass vials (about 15 mL) with deionised water (5 mL). The gas and liquid phase were analysed after three months using GC and LSC respectively.

Dynamic leaching

Samples of 1 g of FZJ-A or FZJ-B SIERs were filtered to remove water using a funnel and paper filter (blue band). Then 10 mL of deionised water (a) or 0.85 M NaCl solution (b) was poured over the SIERs and the filtrate was collected in a separate vial. The liquid phase was analysed by LSC (FZJ-A) and HPLC (FZJA-B) to provide for a quantification and, possibly, a speciation of the released compounds.

On-line gas and pH evolution

A sample of 1.5 g of FZJ-B SIERs was mixed in air-tight vials (15 mL) with 5 mL “cement pore water” solution, modified from WIELAND *et al.* [1998], *i.e.* 0.11 M NaOH and 0.18 M KOH — $Ca(OH)_2$ was not used here. The aim of these experiments was to study the kinetics of ^{14}C release from SIERs under cementitious conditions.

A study of the pH evolution of FZJ-B SIERs in contact with an alkaline solution was additionally performed by mixing 1 g SIERs either with 10 mL cement pore water or with increasing amounts of alkaline solution (XOH, with X=K, Na).

Another experiment, implying a very concentrated NaOH solution, was established to simulate a realistic scenario where cement is in contact with SIERs.

3.1.3 RATEN-ICN

At Cernavoda NPP the SIERs are currently stored under water and no decision regarding the final treatment and conditioning of SIERs in view of their disposal has been taken. For this reason, the experimental tests to estimate the ^{14}C release under chemical conditions relevant to geologic disposal were carried out on un-conditioned SIERs in alkaline solution (relevant to cementitious environment). Desorption tests were carried out in aerobic conditions, using two sub-samples from the SIERs received from Cernavoda NPP, in alkaline solution (NaOH 0.1 M, with pH ~ 13).

For the desorption tests (Test #1 and Test #2), 0.4 g of SIERs was put in contact with 40 mL of NaOH 0.1 M in borosilicate glass bottles with polyketone (PP) lids that were adapted to allow N_2 introduction in the desorption vessels and outgas washing through alkaline gas washing bottles (see Figure 3).

Desorption tests were performed at room temperature (23 ± 3°C), for liquid to solid ratio of 0.01 $g.mL^{-1}$, in semi-dynamic conditions: 5 mL of leachate were sampled at each time step and 5 mL of fresh NaOH were added. The leachate solution was sampled daily in the first 4 days, and after 9, 17, 24, 45, 95, 122 and 174 days of desorption. At the end of the desorption tests not only ^{14}C activity in liquid and gas phase was measured but also the residual ^{14}C activity in the SIER sample subject to desorption test.

Before sampling the desorption solution, at each sampling time N_2 gas was purged in the space above the liquid level and the outgases were washed through the two gas bubblers, one with 3 mL of NaOH 2 M and one with 15 mL of NaOH 2 M, in order to absorb the potential inorganic ^{14}C released as gas phase during the desorption test.

Since at the beginning of the desorption tests it was not clear whether the ^{14}C released in gas phase could be measured by washing outgases through alkaline bubblers, the nitrogen gas was introduced through both parallel desorption vessels in the same time. To get the amount of gaseous ^{14}C released from one vessel, the amount measured in the alkaline solution from the gas bubblers was divided by two assuming the ^{14}C released in gas phase was equal from the two parallel tests.

Figure 3. The glass vessels adapted for desorption tests

3.1.4 ÚJV

Leaching/desorption experiments were performed on two types of SIERs, the real SIERs samples from nuclear reactor operation (samples EDU, ETE, ÚJV) and artificial SIERs samples prepared in laboratory (Amberlite resin saturated by ^{14}C tracer).

In desorption experiments two types of leaching liquids were used: synthetic granitic water (SGW), and 0.02 M NaOH solution. The composition of synthetic granitic water, which should simulate the average composition of ground waters present at a depth relevant to deep geological repository placed in granitic massif in the Czech Republic, is shown in Table 2. NaOH solution simulated the alkaline leachate from cemented wastes in the repository. In desorption experiments the solid to liquid ratio was S/L = 1/20, which means the amount of SIER recalculated to 0.5 g of dry resin and 10 mL of leaching liquid. The testing tubes were placed in continuous shaker to ensure full contact of liquid and solid phases for mutual interaction. The experimental time was set up to 1 month of leaching.

Table 2. Synthetic granitic water composition.

SGW composition (mg/l)										
Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	NO_3^-	HCO_3^-	F^-		pH
10.6	1.8	27.0	6.4	42.4	27.7	6.3	30.4	0.2		8.3

The activity of ^{14}C in leachate was determined by liquid scintillation counting (LSC) method. For the LSC measurement the sample in testing tube was centrifuged and if necessary the liquid phase was filtered to separate the solid phase particles. From this separated liquid the 0.5 mL was sampled into the 5 mL scintillation vial and scintillation cocktail was added.

3.2 *Solidified SIERs leaching*

3.2.1 ÚJV

Solidification of SIERs into the cement matrix is one of the supposed procedures for radioactive wastes immobilisation. In current research the solidification was followed by subsequent leaching tests studying the release of ^{14}C species. Leaching tests were based on ANSI/ANS-16.1-2003 methodology - Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure [ANSI/ANS, 2003]. This methodology defines some required parameters and rules for performing a leaching test. Prepared samples have to be homogeneous and representative for solidified waste. The test specimen geometry should be cylindrical, if possible. The minimum specimen dimension recommended should be 1 cm. In case of cylindrical-shaped specimens, the cylinders shall have a length to diameter ratio in range of 0.2 to 5. In case of ÚJV samples the ratio was approximately 2 (diameter 26 mm, height 55 mm). Sufficient leachate shall be used so that the ratio of the leachate volume (V_L) and the specimen geometric surface area (S) is maintained constant during the leaching test. The vessel, in which leaching test takes place, should be made of non-reacting material and shall be constructed to prevent excessive evaporation of the leachate. The dimensions of the vessel shall permit the sample to be immersed in the liquid such that the whole surface of the specimen is in the contact with the leachate during the test. It is required that the specimen is immersed in the leaching media without the contact between the walls or bottom of the vessel and specimen surface. In case of ÚJV tests, the plastic vessels with lid were used and specimens were hung on the polyamide fibre (see Figure 4). For leaching tests three types of leaching liquids were used: distilled water, SGW, and 0.02 M NaOH solution, same as for desorption tests with SIERs.

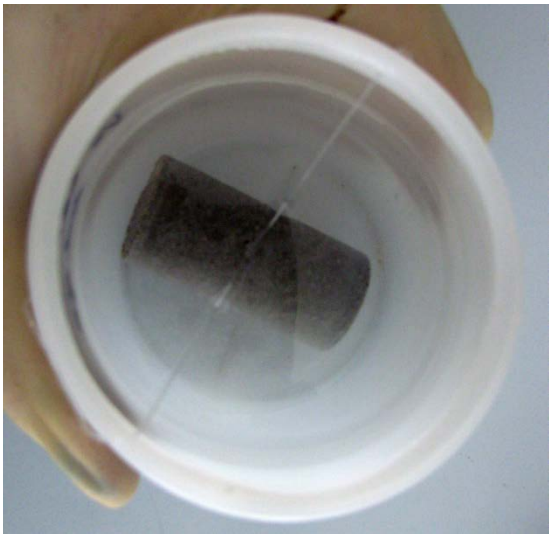

Figure 4. Sample of solidified SIER prepared for leaching experiment.

The activity of ^{14}C in leachate was determined by liquid scintillation counting (LSC) method. For the LSC measurement the liquid phase was sampled and if necessary the liquid phase was filtered to separate the solid phase particles (possible precipitates). For every measurement 0.5 mL of liquid phase was sampled into the 5 mL scintillation vial and scintillation cocktail was added.

4 Analytical and Measurement Methods

For SIERs characterisation sample preparation and ^{14}C activity determination, various analytical methods and procedures were used based on the purpose of the analyses and available analytical techniques in each CAST project participant laboratory.

4.1 *CEA*

4.1.1 Liquid scintillation measurements of ^{14}C

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

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

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

Counting time: 3600 seconds

Scintillating liquid: Oxysolve C400- Zinsser Analytical

4.1.2 ^{14}C standard solutions

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

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

4.1.3 Analytical method for determination of organic matter

The aim is to identify organic compounds potentially retained on resins (SIERs experiments) and check the presence of degradation products (SIERs and virgin resins experiments). To answer this question, an analytical approach has been developed by CEA-LRMO. This analytical strategy has been already used in LEGAND *et al.* [2014].

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[*] http://www.lea-cerca.com/en/areva-lea-cerca.html

During this project [REILLER *et al.*, 2014; BUCUR *et al.*, 2015], the analytical strategy has evolved. The sample's activity limits the analytical possibilities. Moreover, the laboratory experiments have shown that the desalination step of sample by filtration — elimination of the desorption matrix — does not give good results so these results limit the analytical possibilities too.

The final strategy is focused on the global organic carbon analysis by:

1. partition of organic and inorganic total carbon by Total carbon analyser (TC),
2. quantification of low molecular mass carboxylic acids by anionic chromatography (aIC),
3. quantification of amines by cationic chromatography (cIC),
4. detection of low molecular mass molecule by Gas Chromatography coupled with Mass Spectrometry (GC-MS),
5. detection of molecules with higher molecular mass by Electrospray-Mass Spectrometry analysis (ESI-MS).

If this first study shows specific organic compounds, we will apply dedicated experiments to determine ^{14}C speciation.

4.1.3.1 Organic and inorganic total carbon partition

The concentration of Total Organic Carbon (TOC) and Total Inorganic Carbon (TIC) dissolved in solution is determined on a total carbon (TC) analyser in glove box. This quantification will also help at the end of the study to control the mass balance of each sample.

A 250 µL aliquot is injected into a chamber. After acidification with phosphoric acid, the TIC dissociates to CO_2. The CO_2 produced is quantified by infrared spectroscopy. Then, the TOC is oxidized with sodium persulfate to produce CO_2, also quantified by infrared spectroscopy.

Under our conditions, a detection limit around 1 $mg_C.L^{-1}$ in TOC and TIC (without sample dilution) is obtained. The quantification limit is determined by the lowest measurement for which the signal to noise ratio is above 5. The available volume of sample and the background noise of the device are the limiting factors. Several repetitions are realized.

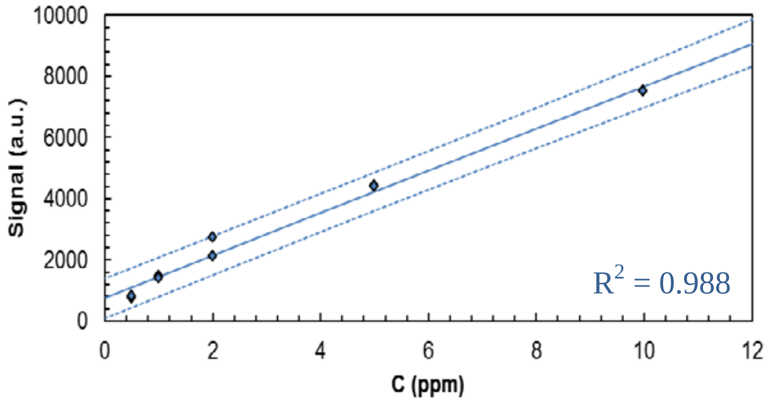


Figure 5. TOC Calibration curve.

4.1.3.2 Anionic chromatography

Ion chromatography is used to quantify low molecular mass carboxylic acids. This device is equipped with a conductivity detector. The carboxylic acids are identified by comparison of retention times of their standards. One method has been developed for the detection of carboxylic acids in high NaOH concentrations and inorganic anions in aqueous solution.

The chromatographic system used was an ICS-3000 High Performance Ion Chromatography System (Dionex, Sunnyvale, CA, USA) in glove box. The sample is diluted in water before analysis. The chromatographic separation of carboxylic acids was performed on an IonPac AS15 Hydroxide-Selective Anion-Exchange analytical column (250 mm × 2 mm i.d. Dionex) and an IonPac AG15 guard column (50 mm × 2 mm i.d. Dionex) with KOH as eluent at a flow-rate of 0.3 mL min-1. The sample injection volume was fixed at 10 µL. The separation is performed with a gradient elution: 0-7.5 min with 10 mM KOH, 7.5-8 min 10-15 mM KOH, 8-13 min 15-25 mM KOH and 13-39 min 25 mM. The carboxylic acids were detected by conductivity.

The chromatogram represents separations obtained for two standard solutions, used to build the calibration curve. In red, the separation of 9 carboxylic acids at 2 mg.L^{-1} and in blue, 7 inorganic anions at 2 mg.L^{-1}.

Under our conditions, a detection limit around 0.1 mg$_{acid}$.L^{-1} is obtained. The quantification limit is determined by the lowest measurement for which the signal to noise ratio is above 5. The available volume of sample and the background noise of the device are the limiting factors.

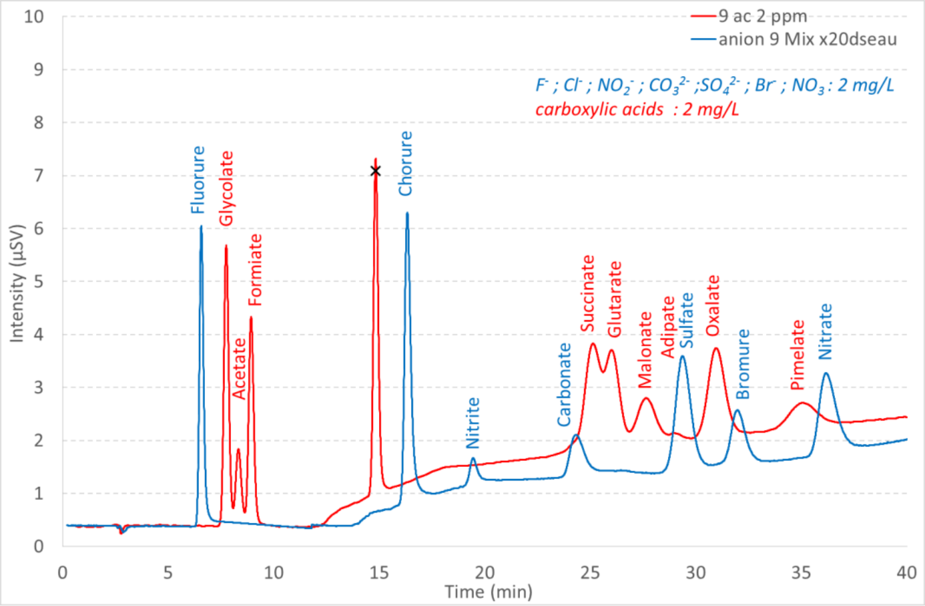


Figure 6. Example of chromatogram: 9 carboxylic acids at 2 mg.L^{-1} and in red and 7 inorganic anions at 2 mg.L^{-1} in blue.

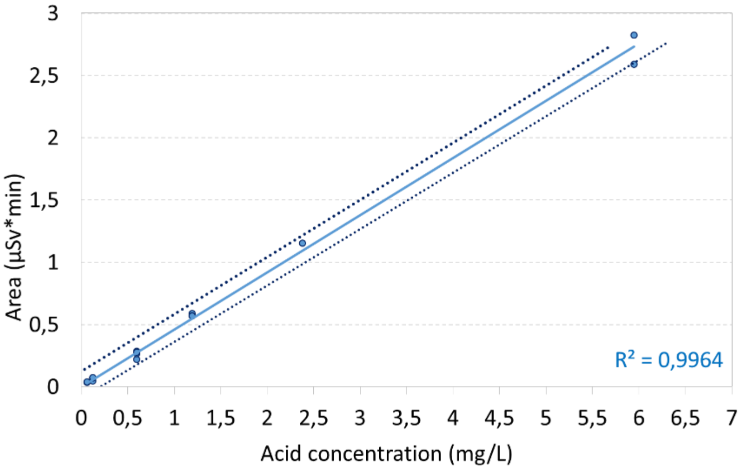


Figure 7. Example of calibration curve (Formic acid).

4.1.3.3 Cationic chromatography

Studying the radiolytic and chemical degradation of organic ion exchange resins under alkaline conditions, VAN LOON AND HUMMEL [1995] have shown the presence of different amines such as methylamine, dimethylamine and trimethylamine in the leaching solution (highly irradiated resins at 1.7 MGy). Thus, one method has been developed for the detection of amines by using two standards, ethylamine (EA) and diethylamine (DEA) in NaOH at 5 mg.L^{-1}.

The chromatographic system used was an ICS-3000 High Performance Ion Chromatography System (Dionex, Sunnyvale, CA, USA). The chromatographic separation of amines was performed on an IonPac CS16 cation-Exchange column (250 mm × 3 mm i.d. Dionex) and an IonPac CG16 guard column (50 mm × 3 mm i.d. Dionex) with methane sulfonic acid (MSA) eluent at 30mM in water at a flow-rate of 0.3 mL min^{-1}. The sample injection volume was fixed at 10 µL. The isocratic elution is performed. The sample is diluted before analysis.

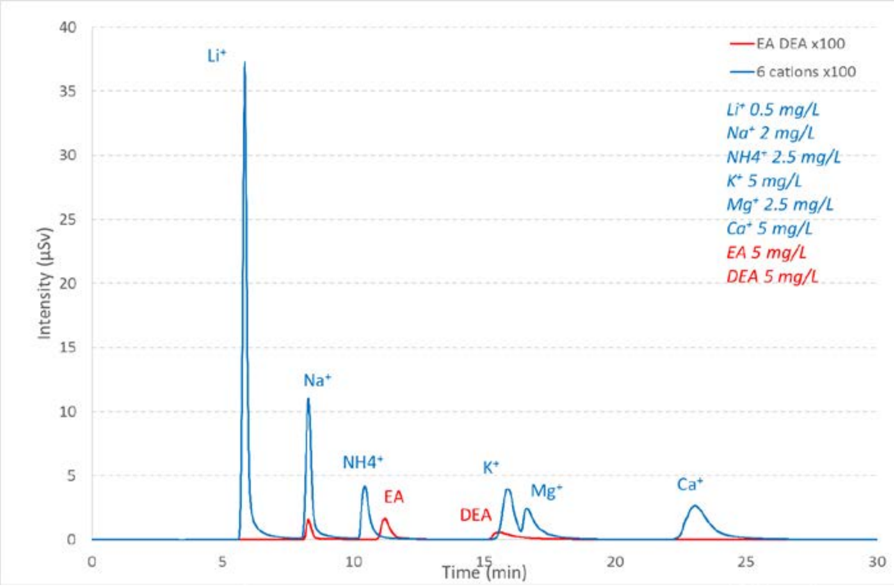


Figure 8. Example of chromatogram: 2 amines at 5 mg.L^{-1} and in red and 6 inorganic cations between 0.5 and 5 mg.L^{-1} in blue

4.1.3.4 *Gas chromatography coupled with mass spectrometry*

To identify semi-volatiles (organic compounds with mass between 100 - 500 amu) molecules by GC-MS, a derivatization reaction is performed. The aim of this derivatization is the substitution of polar groups with trimethylsilylated groups to increase their volatility before analysis by GC-MS.

The desorption solutions are acidified with HCl 1 M, evaporated at ambient temperature under N_2, diluted in pyridine and derivatized during 1 hour to 70°C by BSTFA-TMCS (N,O-Bis(trimethylsilyl)trifluoroacetamide with trimethylchlorosilane).

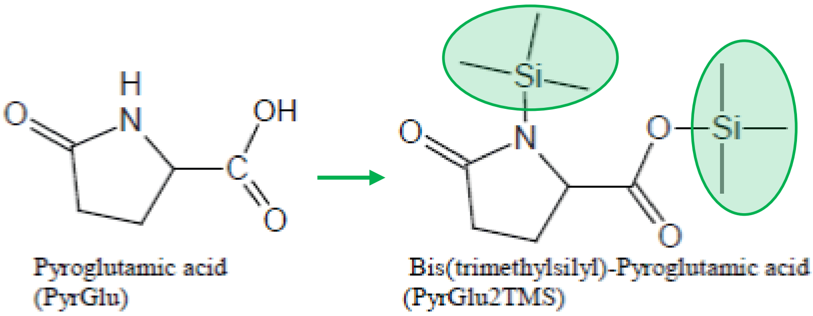


Figure 9. Derivatization reaction on amine and acid functions with BSTFA-TMCS

After this derivatization step, the sample is analysed by Gas Chromatography (GC) coupled to Mass Spectrometry (MS). The system used is a Trace ultra GC coupled with a DSQ II MSD (dual stage quadrupole mass selective detector, Thermo) equipped with an electron impact ionization source.

Gas chromatographic separations were performed on a TR1-MS capillary column (30 m length, 0.32 mm i.d., 0.20 µm df, Thermo). The oven was maintained at the initial temperature of 60°C for 5 min, heated to 280°C at the rate of 7.5°C min^{-1}, and then held at 280°C for 20 min. The inlet temperature was 250°C and the transport line maintained at 300°C. Helium was used as the carrier gas at a flow rate of 1.6 mL min^{-1}. The injection volume was 1 µL in split less mode. The ion source and quadrupole temperatures were 230°C and 150°C, respectively. An electron energy of 70 eV was used. The full scan MSD was operated over the range of 10 – 600 amu.

4.1.3.5 Electrospray-mass spectrometry

For the detection of molecules with molecular weight higher than 100 g.mol^{-1}, electrospray-mass spectrometry technique is used (Nano-ESI mass spectrometer equipped with a quadrupole mass analyser, Micromass). The sample is introduced into a nano-capillary. By application of a high voltage on this capillary, analytes are transferred as ions in an aerosol. After desolvation, *i.e.* solvent evaporation, a stream of charged ions is produced. Ions are afterwards transferred in the mass analyser, a quadrupole. This ambient pressure soft ionization technique allows the detection of intact polar molecules with higher molecular weight than GC/MS technique in complex mixture[PLANCQUE *et al.*, 2001]. ESI is also widely used in studies of non-volatile organic compounds, thermally labile inorganic compounds and biomolecules, which are difficult to analyse using Electronic Impact (EI) source. The ESI source allows the detection of intact polar molecules.

4.2 *FZJ*

4.2.1 Radionuclide inventory

The radionuclide inventory of FZJ-A/B SIERs and of the suspension water in contact with FZJ-A were performed by gamma spectrometry, by means of an HPGE detector GR 3018 (Canberra), and by LSC (PerkinElmer), provided with two photomultiplier tubes.

Samples for gamma spectrometry were prepared in standard 20 mL LSC plastic vials and the self-absorption of every sample was considered through a proper calibration with a ^{152}Eu source.

Samples for LSC were prepared in transparent 20 mL LSC glass vials, mixed with the scintillation cocktail “Goldstar Multipurpose” and then loaded into the instrument after proper homogenization and a resting time of several hours.

4.2.2 Speciation of the liquid phase

High Performance Liquid Chromatography (HPLC) has been adopted for the speciation of carbonaceous species released by the SIERs in solution. The HPLC, produced by Knauer, was furnished with an UV/Vis detector, a RI detector and an activity detector from Raytest. A 240mm organic acid resins column, optimised for the detection of some organic anionic species, has been adopted. An oven allowed the precise set-up of the column temperature, chosen at 20°C in the present work. H_2SO_4 0.01 N has been used as mobile phase, with a flow rate of 0.8 $mL.min^{-1}$ and isocratic analysis. The injected sample volume for a single analysis was 100 μL. The system has been calibrated with some species of potential interest, as reported by MAGNUSSON *et al.* [2008], in particular formic and acetic acid.

A limitation of the equipment was represented by the pH of the sample, which in extreme cases was not able to provide a stable background. Therefore, nearly neutral solutions were selected for the HPLC analyses, focused mainly on the samples FZJ-A, and in particular, on:

- species released by FZJ-A/B SIERs in contact with deionised water;
- species released by FZJ-A SIERs in contact with NaCl (0.85 M) solution.

4.2.3 On-line gaseous releases at high pH

On-line gaseous releases from FZJ-B SIERs in contact with an alkaline solution implied a sample of about 1 g (FZJ-B-2), loaded in a reactor vessel, and 10 mL of cement pore water (0.114 M NaOH and 0.18 M KOH). The vessel was connected to an argon bottle, provided with a flow regulator, and to a series of so-called “washing bottles” (Figure 10). A vacuum pump was connected at the end of the line to ensure a pressure below the atmospheric one in the whole line and, consequently, to avoid any escape of radioactivity. The washing bottles were exchanged every 24 hours and new solution was added to the sample at every step, until the activity in the washing bottles´ solutions was below the detection limit of the LSC.

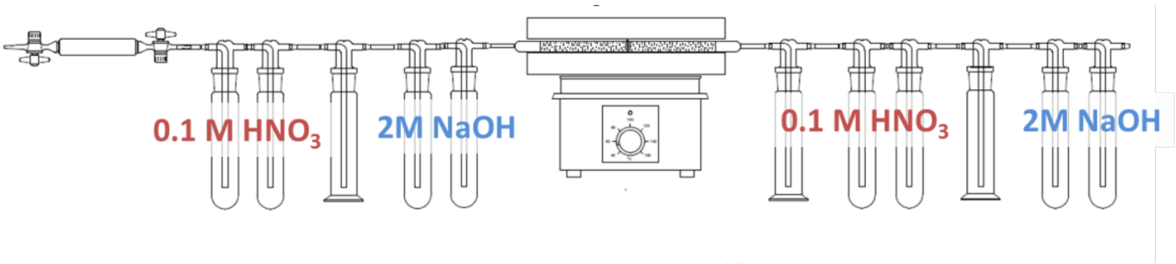


Figure 10. Experimental setup for the analysis of ^{14}C in FZJ, with a catalyzer to convert HT to HTO, CO and organics to CO_2.

A similar approach (on-line) was adopted to investigate the variations in the pH of the cement pore water in contact with SIERs, focussing on the transient pH value at a well-defined sample-to-solution ratio (1 g SIERs and 10 mL 0.1 N NaOH) and on the equilibrium pH value at different ionic strengths of the alkaline solution.

4.3 *RATEN-ICN*

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

The analytical method used for inorganic and organic ^{14}C measurement in liquid samples resulted from the desorption tests consists in a sequential extraction of inorganic ^{14}C and organic ^{14}C using acid stripping and wet oxidation, adapted after the method developed by MAGNUSSON *et al.* [2008] for ^{14}C measurement in spent ion exchange resins and process waters.

The experimental set-up used for release and separation of inorganic and organic ^{14}C is schematically presented in Figure 11. It consists in a reaction vessel, a separator funnel, a nitrogen supply and a vacuum pump, and two gas washing lines with a catalytic furnace between them.

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

To ensure that no gases are released from the system, all acid stripping/wet oxidation experiments were carried out under vacuum (0.2 bar below atmospheric pressure) and the carrier gas (N_2) was introduced into the system with a flow rate between 60 and 80 $mL.min^{-1}$ (controlled by a flow meter).

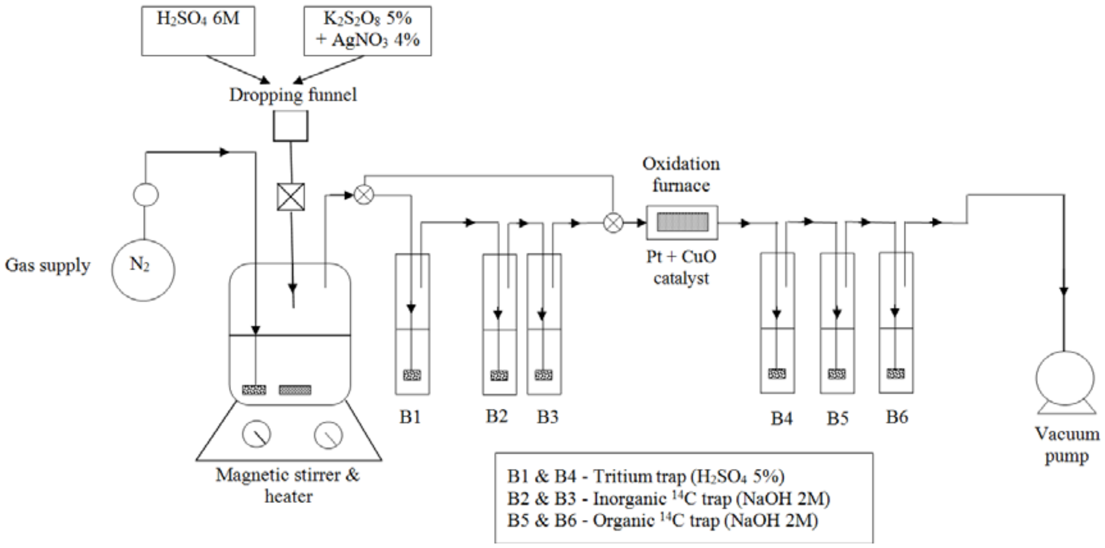


Figure 11. The experimental set-up for separation and purification of inorganic and organic ^{14}C from desorption solution.

Since from the SIERs not only ^{14}C is released but also tritium and other beta-gamma emitters that interfere with ^{14}C at its measurement by LSC, the two gas washing lines of the experimental set-up consists of a slightly acidic trap (5% H_2SO_4) for absorption of tritium and other gamma radionuclides and four alkaline traps (two placed before the catalytic furnace and two after it) with 2M sodium hydroxide [COMTE *et al.*, 2017]. Four small gas bubblers were used as alkaline gas washing bottles: 2 with 3 mL of NaOH 2 M (B2 and B5 and 2 with 10 mL of NaOH 2 M (B3 and B6), while for tritium and beta-gamma emitters absorption 50 mL gas bubblers were used.

The iodine traps were not used in this experimental set-up since in the radiochemical characterisation of the SIER sample received from Cernavoda NPP this element was not identified [RIZZO *et al.*, 2017].

The inorganic ^{14}C compounds, *i.e.* carbonates and bicarbonates, are easily decomposed by weak acids to carbon dioxide and the inorganic ^{14}C is released during acid stripping step of the analytical method mainly as $^{14}CO_2$. The gases released during the acid stripping are carried by the N_2 gas through the first gas washing line (Figure 10). If any ^{14}C is released during this step as CO or other organic molecules, it passes through the scrubbing bottles of the first gas washing line and is oxidized to CO_2 in the catalytic furnace and subsequently absorbed in the scrubbing bottles of the second gas washing line. After the acid stripping step is accomplished the first gas washing line is isolated from the system by means of three ways valves placed before the first scrubbing bottle and the third one.

Because the organic compounds have high bounding energies between atoms they are decomposed by strong oxidants such as potassium persulphate ($K_2S_2O_8$). Presence of a catalyser such as silver nitrate ($AgNO_3$) enhances the decomposition of the organic compounds. During the wet oxidation step the temperature of the solution in the reaction vessel is slightly increased to 90°C.

The mechanism of ^{14}C-labelled organic compounds decomposition is based on the $OH^{(*)}$ radicals and can be expressed by the following equations [AHN *et al.*, 2013].

$$K_2S_2O_8 \xrightarrow{H_2O} 2K^+ + S_2O_8^{2-} \quad (1)$$

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

$$^{14}C_nH_m + (4n-m)OH^* \longrightarrow n^{14}CO_2 + (2n+m)H_20 \quad (3)$$

The ^{14}C released during wet oxidation step of the analytical procedure (both as CO_2, but also as CO or CH_4) is carried by the N_2 gas through a catalytic furnace that ensures oxidation of any reduced compounds to CO_2 that is after that absorbed in the scrubbing bottles of the second gas washing line (Figure 10).

Two wet oxidation steps were carried out in order to ensure the complete decomposition of the organic ^{14}C-labelled compounds that could be desorbed from the Cernavoda SIERs, and the carrier gas was purged into the system for 1 hour in each step to allow all gaseous ^{14}C to be absorbed in the alkaline solution contained in the scrubbing bottles. The ^{14}C activity in the alkaline traps as well as the ^{3}H activity in solutions sampled from the acid scrubbing bottles were measured by liquid scintillation counting (LSC), using a Tri-Carb® analyser Model 3110 TR.

Hionic Fluor liquid scintillation cocktail was used for ^{14}C measurement by LCS, and Ultima Gold AB liquid scintillation cocktail for tritium measurement. The ratio between sample and scintillation cocktail was 1 to 10. All samples were kept in darkness over night before their counting to decrease the chemoluminescence effect. Aliquots from the reaction vessel solution, as well as from all scrubbing bottles were sampled for gamma measurements. Each sample was counted for more than 4 hours. The experimental data obtained for ^{14}C recovery are reported in CAST report D4.5 [RIZZO *et al.*, 2017].

A similar analytical method was applied to measure the inorganic and organic ^{14}C in SIERs samples subject to desorption test, while the total ^{14}C in these SIERs samples was measured by non-catalytic combustion using Sample Oxidizer, Model 307 PerkinElmer®. These methods are also described in CAST report D4.5 [Rizzo *et al.*, 2017].

4.3.2 Influence of thermal degradation of ion exchange resin on ^{14}C uptake

Up to now, for the spent ion exchange resins generated at Cernavoda NPP no conditioning technology was decided: a widely-used option for SIERs immobilization is cementation. Even if the cementation process is carried out at room temperature cementation can generate temperatures up to 100-120°C in the solidification product during the curing period [Aittola *et al.*, 1982].

The influence of the thermal degradation of the ion exchange resin (IER) on ^{14}C uptake were studied by batch sorption experiments carried out on fresh resin and on resins dried for 5 hours at two different temperatures: 50°C and 80°C, respectively (Figure 12). Since the ^{14}C is predominantly sorbed on the anionic fraction of a mixed bed resin, only IRN 78 resin (a strong base anion-exchange resin) was used in these experiments.

Figure 12. The resin samples used in the sorption tests at RATEN-ICN

To calculate the resin mass used in the sorption tests so that to have the same dry mass in the tests performed with the three types of IER (fresh IRN 78, IRN 78 dried at 50°C and IRN 78 dried at 80°C), the residual water content of the fresh IER and dried ones were determined based on the water loss at 105°C by using a thermobalance.

Both inorganic and organic ^{14}C uptake on fresh and dried resin samples were evaluated. A solution with ^{14}C in the form of carbonate ($^{14}CO_3^{2-}$), with activity of 1.23×10^3 Bq.mL^{-1} and one with ^{14}C as sodium acetate, with initial ^{14}C activity of 1.08×10^{3} Bq.mL^{-1}, were used as contact solutions.

The batch tests were carried out for a solid to liquid ratio of 0.1 g.mL^{-1} (0.6 g of resin expressed as dried mass to 6 mL of contacting ^{14}C-labelled solution), at room temperature (23±3°C) in 15 mL polypropylene centrifuge tubes. All experiments were carried out in duplicate samples. Blank batches were prepared to measure the ^{14}C background in resin samples and the ^{14}C sorption on the tubes walls was checked.

Eighteen test tubes were prepared for each type of resin and each form of ^{14}C — 2 for each sampling time: 1, 2, 3, 4, 5, 6, 18, 24, and 48 hours — to assess the kinetic of the ^{14}C uptake on the resin samples. During the equilibration time, the test tubes were placed on an orbital shaker at 70 rpm. At the established contacting time, 2 mL of solution was sampled and the residual ^{14}C activity in solution was measured by liquid scintillation counting (LSC) using Hionic Fluor scintillation cocktail. For each batch solution, two parallel LSC glass counting vials were measured. The sample to scintillation cocktail ratio was 1mL to 10mL and the counting time was at least 2 hours. All glass vials containing the ^{14}C solutions and LSC cocktail were kept in dark overnight before counting.

4.4 *ÚJV*

Experiments in ÚJV were focused mainly on the total ^{14}C activity measurements released by leaching/desorption processes. Neither separation techniques for separation of organic and inorganic forms of carbon species nor organic species characterisation techniques were applied. Organic/inorganic ^{14}C species determination was only used for initial characterisation of used SIERs.

In these measurements the inorganic ^{14}C species were analysed in the first step, the inorganic species (carbonates) were separated by acidification of the SIER sample and released CO_2 was collected and ^{14}C activity was determined, this activity value corresponded to the activity of inorganic ^{14}C. In second step the total digestion of the rest of SIER sample took place and the ^{14}C activity was determined, this activity value corresponded to the activity of organic ^{14}C. These analyses were performed in Central Analytical Laboratory of ÚJV and for activity measurement the Wallac Guardian 1414 LSC device was used.

4.4.1 LSC measurements of ^{14}C

Liquid scintillation counting (LSC) method was applied to determine of ^{14}C activity measurement. This method does not distinguish the chemical form of ^{14}C species and determines the total ^{14}C activity.

For LSC measurement the HIDEX 300 SL counter (Hidex oy, Finland) was used and liquid samples were mixed together with LSC universal cocktail Rotiszint eco plus. From every sample, before any measurement the liquid phase was collected and mixed together with the LSC cocktail. The ratio of the sample/cocktail for LSC measurement varies depending on experiment type and activity measurement, the most used sample/cocktail ratios were 1/2, 1/4 and 1/8, that means 1 mL of liquid sample/2 mL of cocktail, 1 mL of liquid sample/4 mL of cocktail and 0.5 mL of liquid sample/4 mL of cocktail respectively. The measurement parameters were used as set by Hidex oy company in counter software for ^{14}C measurement. The counting time was set for 5 or 10 minutes, every sample counting was triplicated.

4.4.2 Liquid phase characterisation

In leaching/desorption tests the characterisation of the leachates and also the input liquids (SGW) were performed. The SGW was prepared as described in HAVLOVÁ *et al.* [2010] and the composition of prepared synthetic granitic water was confirmed by analysis, concentration of cations were determined by atomic absorption spectrometry (AAS), anions concentration was determined by ion chromatography (IC). Also the pH value was checked during the SGW preparation and in the final solution. Because of radioactivity present in the solution after the leaching experiments, it was not able to analyse any leachate by AAS and IC methods due to radioactive safety protection.

The pH measurements were performed on pH-meter Metrohm equipped by standard pH electrode, which was calibrated by Fluka standards on pH values 7, 9, 11 and 13. The pH measurements were performed mainly in cemented SIERs leaching experiments into distilled water, SGW and NaOH solution to study the behaviour of liquid phase in interaction with cement matrix of solidified sample and to evaluate the influence of leachate characteristics of desorption process.

The second parameter which was studied, mainly in cemented SIERs leaching experiments into distilled water, SGW and NaOH solution, was the conductivity measurement of the liquid phases. For conductivity measurements the device of Gryf company equipped by standard platinum cell conductivity probe with temperature correction of measurement was used. The KCl solutions with conductivity 1413 and 12880 µS.cm^{-1} — *i.e.* 0.01 and 0.1 mol.L^{-1} respectively at 25°C — were used for calibration. The conductivity of liquid phase in interaction with cement matrix of solidified sample is also an important parameter for evaluating the influence of leachate characteristics on desorption process.

4.4.3 Leachability determination

For leaching of radionuclides from cemented samples, diffusion is considered as the main controlling process of contaminant release, other important processes such as dissolution, corrosion, etc. can only be determined with long-term leaching of the samples. Therefore, the rate of leaching in accelerated tests is determined by effective diffusivity. The diffusivity can be evaluated as:

$$D = \pi \left[\frac{a_n / A_0}{(\Delta t)_n} \right]^2 \left[\frac{V}{S} \right]^2 T \tag{4}$$

where D is effective diffusivity (cm^2.s^{-1}), a_n - the quantity of a nuclide released from the specimen during leaching interval n, A_0 - the total quantity of a given contaminant in the specimen at the beginning of the first leaching interval, $(\Delta t)_n$ - is the duration of the n^{th} leaching interval (s), V - volume of the specimen (cm^3), S - geometric surface area of the specimen (cm^2) as calculated from measured dimensions, T - leaching time (s) representing the "mean time" of leaching interval as follows:

$$T = \left[\frac{1}{2} (t_n^{1/2} + t_{n-1}^{1/2}) \right]^2 \tag{5}$$

Applicability of the method: assuming that less than 20% of the original radionuclide is released, its half-life is sufficiently long and the process is controlled only by diffusion. In this case it is possible to calculate effective diffusivity according to the above formula an it can be applied for calculation of leachability index.

The leachability index is a dimensionless value calculated from the experimentally obtained effective diffusivity for a defined radionuclide and is suitable for comparing different types of materials and characterizes the leaching properties of the solidified material. The leachability index of a nuclide *i* of concern in a material is defined as follows.

$$L_i = \frac{1}{n}\sum_{1}^{n}\left[\log(\beta / D_i\right] \tag{6}$$

where β is a defined constant (1.0 $cm^2.s^{-1}$) and D_i is the effective diffusivity ($cm^2.s^{-1}$) of radionuclide *i* calculated from the test data.

These calculations are recommended by ANSI/ANS [2003] methodology for the standard 5 days test with 7 sampling intervals or 90 days interval with 10 sampling intervals.

In performed leaching experiments not all of required conditions of sampling intervals were fulfilled, nevertheless the leachability index and diffusion coefficient were calculated based on ANSI/ANS-16.1-2003 methodology equations.

In the leaching tests the ratios of liquid volume (cm^3)/sample surface (cm^2) = 10 or 5 and 2.2 (cm) were used. The recommended ratio value = 10 was used in the first leaching test of cemented artificial SIER labelled by ^{14}C bicarbonate. Because of very slow leaching of the tracer it was suggested to increase of the leaching medium amount and try to reach the higher activity values in the leachate for better evaluation of the leaching process. Therefore the ratio of liquid volume/sample surface = 5 and 2.2 was used in all other leaching tests.

5 Results and Discussion

5.1 *CEA*

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

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

Desorption experiments, which are evaluated in following text, were performed for sample EDF- B.

5.1.1 Total ^{14}C

The activities obtained on December 5th 2014 on dry and wet samples in $Bq.g^{-1}$ are indicated in Table 3.

Table 3. ^{14}C total determination in SIERs (December, 5th 2014).

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

5.1.2 ^{14}C partition between mineral and organic forms

The activities obtained on December 5th 2014 in $Bq.g^{-1}$ on dry and wet same samples are presented in Table 4.

Table 4. ^{14}C determination for the repartition between mineral and organic forms in SIERs (December 5th 2014).

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

5.1.3 ^{14}C desorption

The behaviours of the mineral and organic ^{14}C forms are shown in tables and figures below. 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 < 1.3 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).

Table 5. Determination of the speciation ^{14}C remaining in SIERs after desorption from sample EDF-B.

Experiment		^{14}C Bq.g^{-1} After experiment
1	Sub sample1	209 ± 12
	Sub sample2	153 ± 8
	Average	*180 ± 80*
2	Sub sample1	175 ± 12
	Sub sample2	150 ± 8
	Average	*162 ± 38*

No radiochemical measurements have been performed on the solutions coming from the “blank” and “virgin resins” experiments.

Table 6. Desorption and cumulative desorption of ^{14}C (total, mineral, and organic forms) during desorption experiments for sample EDF-B experiment 1 — activities measured on July 1st 2016.

Sample		**EDF-B**					
Experiment		N°1					
Mass		1.0973 ± 0.0004 g					
^{14}C		Mineral form		Organic form		Total	
Seq	Media	Desorption Activity Bq.seq^{-1}g^{-1}	Cumulative Desorption Bq.g^{-1}	Desorption Activity Bq.seq^{-1}g^{-1}	Cumulative Desorption Bq.g^{-1}	Desorption Activity Bq.seq^{-1}g^{-1}	Cumulative Desorption Bq.g^{-1}
1	LiOH 10^{-3}M	<3	<3	<3	<3	<3	<3
2	LiOH 10^{-3}M	<3	<3	<3	<3	<3	<3
3	LiOH 1M	447 ± 73	447 ± 73	259 ± 37	259 ± 36	705 ± 63	705 ± 63
4	LiOH 1M	221 ± 30	668 ± 79	114 ± 20	372 ± 41	335 ± 23	1040 ± 67
5	LiOH 1M	98 ± 14	766 ± 80	51 ± 11	423 ± 43	149 ± 9	1189 ± 67
6	LiOH 1M	46 ± 9	812 ± 80	31 ± 8	454 ± 44	77 ± 5	1266 ± 67
7	LiOH 1M	20 ± 12	832 ± 81	29 ± 11	483 ± 45	50 ± 5	1315 ± 68
8	LiOH 1M	11 ± 9	843 ± 82	19 ± 9	502 ± 46	30 ± 3	1345 ± 68
9	H_2O	<1,3	843 ± 82	<1,3	502 ± 46	<1,3	1345 ± 68
10	H_2O	<1,3	843 ± 82	<1,3	502 ± 46	<1,3	1345 ± 68

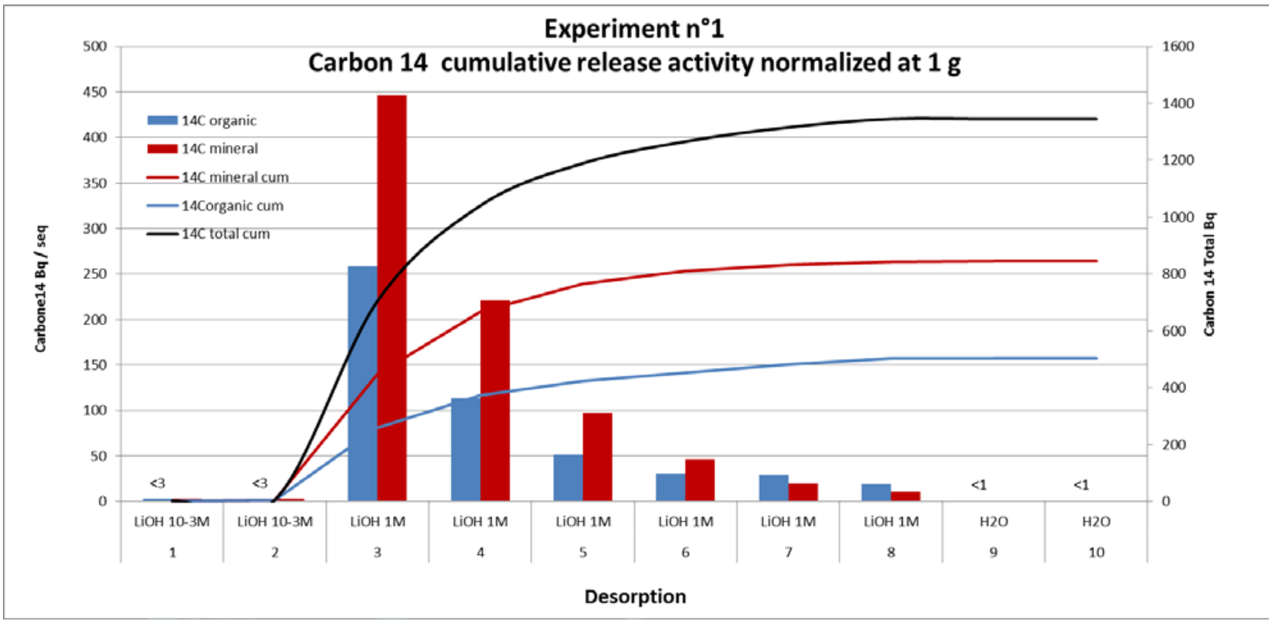


Figure 13. Desorption and cumulative desorption of ^{14}C (total, mineral, and organic forms) during desorption experiments for sample EDF-B experiment 1.

Table 7. Desorption and cumulative desorption of ^{14}C (total, mineral, and organic forms) during desorption experiments for sample EDF-B experiment 2 — activities measured on July 1st 2017.

Sample		**EDF-B**					
Experiment		N°2					
Mass		1.1864 ± 0.0004g					
^{14}C		Mineral form		Organic form		Total	
Seq	Media	Desorption Activity Bq.seq^{-1}g^{-1}	Cumulative Desorption Bq.g^{-1}	Desorption Activity Bq.seq^{-1}g^{-1}	Cumulative Desorption Bq.g^{-1}	Desorption Activity Bq.seq^{-1}g^{-1}	Cumulative Desorption Bq.g^{-1}
1	LiOH 10^{-3}M	<3	<3	<3	<3	<3	<3
2	LiOH 10^{-3}M	<3	<3	<3	<3	<3	<3
3	LiOH 1M	406 ± 51	406 ± 51	263 ± 34	263 ± 34	669 ± 38	669 ± 38
4	LiOH 1M	211 ± 26	617 ± 57	110 ± 17	373 ± 38	321 ± 20	990 ± 43
5	LiOH 1M	90 ± 13	707 ± 59	52 ± 10	425 ± 39	142 ± 9	1132 ± 44
6	LiOH 1M	41 ± 11	748 ± 60	29 ± 9	454 ± 40	70 ± 5	1202 ± 44
7	LiOH 1M	19 ± 7	767 ± 60	28 ± 5	482 ± 40	47 ± 4	1249 ± 45
8	LiOH 1M	10 ± 5	777 ± 60	18 ± 4	500 ± 41	28 ± 3	1277 ± 45
9	H_2O	<1,3	777 ± 60	<1,3	500 ± 41	<1,3	1277 ± 45
10	H_2O	<1,3	777 ± 60	<1,3	500± 41	<1,3	1277 ± 45

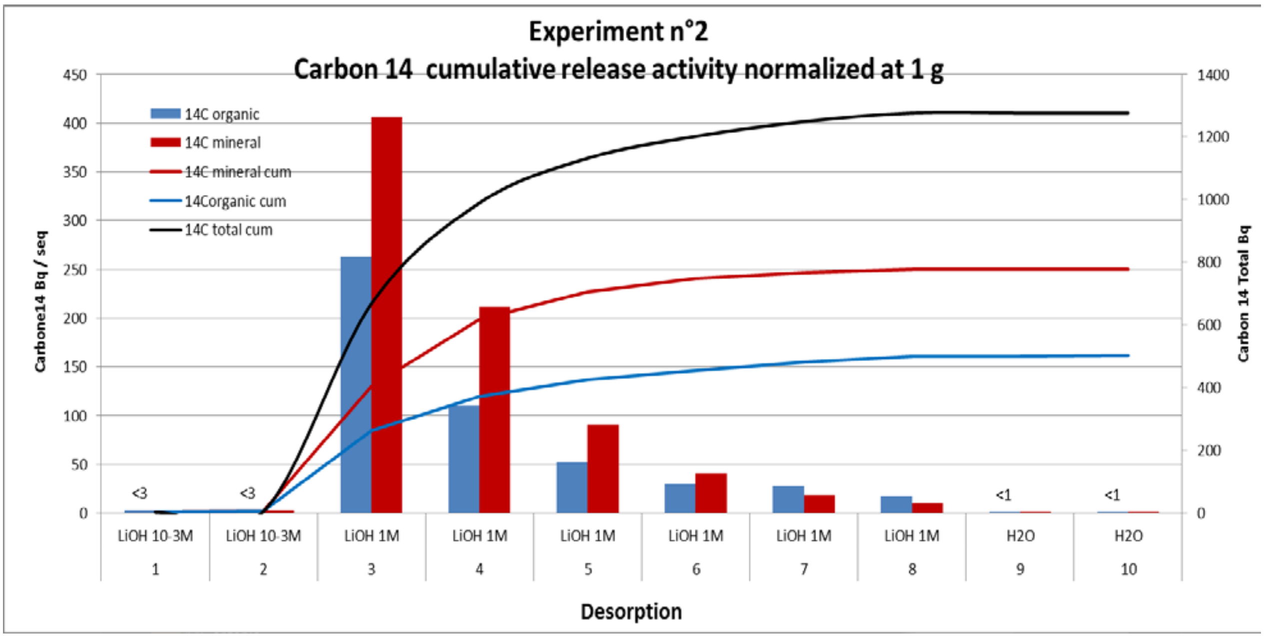


Figure 14. Desorption and cumulative desorption of ^{14}C (total, mineral, and organic forms) during desorption experiments for sample EDF-B experiment 2.

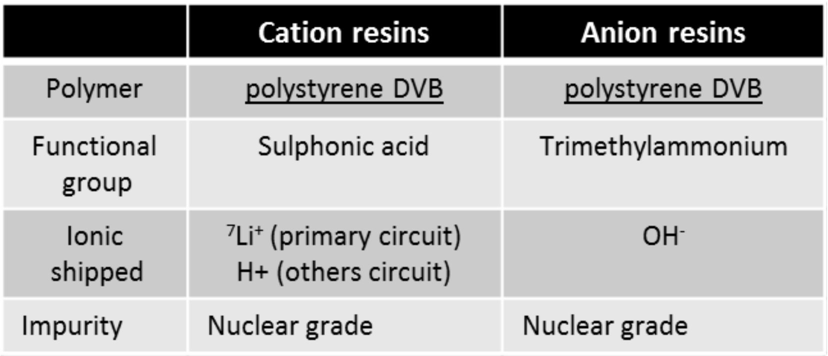
5.1.4 Organic carbon speciation

Only experiments carried out in LiOH 1 M medium were analysed. Three kinds of desorption solutions are prepared:

- LiOH at 1 mol.L^{-1} alone (Blank);
- Mixed bed inactive virgin resin "IERs" (experiment 1 and 2 for the repeatability), noted V;
- Mixed bed active resins from EDF "SIERs" (experiment 1 and 2 for the repeatability), noted F.

The mixed bed resin is presented in Table 8.

Table 8. Mix bed resin description



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

After 30 min, the liquid is removed for analysis and a new alkaline solution is re-introduced. 6 sequences in LiOH 1 M are realized every 30 min.

The samples are named by the experiment/sample/sequence.

(For example "1F6" - It is the desorption solution of active SIERs coming from experiment 1 and sequence 6)

5.1.4.1 Organic and inorganic total carbon partition

All desorption resin solutions have been analysed by total carbon analyser to determine TOC concentration. The TIC is not presented because the concentration has changed with the carbonation of solutions during all the study.

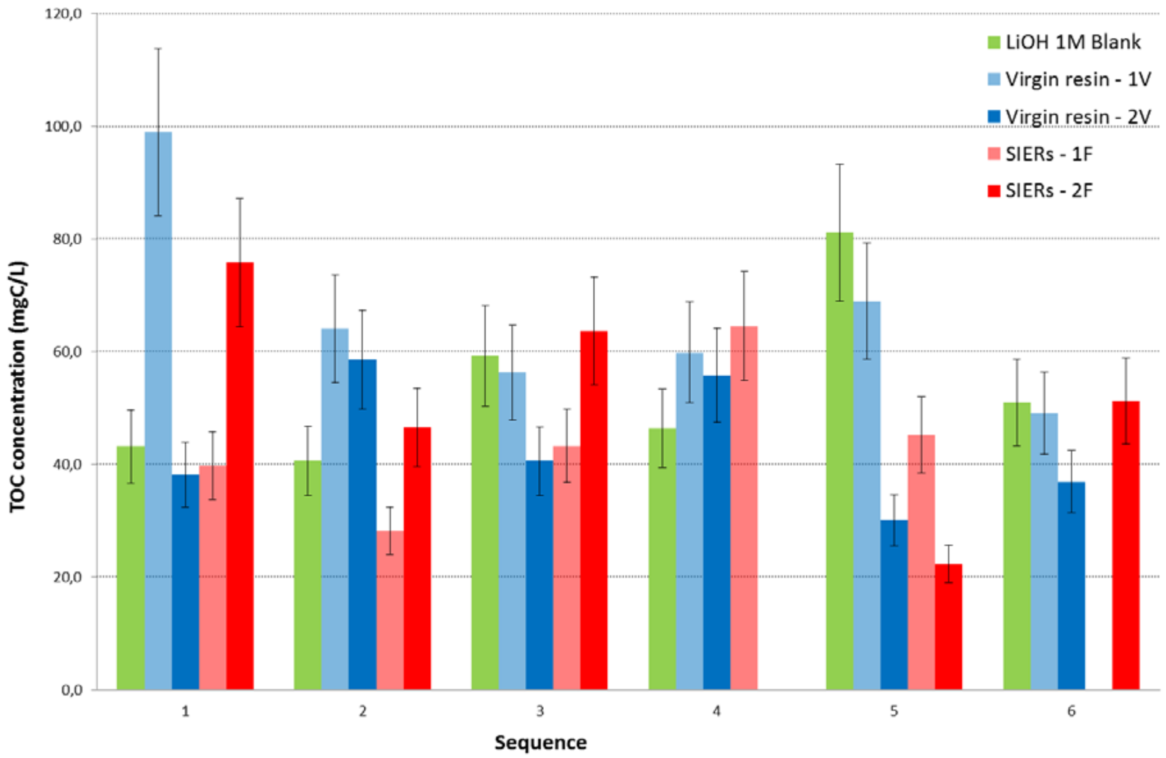


Figure 15. TOC results from LiOH leaching of EDF resins in CEA.

The presence of TOC is observed in LiOH solutions (blank) represented in green on the previous figure. This results shows that there is a carbon contamination. This contamination is variable and not controlled.

The TOC concentration in resin desorption solutions is in the same order of magnitude than in LiOH "blank" solutions (in blue from virgin resin and in red from SIERs resin). The point 1V1 is very different with the other sample, 2V1, realized in the same conditions, maybe because of contamination.

The TOC contamination is high and by comparison the TOC in resin desorption solutions is not significant. Thus it is difficult to conclude on organic carbon coming only from resin desorption. Analytical techniques will now be carried out in order to identify organic carbon in desorption solutions.

5.1.4.2 Quantification of carboxylic acids by aIC

Different resin desorption solutions have been analysed by anionic chromatography to quantify carboxylic acids:

- 2 samples of virgin resins – experiment 1 - sequences 1 and 6;
- 6 samples of virgin resins - experiment 2 - sequences 1 to 6;

- 2 samples of SIERs - experiment 1 - sequences 1 and 6;
- 6 samples of SIERs – experiment 2 - sequences 1 to 6.

The retention time can slightly change during the analysis sequence. Some standard molecules are regularly analysed to verify the identification.

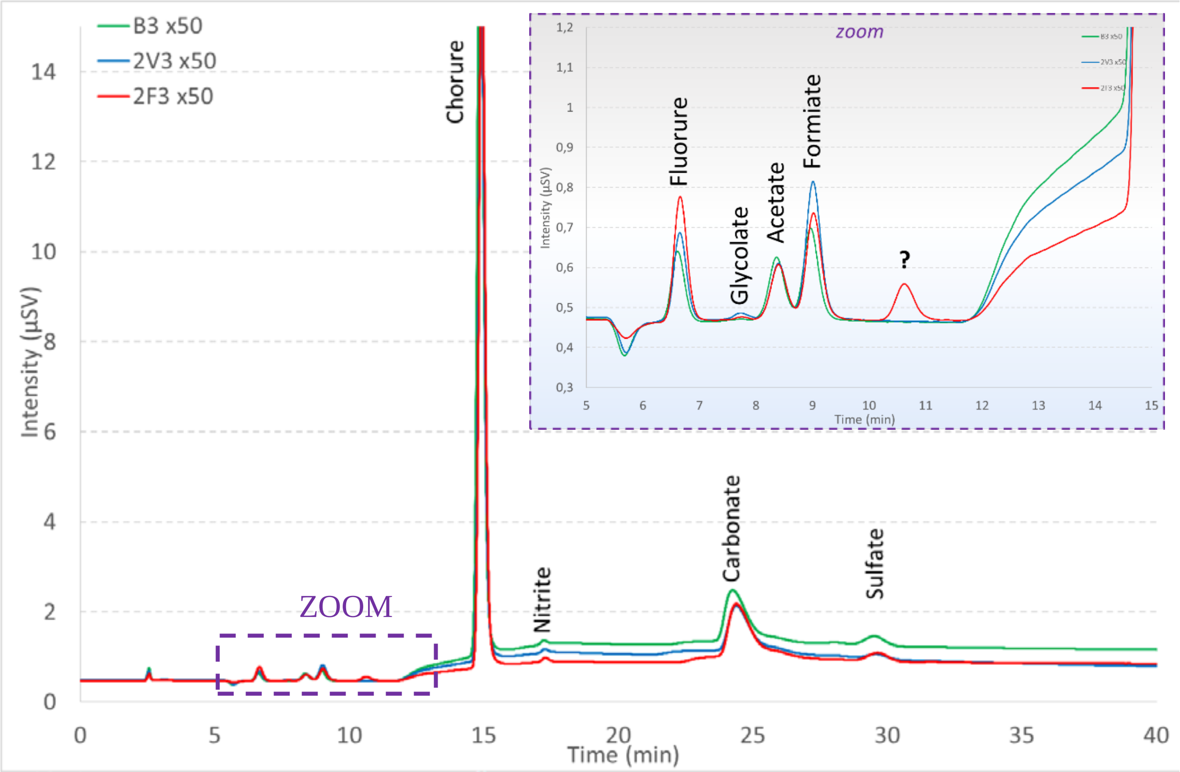


Figure 16. Example of chromatograms obtained by anionic chromatography (Comparison of LiOH blank in green, virgin resin in blue and SIERs in red desorption solutions from sequence 3).

Different molecules have been observed:

1. inorganic anions like fluoride, chloride, nitrite, sulphate and nitrate,
2. one molecule with TIC : carbonate in significant concentration, due to carbonation of solution,
3. molecules with TOC as glycolate, acetate and formate. These two last compounds, acetate and formate, are also detected in LiOH “blank” solutions. Only glycolate ($C_2H_3O_3^-$) seems to come from virgin resins and SIERs desorption,
4. one peak at retention time of 11 min only observed in SIERs desorption solutions. This molecule is not identified, so we cannot conclude if it is an organic or inorganic compound.

The quantification has been realized on three complete sequences of LiOH solutions, virgin resins and SIERs. It is difficult to conclude on the acetic and formic concentrations coming from resin desorption because some quantities come from variable LiOH solution.

Table 9. Carboxylic acids concentrations in desorption solution — uncertainty 15%, activities measured on July 1st 2016.

Sample	**$mg_{acid}.L^{-1}$**		
	Glycolic acid	**Acetic acid**	**Formic acid**
B1	< 1	5	8
B2	< 1	10	5
B3	< 1	4	6
B4	< 1	3	5
B5	< 1	4	5
B6	< 1	17	9
2V1	8	5	32
2V2	4	7	15
2V3	2	3	10
2V4	< 1	< 1	2
2V5	< 1	< 2	16
2V6	< 1	8	10
2F1	3	4	13
2F2	2	11	8
2F3	2	3	8
2F4			
2F5	2	< 2	10
2F6	< 1	15	11

5.1.4.3 Quantification of amines by cIC

Due to the structure of resins (trimethylammonium functional groups), molecules with amine functions can be formed. So different resin desorption solutions have been analysed by cationic chromatography to quantify amines:

- 2 samples on virgin resins - experiment 2 – sequences 1 and 6;
- 2 samples on SIERs - experiment 2 - sequences 1 and 6.

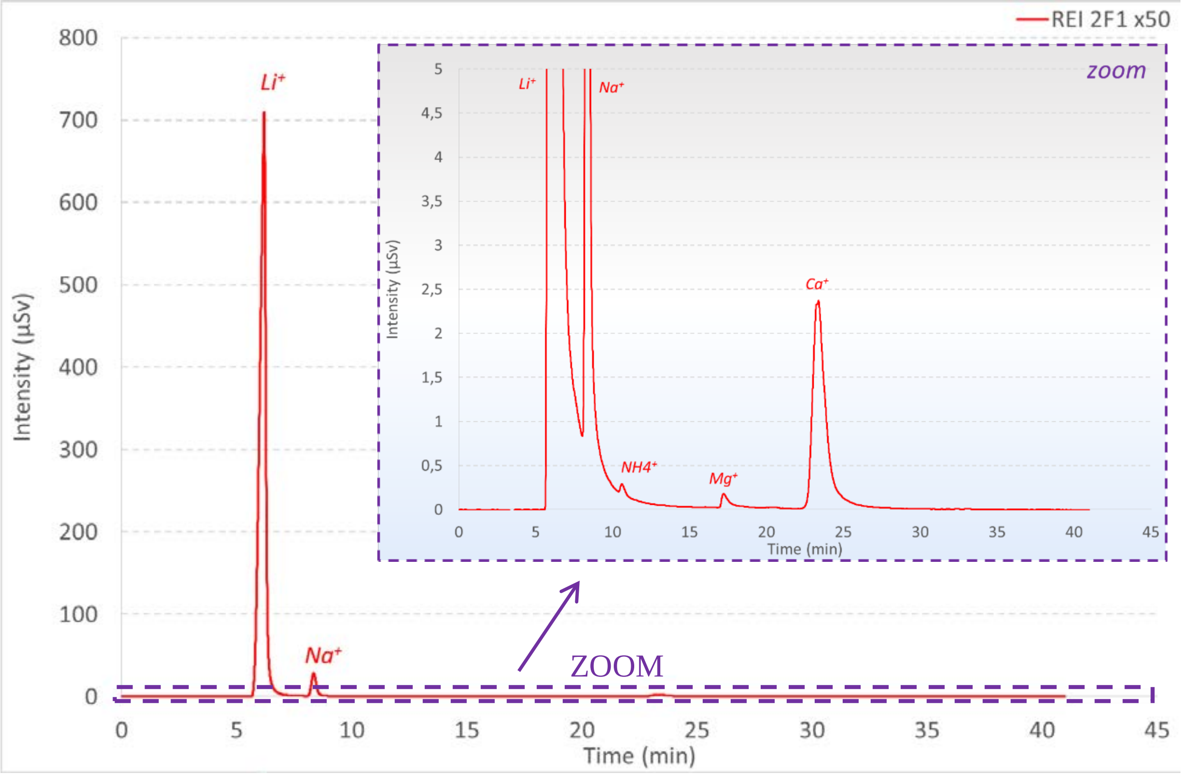


Figure 17. Example of chromatograms obtained by cationic chromatography (Active SIERs desorption solution of experiment 2 and of sequence 1).

Different inorganic species like lithium, sodium, ammonium, magnesium and calcium cations are observed but no peak corresponding to amines. These results are consistent with those observed by van Loon and Hummel [1995]. In this publication was presented analyses of desorption solutions of highly irradiated resins (1.7 MGy). Moreover, the sulphate concentration is the same between virgin resins and SIERs solutions. We don't observe the chemical degradation of functional groups (sulphonic acid or trimethylammonium) under these conditions.

5.1.4.4 Detection of low molecular weight volatile molecules by GC-MS

Different resin desorption solutions have been analysed after derivatization by GC-MS to detect low semi volatile molecules:

- 1 sample of LiOH solution - sequence 2;
- 1 sample of virgin resins – experiment 2 - sequence 2;
- 1 sample of SIERs – experiment 2 - sequence 6.

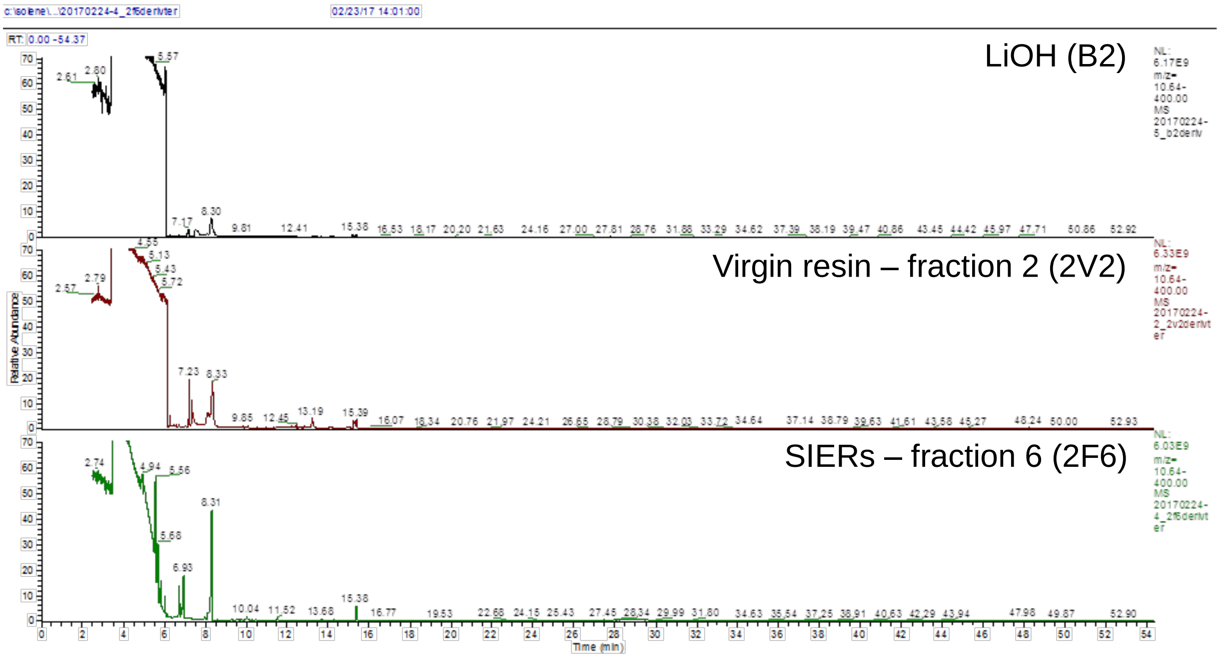


Figure 18. Comparison of three GC-MS chromatograms of LiOH and two resin desorption solutions (Virgin resin and SIERs desorption solutions).

Some peaks have been detected for all samples but no difference between resin desorption solutions and LiOH solutions is observed. Main of these peaks, before 9 min, are due to derivatization compound and not directly from samples. This analytical method did not allowed us to identify precisely organic compounds with low molecular mass in resin desorption solutions, such as carboxylic acids, alcohols, primary and secondary amines. In the absence of identified compounds, it is not possible to calculate a quantification limit.

5.1.4.5 Detection of molecules with higher molecular mass by ESI-MS

The laboratory experiments have shown that the desalination step of sample by filtration has not given good results. Salts are removed after filtration but a decrease of organic carbon content around 30-40% has also been observed. As it was shown that the desalination is not conclusive, the sample is only diluted in methanol to improve the ionization and directly analysed, even if the presence of salts in high concentration hides detection of organic compounds.

Different resin desorption solutions have been analysed after dilution in methanol by ESI-MS in positive and negative modes to detect organic compounds with higher molecular weights:

- 1 sample of LiOH solution - sequence 6;
- 1 sample of virgin resins – experiment 2 - sequence 2.

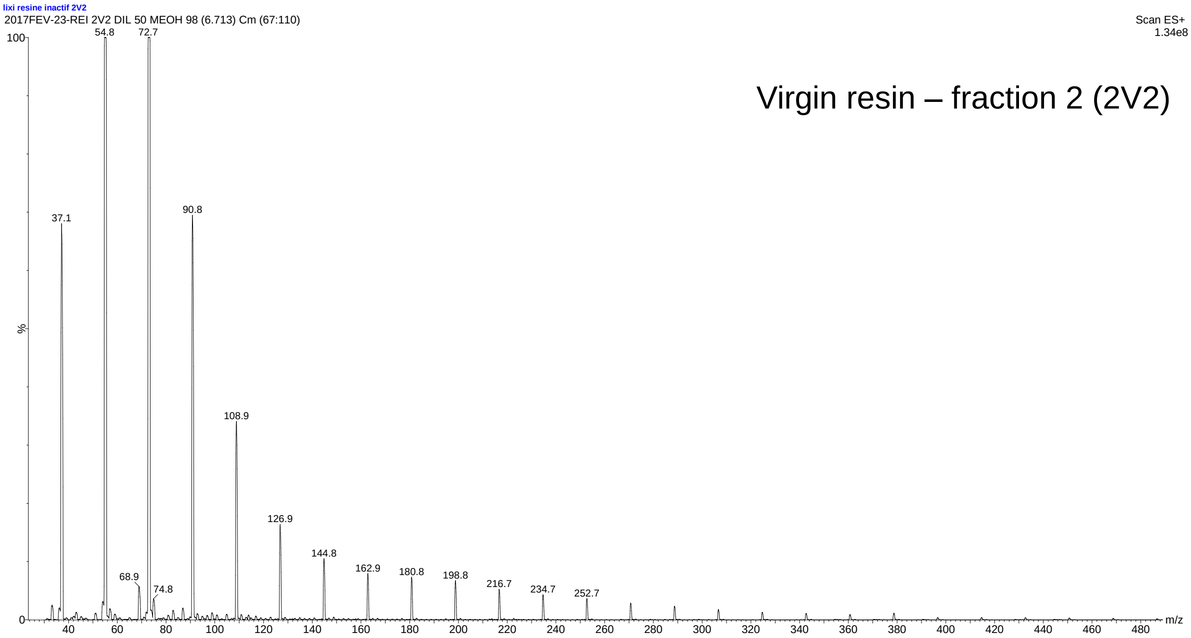


Figure 19. Example of ESI spectrum in positive mode of a virgin resin desorption solution.

This analysis shows only the ionization of LiOH/MeOH matrix and no organic compound with higher molecular weight in solution is detected in these conditions. If the sample contains organic compounds, they are probably hidden by the signal of LiOH.

5.1.5 ^{14}C desorption experiment interpretations

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 3), evidence a loss of ^{14}C during desorption experiments. A difference about 30% is measured. The organic fraction determined during desorption tests represents around 38% of the total desorbed activity, showing an apparent loss of inorganic ^{14}C during the desorption protocol.

Table 10. ^{14}C desorption assessment of the experiment with wet EDB-B SIER.

Experiment **Sample EDF-B**	**1**	**2**
Mineral Form (Bq.g^{-1})	843 ± 82 (63%)	777 ± 60 (60%)
Organic form (Bq.g^{-1})	502 ± 46 (37%)	500 ± 41 (39%)
Total desorbed fraction(Bq.g^{-1})	1345 ± 68	1277 ± 45
Final activity (Bq.g^{-1})	180 ± 80	162 ± 38
Estimated initial activity (Bq.g^{-1})	1525 ± 200	1440 ± 80

Desorption tests allow obtaining solutions with organic ^{14}C from SIERs, which was 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 possible volatilization of organic or mineral forms of ^{14}C during the experiments in reason of chemical reactions of the solution on minerals or organic compounds.

5.1.6 Interpretation of organic carbon speciation in resin desorption solutions

Carbon mass balance is calculated: around 12% of carbon mass balance is identified in LiOH "blank", virgin resins and SIERs solutions. The only organic identified compounds in resin desorption solutions, glycolate, stays in very low concentration around 1% of TOC. The identified carboxylic acids doesn't complete the carbon mass balance, even in LiOH solution. So, others molecules are in solution and probably contamination in high concentrations.

Table 11. Total carbon mass balance results.

Sample	**mg$_C$.L^{-1}**				**Identified carbon (%)**
	Glycolic acid	**Acetic acid**	**Formic acid**	**TOC**	
B1	< 1	2	2	43	9
B2	< 1	4	1	41	12
B3	< 1	2	2	59	5
B4	< 1	1	1	46	5
B5	< 1	1	1	81	3
B6	< 1	7	2	51	18
2V1	3	2	8	38	34
2V2	1	3	4	59	13
2V3	1	1	3	41	11
2V4	< 1	< 1	1	56	1
2V5	< 1	< 1	4	30	14
2V6	< 1	3	3	37	16
2F1	1	2	3	76	8
2F2	1	4	2	47	15
2F3	1	1	2	64	6
2F4	-	-	-	-	-
2F5	1	< 1	3	22	15
2F6	< 1	6	3	51	18

No amine derivate is observed and ammonium is in very low concentration by ionic chromatography. So these observations can confirm that no or very little degradation of resin occurs in these conditions. Moreover, the contamination in LiOH makes difficult the characterization of organic molecules in resin desorption solutions.

5.2 *FZJ*

5.2.1 Radionuclide inventory of SIERs

The analysis of radionuclide inventory of SIER samples used for leaching experiments is reported in Table 12.

Table 12. Radionuclide inventory of the investigated SIERs samples.

Sample	**Total ^{14}C [Bq.g^{-1}]**	**^{60}Co [Bq.g^{-1}]**	**^{137}Cs [Bq.g^{-1}]**	**^{134}Cs [Bq.g^{-1}]**	**^{54}Mn [Bq.g^{-1}]**
FZJ-A	1906 ± 256	360.7 ± 10.8	72.0 ± 3.6	4.75 ± 0.48	17.6 ± 1.2
FZJ-B-2	553*	138.1 ± 4.1	276.5 ± 8.3	0.80 ± 0.16	< 0.1

*only one sample was analysed

5.2.2 Radionuclide inventory of suspension water

The suspension water in contact and delivered together with FZJA was characterised. Results are reported in Table 13. Due to the very low activities, the amount of suspension water has been maximized to possibly overcome the detection limits of the instruments. LSC samples´ volume was 5 mL, while 20 mL were used for gamma spectrometry. Despite that, no measurable activity was found above the background, except for ^{3}H. HPLC analyses did not reveal any measurable compound in solution.

Table 13. Radionuclide inventory of suspension water from FZJ-A

Radionuclide	**^{3}H**	**^{14}C Total**	**^{60}C**	**^{137}Cs**	**^{134}Cs**	**^{54}Mn**	**^{152}Eu**	**^{154}Eu**	**^{125}Sb**
Concentration [Bq.mL^{-1}]	≈ 5.7	< 0.02	< 0.002	< 0.004	< 0.004	< 0.004	< 0.01	< 0.007	< 0.013

5.2.3 Batch leaching FZJ-A

Static leaching of FZJ-A SIERs in contact with deionised water (in air) lasted for three months, after which the gas phase and the leachate were analysed. Very small amounts of inorganic ^{14}C (in the order of 0.1 Bq.g^{-1}) were detected in the gas phase, while no activity was found in the liquid phase. The gas phase was completely collected in washing bottles by inert gas flushing [BUCUR *et al.*, 2017]. Since only 0.5 mL of the leachate were used for LSC, assuming an equilibrium of the system SIERs/water/gas, the expected activity in the liquid phase would be below the LSC detection limit.

The amount of ^{14}C retained in the FZJ-A SIERs is, however, considerable. Considering the leaching mechanism of ^{14}C, *i.e.* ion-exchange and possibly isotope-exchange, activities expected in the liquid and gas phase should be higher. FZJ-A SIERs were, however, stored in a (probably) open system in contact with air for several years, leading to a possible leaching during intermediate storage. The very low release of ^{14}C, despite the significant amount of ^{14}C retained in FZJ-A SIERs, could be explained by inorganic forms with different electrostatic interaction strengths, as *e.g.* divalent and monovalent ions (CO_3^{2-} and HCO_3^-). Such a hypothesis should be, however, verified.

The results of HPLC analysis of suspension water in contact with FZJ-A showed no measurable compound above the background.

5.2.4 Dynamic leaching of FZJ-A/B

Results of the dynamic leaching are reported in Figure 20 (deionised water) and Figure 21 (NaCl solution). A well-defined peak can be noticed in both chromatograms, with a retention time of 12.7 min. The HPLC calibration with standard solutions allowed the identification of the compound corresponding to the measured peak: formic acid. This organic molecule was hypothesized by MAGNUSSON *et al.* [2008]. However, possible interferences with other compounds should be further verified.

It is not clear whether such a molecule arises from the water circuit of the BWR (^{14}C-labled) or from the degradation of the ion-exchange resins. A separation of sufficient amount of this compound using HPLC was, however, not possible, so an activity determination of this fraction was not performed. In fact, the concentration of formic acid, obtained from the HPLC calibration with standard solutions, resulted to be about $0.01 \cdot 10^{-3}$ mmol.g_{resin}^{-1} for the deionised water and about $0.5 \cdot 10^{-3}$ mmol.g_{resin}^{-1} for the NaCl solution. A direct LSC analysis with deionised water did not reveal any detectable activity. For SIERs leached in 0.85 M NaCl solution other radionuclides (mainly gamma/beta emitters) were released along with ^{14}C, therefore a quantification of the ^{14}C fraction was not possuble due to the presence of other interferring radionuclides.

Similar experiments with deionised water in contact with FZJ-B SIERs did not provide any measurable results above the background. Most probably, the drying process of FZJ-B SIERs influenced these results. Regeneration tests with NaCl on FZJ-B SIERs were not performed.

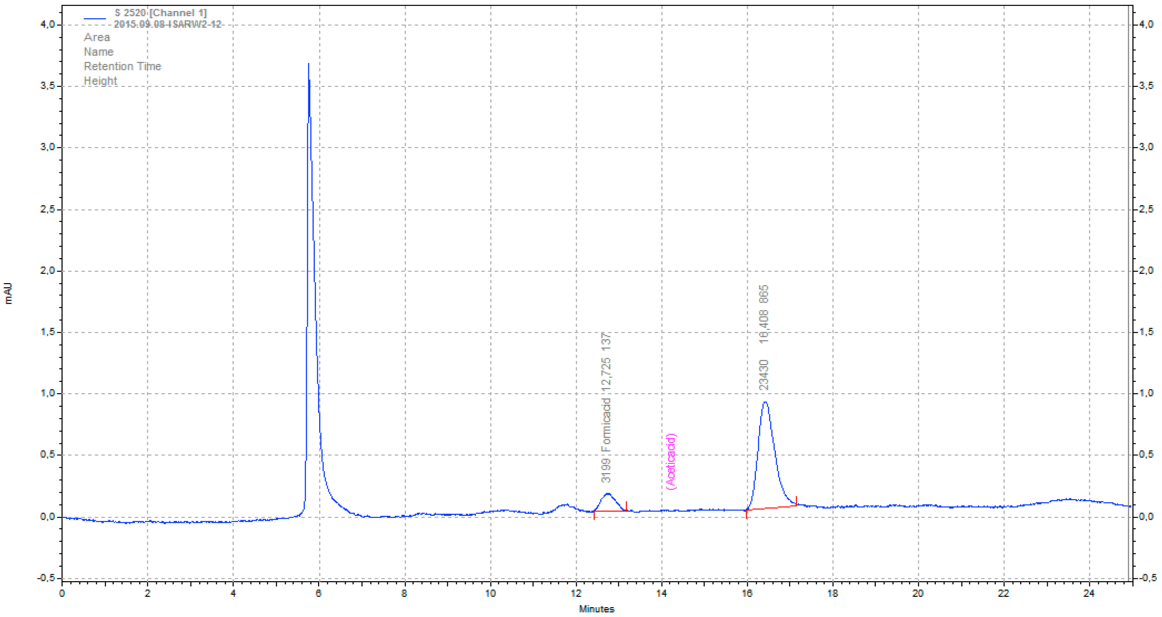


Figure 20. Chromatogram of deionised water in contact with FZJ-A SIERs.

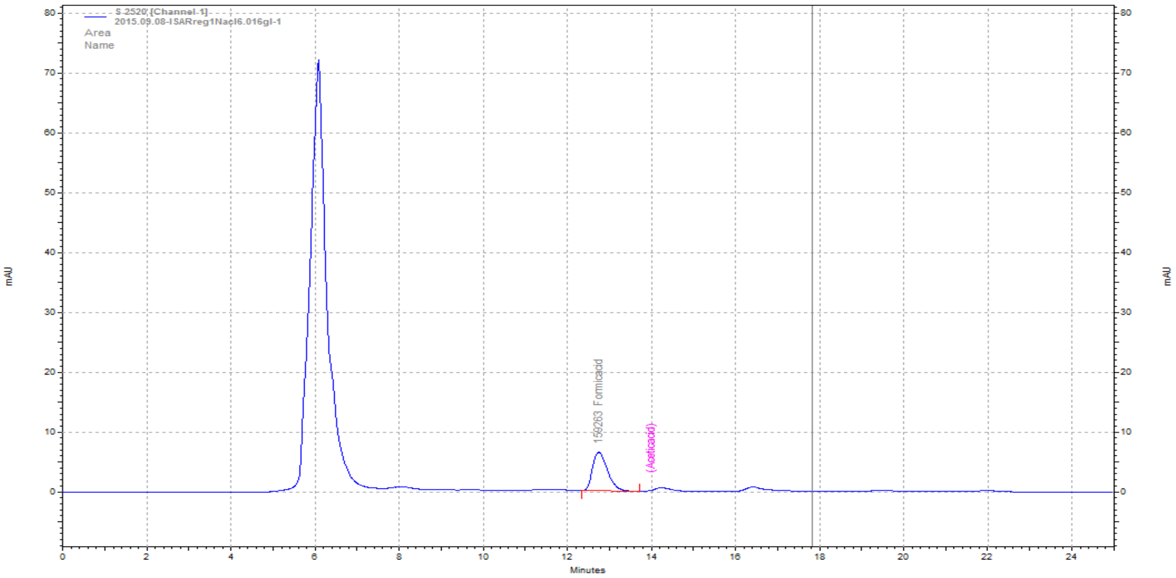


Figure 21. Chromatogram of NaCl solution in contact with FZJ-A SIERs.

Formic acid is a diprotic acid and it can be bound to the anion-exchange resins in ionic form ($HCOO^-$). Earlier reports [BARRON AND FRITZ, 1984; DUVAL AND FRITZ, 1984; DOW, 2016] demonstrate selectivity values for formate ions bound to the resins to be between those for OH^- ions and the HCO_3^- ones (Table 14). In general, any disturbance of the system's equilibrium (SIERs/liquid phase/gas phase) is likely to result in releases, depending on the selectivity coefficients of the single compounds. The presence of formic acid (^{14}C-labeled) bound to the SIERs has been reported also in RIZZO *et al.* [2017], corresponding to about 89% of the ^{14}C organic fraction's activity.

Table 14. Ion selectivities for SBA IERs reported in literature [DOW, 2016]

Ion	Reference
OH^- (reference)	1.0
CH_3COO^-	3.2
$HCOO^-$	4.6
HCO_3^-	6.0

Other compounds as *e.g.* TMA, oxalic acid, SIERs' degradation products, could be expected to be found in solution. Dedicated analytical methods should be implied for their identification, considering the presence of possibly high activities in solution and interfering compounds.

After regeneration, a separation of the leachate from the SIERs by *e.g.* filtration could allow evaluating the total ^{14}C released in the liquid phase and the fraction left in the resins. Additionally, the inorganic and organic ^{14}C fractions released in solution could be evaluated by applying a method as the one reported by MAGNUSSON *et al.* [2008].

5.2.5 Online gas releases from SIERs at high pH

The experiment of static leaching, implying FZJB SIERs and cement pore water, was abandoned, since an evolution of gas was observed during sample preparation as soon as the alkaline solution became in contact with the sample. Consequently, an on-line measurement of the eventual releases in the gas phase was performed, as reported in D4.7 [BUCUR *et al.*, 2017].

Results from the on-line analyses of the gas phase, resulting from FZJB-2 SIERs in contact with cement pore water, revealed a consistent release of ^{14}C within the first 24 hours (Figure 22).

^{14}C was retained exclusively in the third washing bottle (alkaline), therefore the gaseous releases from SIERs in a high pH environment were indicated to be in form of $^{14}CO_2$ (no organic ^{14}C was detected). This seems to be inconsistent with CO_2 release from a solution with high pH, since at high pH no CO_2 should be in gas form, but remained in the solution in the carbonate form.

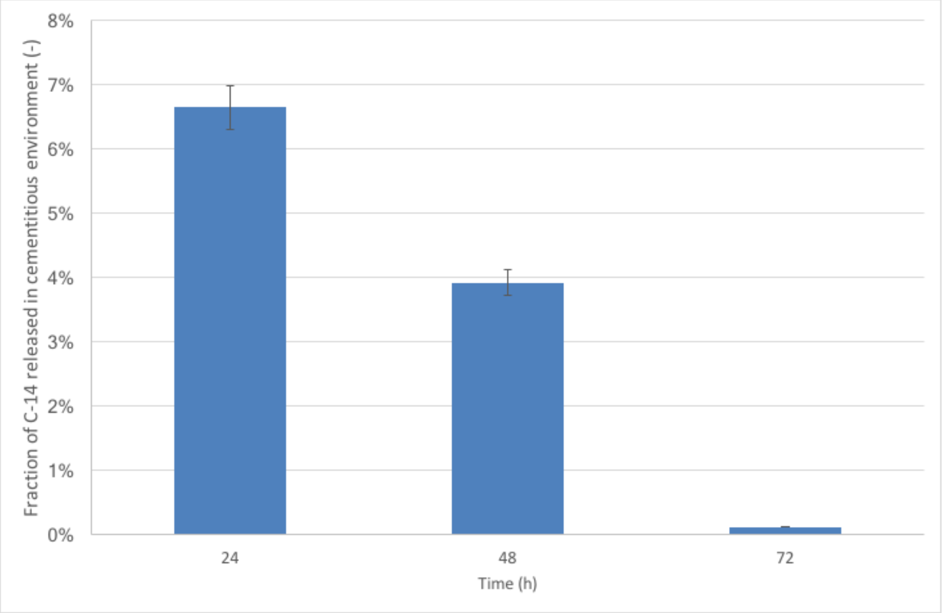


Figure 22. On-line gaseous release of inorganic ^{14}C from FZJ-B-2 SIERs in contact with cement pore water. Values referred to the total sample´s mass as delivered.

A possible mechanism, leading to the release of CO_2, could imply a decrease in the pH value, in a transient or permanent way. Once SIERs are in contact with the solution, cations like Na^+ or K^+ (relatively big compared to the anions OH^-) are exchanged with a faster kinetics compared to the anions. Assuming that cation-exchange groups are not saturated with counter-ions (*e.g.* in the original H^+ form) or that the same groups are containing hydrogenated compounds, the release of such cations in solution would be faster compared to the release of anions. In this case, the solution would experience a local decrease in the pH that could result in a transient — in case the solution has a sufficient molarity to overcome the released cations. When the molarity of the alkaline solution is not sufficiently high to compensate the release of H^+ ions, instead of a transient phenomenon the decrease of the pH would be permanent. Another hypothesis would imply the release of cation-exchange groups (-SO_3H) in solution due to a degradation of the resins. Measurements of the residual cation-exchange capacity of SIERs seem to disprove this hypothesis, but small releases cannot be excluded – more details in RIZZATO [in prep.].

To clarify the mechanism leading to the release of $^{14}CO_2$ in alkaline conditions, two additional experiments were performed on FZJ-A. The first one consisted in mixing 1 g FZJ-B SIERs with 10 mL cement pore water solution and on measuring the evolution of the pH with a pH-meter. A transient (in the order of minutes) was in fact observed in all cases (all FZJ-B samples), with pH values down to 7.3, value low enough to allow the presence of gaseous CO_2. The second experiment, more detailed, consisted of mixing 1 g of FZJB SIERs with increasing amounts of alkaline solution (XOH, with X = K, Na), at a well-defined molarity. The pH was then measured after several minutes, allowing the system to equilibrate. Results are shown in Figure 23, reporting the pH as a function of the equivalent volume of added solution at 0.029 M. One can notice that the pH value, in all cases, is very low for low amounts of volume added, since OH^- ions in the original solution are not sufficient to compensate the released H^+ ions. By increasing the volume of solution added, the pH increases accordingly, up to the original pH of the cement pore water solution (13.2).

In conclusion, the mechanism implying a drop in the pH when an alkaline solution is in contact with SIERs seems to be confirmed. A more detailed description of the mechanism would require additional investigations. Considering the experimental conditions, however, and considering a cementation process of the SIERs, the number of anions present in a real cement mixture would be much higher than the ones employed here. Consequently, a test with a high-molarity alkaline solution (4.7 M NaOH) was performed to simulate a more realistic scenario. In this case, SIERs were placed in a glass column and the solution was let through from the top to the bottom, keeping the samples always covered. A local evolution of gases was observed (Figure 24), but the solution had enough OH^- ions to avoid any release of gases. In Figure 24 one can observe the evolution of the reaction front going through the resins, accompanied by the gas bubbles.

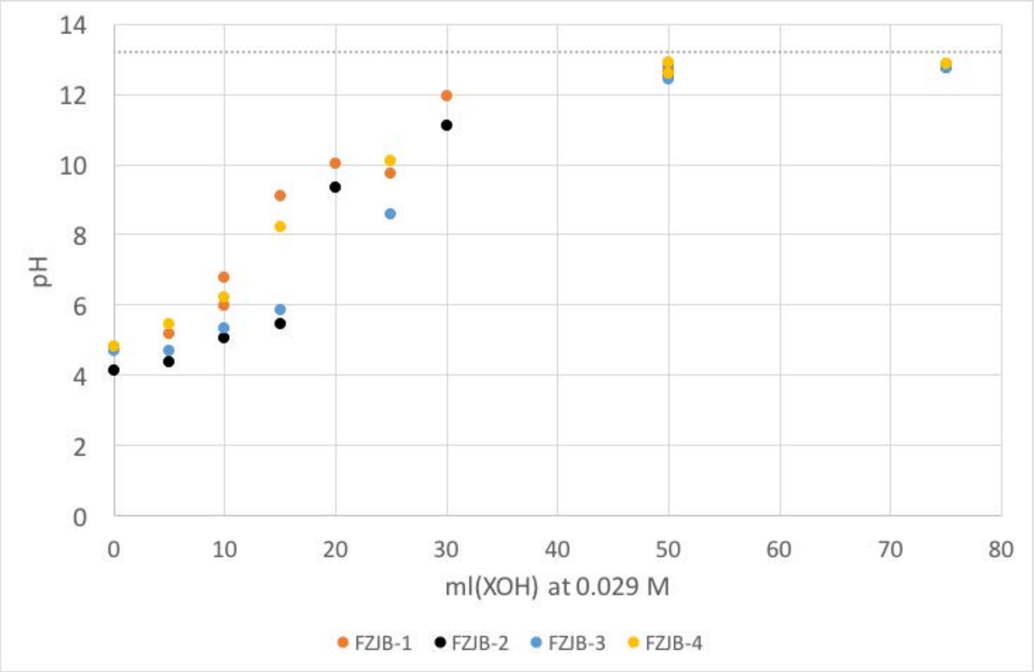


Figure 23. Static pH values of the solution in function of the equivalent volume in contact with FZJ-B SIERs. The initial point relates to the pH of deionized water in contact with SIERs.

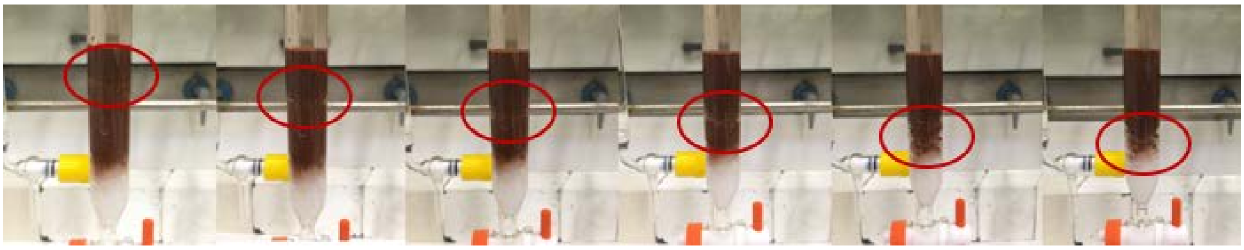


Figure 24. Evolution of gas at the reaction front of the alkaline solution in contact with FZJ SIERs.

5.3 *RATEN-ICN*

5.3.1 ^{14}C desorbed from the Cernavoda SIERs in alkaline solution

As presented earlier (c.f. §3.1.2), ^{14}C desorption tests were carried out in semi-dynamic conditions. In the first 4 days, 5 mL of leachate solution was sampled daily and replaced — in order to have the same resin to liquid ratio — with 5 mL of fresh NaOH 0.1 M solution. The same procedure was applied after 9, 17, 24, 45, 95, 122, and 174 days. The sampled solutions were analysed by acid stripping-wet oxidation method to measure the inorganic and organic ^{14}C content. The initial concentration activities of radionuclides in the SIER samples used for desorption tests are reported in Table 15.

Table 15. The initial radionuclide content in 5.3 RATEN-ICN SIER sample.

Radionuclide	Activity*, Bq.g^{-1} in wet SIERs (ω = 60.10%)
Total ^{14}C	$(3.37 \pm 0.12) \times 10^4$
Inorganic ^{14}C	$(3.14 \pm 0.15)\ 10^4$ (93.18%)
Organic ^{14}C	$(2.31 \pm 0.86)\ 10^3$ (6.85%)
^{3}H	$(1.43 \pm 0.49) \times 10^5$
^{137}Cs	$(1.72 \pm 0.07)\cdot 10^4$
^{60}Co	$(9.78\cdot \pm 2.25)\cdot 10^2$
^{134}Cs	$(3.48\cdot \pm 0.16)\cdot 10^2$

* *these data represent the average value of measurements carried out on 5 sub-samples from the SIER sample transferred from Cernavoda NPP* [RIZZO *et al.*, 2017].

The experimental data obtained from the desorption tests for the ^{14}C activity, expressed as total ^{14}C and inorganic and organic partition, measured at each sampling time in solution and gas, are reported in Table 16. As it can be seen from the experimental data presented in Table 16, the ^{14}C measured in desorption solution is mainly in inorganic form and only insignificant fraction was found to be in organic forms, at least for desorption times less than 24 days. After this time, the organic ^{14}C measured in desorption solutions represents around 8% from the total ^{14}C.

Table 16. The row data measured in desorption tests.

Time, days	Total ^{14}C measured in solution, Bq	Inorganic ^{14}C, Bq	Organic ^{14}C, Bq	Inorganic ^{14}C released in gas* Bq
1	4.96×10^3	4.95×10^3 (99.93%)	3.34 (0.07%)	96.83
2	6.10×10^3	6.09×10^3 (99.94%)	3.77 (0.06%)	82.75
3	5.93×10^3	5.93×10^3 (99.92%)	4.63 (0.08%)	79.02
4	5.63×10^3	5.63×10^3 (99.93%)	3.98 (0.07%)	99.10
9	4.93×10^3	4.93×10^3 (99.93%)	3.34 (0.07%)	92.70
17	4.72×10^3	4.72×10^3 (99.92%)	3.98 (0.08%)	95.91
24	4.22×10^3	3.87×10^3 (91.71%)	3.50×10^2 (8.29%)	86.80
45	4.35×10^3	3.98×10^3 (91.51%)	3.69×10^2 (8.49%)	84.16
174	3.35×10^3	3.08×10^3 (91.91%)	$2,71 \times 10^2$ (8.09%)	80.04

** these values were measured in the alkaline solution from the gas washing bottles used to wash the outgases from the desorption vessels before their opening to sample the leachate solution and represent only the inorganic ^{14}C released as gas phase.*

At each sampling time the ^{14}C is released mainly as dissolved species and less than 2% was measured as inorganic gas. No organic ^{14}C released as gas phase was measured during these desorption tests.

The row data presented in Table 16 were computed to keep account on the dilution introduced at each sampling time and the results are presented in Table 17 for the one of the desorption test (the experimental results obtained from the two parallel tests were very similar), and the global inventory of the ^{14}C in different phases of the desorption tests is presented in Table 18. The most part of ^{14}C released as dissolved species was released in the first 2 days (Figure 25).

Table 17. The ^{14}C released in liquid phase.

Time (days)	Initial ^{14}C activity in solution (Bq)	^{14}C released (Bq)
1	0	4.96×10^3
2	4.34×10^3	1.76×10^3
3	5.33×10^3	6.00×10^2
4	5.19×10^3	4.39×10^2
9	4.93×10^3	2.25×10^2
17	4.31×10^3	4.09×10^2
24	4.13×10^3	8.70×10^1
45	3.69×10^3	6.56×10^2
95	3.80×10^3	5.44×10^2
122	3.33×10^3	5.23×10^2
174	2.91×10^3	4.38×10^2

Data presented in Table 18 show that around 79% from the total ^{14}C present in the SIERs sample used for desorption test was released as dissolved species. At the end of desorption test the residual ^{14}C activity in the resin sample was less than 9% from the initial activity. Around 94% of ^{14}C introduced in the experiments was recovered at the end of desorption test. Difference of ~ 6% that was not found neither as dissolved species and inorganic gas species, nor as residual on the SIER sample after desorption test could be due to the inherent experimental errors — the uncertainty of this kind of test was estimated to be 20% — but could also represent the ^{14}C released in gas phase as organic species. But, since no organic ^{14}C in gas phase was measured this is only a hypothesis and further experiments need to be carried out to have a conclusion on organic ^{14}C release in gas phase. The desorption tests was very reproducible since the experimental results obtained in the two parallel tests were similar (Figure 25).

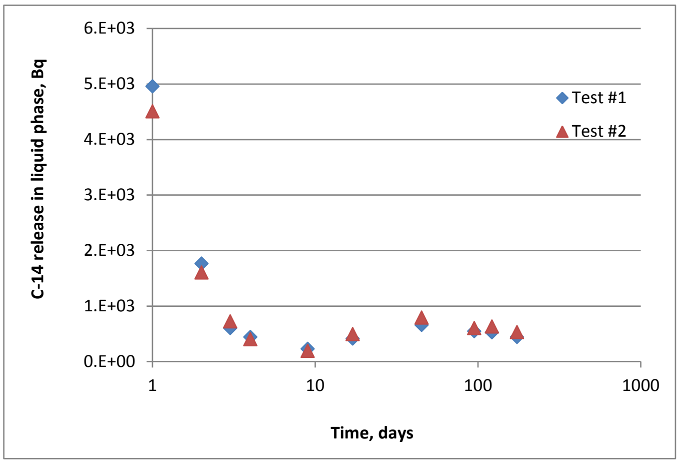


Figure 25. The ^{14}C release in liquid phase during the desorption tests in RATEN-ICN.

Table 18. The total amount of ^{14}C measured on the components of the desorption system.

^{14}C		Activity, Bq	% from the ^{14}C content of the SIER sample use for desorption test
^{14}C activity in SIER sample before desorption	Total ^{14}C	1.35 10^{4}	-
	Inorganic ^{14}C	1.26 10^{4}	-
	Organic ^{14}C	9.24 10^{2}	-
Residual ^{14}C in SIER sample at the end of desorption test	Total ^{14}C	1.12 10^{3}	8.30
	Inorganic ^{14}C	9.66 10^{2}	7.67
	Organic ^{14}C	1.52 10^{2}	16.45
^{14}C cumulative release in solution		1.06 10^{4}	78.52
Inorganic ^{14}C cumulative release in gas phase		980.03	7.26
Total ^{14}C measured at the end of desorption tests (in liquid, gas and residual on the SIERs)		1.27 10^{4}	94.07

5.3.2 ^{14}C uptake on ion exchange resin – the influence of thermal degradation

As it was specified in § 4.3.2, in order to have the same dried resin mass in all sorption tests, the residual water content of the investigated resins (fresh IRN 78 resin, IRN 78 resin dried at 50°C and IRN 78 resin dried at 80°C) was measured by the means of a thermo-balance. The residual water content of these resin samples is reported in Table 19.

Table 19. Residual water content in the resin samples used for ^{14}C sorption experiments.

Resin sample	Water content (%)
Fresh IER	58.43
IER dried at 50°C	21.68
IER dried at 80°C	17.37

The results from the batch sorption experiments carried out to assess the effect of thermal degradation on ^{14}C uptake on ion exchange resins were expressed as the absorption percentage at each contacting time, using the following equation.

$$A_{ti} = \frac{m_s^{ads}(ti)x100}{m_0} \tag{7}$$

where: A_{ti} is the sorption percentage at time ti (%), $m_s^{ads}(ti)$ is the amount of ^{14}C on the IER at the time ti when the analysis is performed (Bq), m_0 is the amount of ^{14}C in the contact solution at the beginning of the test (Bq).

The amount of ^{14}C on the IER at the time ti is expressed as:

$$m_s^{ads}(ti) = m_0 - C_{eq}(ti) \cdot V_0 \tag{8}$$

where: $C_{eq}(ti)$ is the ^{14}C activity in solution at the time ti when the analysis is performed (Bq.mL^{-1}) and V_0 is the volume of the ^{14}C-labelled solution in contact with the IER (mL).

The experimental results obtained for the inorganic ^{14}C uptake on the IRN 78 resin are reported in Table 20. The ^{14}C uptake both on fresh and dried resin samples is characterized by a fast absorption (equilibrium was reached in less than 3 hours), but the absorption percentage is drastically decreased by increasing temperature. If for the IER dried at 50°C the absorption percentage was only slightly reduced (from ~ 99% to ~ 96% - see Figure 26), for the IER dried at 80°C the absorption percentage significantly decreased to around 63%.

Table 20: ^{14}C activity in solution during the kinetic tests and the percentage uptake for sorption tests carried out with ^{14}C-labelled sodium carbonate

Time (hours)	Fresh IER		IER dried at 50°C		IER dried at 80°C	
	C_{aq}, Bq.mL^{-1}	A^{ti}_{eq}, %	C_{aq}, Bq.mL^{-1}	A^{ti}_{eq}, %	C_{aq}, Bq.mL^{-1}	A^{ti}_{eq}, %
1	188.19±37.64	84.70±16.94	201.88±40.38	83.59±16.72	676.43±135.29	45.01±9.00
2	23.93±4.79	98.05±19.61	54.17±10.83	95.60±19.12	513.52±102.70	58.25±11.65
3	13.56±2.71	98.90±19.78	52.52±10.50	95.73±19.15	504.42±100.88	58.99±11.80
4	11.70±2.34	99.05±19.81	48.46±9.69	96.06±19.21	601.05±120.21	51.13±10.23
5	9.85±1.97	99.20±19.84	48.97±9.79	96.06±19.21	495.39±99.08	59.72±11.94
6	9.51±1.90	99.23±19.85	50.04±10.01	95.93±19.19	478.61±95.72	61.09±12.22
18	9.87±1.97	99.20±19.84	52.87±10.57	95.70±19.14	505.65±101.13	58.89±11.78
24	8.22±1.64	99.33±19.87	47.08±9.42	96.17±19.23	457.17±91.43	62.83±12.57
48	7.82±1.56	99.36±19.87	45.54±9.11	96.30±19.26	453.54±90.71	63.13±12.63

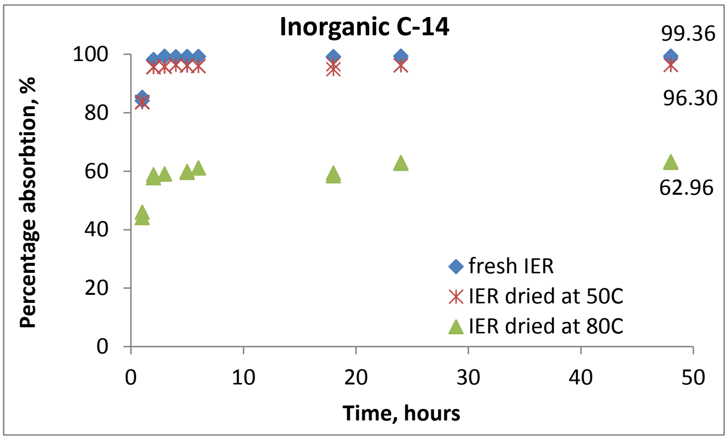


Figure 26. Kinetic of the $^{14}CO_3^{2-}$ uptake on fresh and dried resin samples.

Since the functional groups are responsible for the ion-exchange capacity of the IER, and the bounds between functional groups (quaternary ammonium – $CH_2\text{-}N(CH_3)_3^+$) and the polymer matrix (polystyrene divinylbenzene) are less stable, the decrease of the ^{14}C uptake on the IER dried at 80°C could be due to the rupture of these bounds. High temperature enhances the decomposition of the strong basic quaternary ammonium groups (active sites of anion exchange) to the tertiary amine that could result in decrease of the exchange capacity of the anion exchange resin [PARK *et al.*, 2014].

The decrease of the absorption percentage for the IER dried both at 50°C and 80°C was also observed in the sorption tests carried out with ^{14}C-labelled sodium acetate (Figure 27). In these tests the decrease was even more accentuated: for the IER dried at 50°C the absorption percentage was around 87% from the value obtained for fresh IER and for the IER dried at 80°C only 47% from the value obtained for fresh IER.

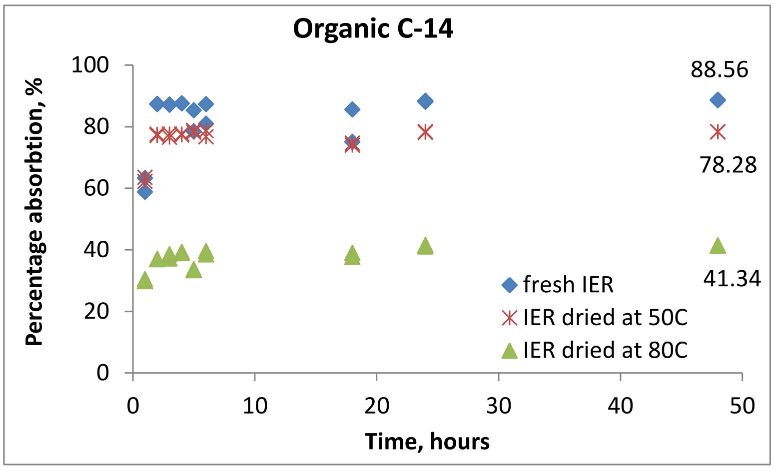


Figure 27. The kinetic of organic ^{14}C uptake on fresh and dried resins.

Since the SIERs generated from moderator purification system of a CANDU reactor contain high amount of ^{14}C a special attention has to be put in selecting the adequate conditioning process to avoid the ^{14}C release from the conditioned matrix.

5.3.3 Uncertainties

The uncertainty of ^{14}C measurement by LSC was around 7%. The uncertainty associated with the sorption tests was estimated as standard deviation of the results (computed as absorption percentage) of 8 parallel batches. The standard deviation of these tests was 17% and a covering uncertainty of 20% was considered for the values reported for the absorption percentage of the sorption tests carried out with ^{14}C-labelled sodium carbonate (Table 20).

To evaluate the uncertainty associated to the analytical procedure for measuring the inorganic and organic ^{14}C, six identical tests were carried out and the standard deviation of the results were below 15% and consequently, a covering uncertainty of 20% has to be considered for the values reported in Table 15, 16 and 18 regarding the ^{14}C measurement in the desorption tests.

5.4 *ÚJV*

For desorption and leaching test real and artificial SIERs were used. Both terms, leaching and desorption, are used in the text, with equal meaning.

5.4.1 SIERs characterisation

The ^{14}C content and major radionuclide activity in studies SIERs is shown in Table 21. The characterisation of ^{14}C activity in artificial SIERs and solidified resins are described in § 2.2.1 and 2.3.1.

Table 21. ^{14}C content and major radionuclide activity in studies SIERs.

Nuclide	**activity (Bq.g^{-1})**		
	EDU	**ETE**	**ÚJV**
^{14}C (total)	**48 ± 5.9**	**43 ± 4**	**2000 ± 280**
^{14}C (inorganic)	**14 ± 2.2**	**16 ± 2**	**2000 ± 280**
^{14}C (organic)	**34 ± 5.5**	**27 ± 4**	**77 ± 11**
^{40}K	-	24 ± 2.1	-
^{51}Cr	-	89 ± 4.8	-
^{60}Co	140 ± 8.3	23 ± 0.9	590 ± 34
^{108m}Ag	-	-	860 ± 64
^{125}Sb	-	2245 ± 70	-
^{125}I	-	1858 ± 62	-
^{134}Cs	-	388 ± 12	-
^{137}Cs	22 ± 2.8	2077 ± 65	-

5.4.2 SIERs samples leaching

Leaching of non-treated SIERs was one of the part of leaching/desorption tests. In this part of experiments the EDU and ÚJV SIERs were leached into the 0.02 M sodium hydroxide solution and synthetic granitic water for the time period of one month. During the leaching test the conductivity and pH of leachate were recorded and ^{14}C activity vas measured. By comparing of total ^{14}C activity presented in the SIERs and activity in leachate the released activity fraction was determined.

5.4.2.1 EDU SIERs

In EDU SIERs leaching/desorption experiments it was observed gradual increase of electrical conductivity of the leachates, no changes were observed in the pH values, for both solutions NaOH and SGW (Figure 29 and 30). These conductivity changes did not affected the releasing of ^{14}C in the leaching tests. When EDU SIER was leached into the 0.02 M NaOH solution, the maximal cumulative released fraction of ^{14}C activity was reached almost 3% after the 14 days of leaching. In case of EDU SIER leaching into the SGW, the released fraction of ^{14}C activity value reach the maximum of cumulative leached activity (3.5%) in the first week, after the reaching this peak, the total cumulative released activity stabilised on the level of 2% during one month experimental interval (Figure 28). In both cases after 14 days of the test, the sorption/desorption ratio was reached and level of cumulative leached ^{14}C activity was stabilised.

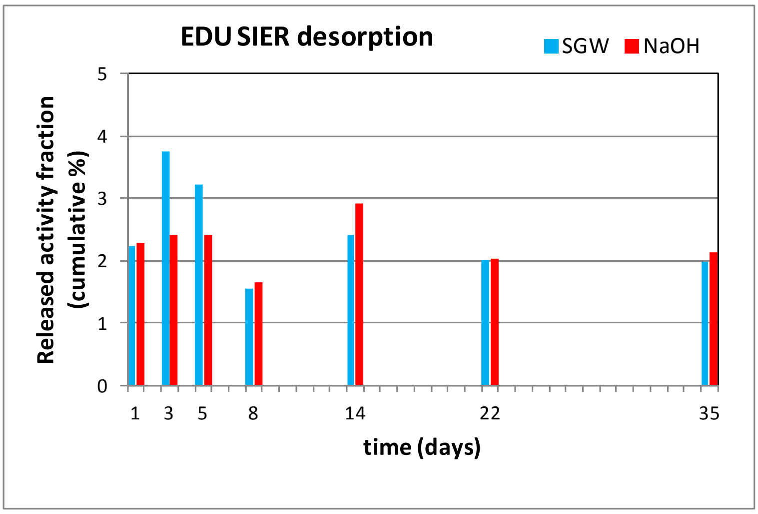


Figure 28. Released fraction of ^{14}C activity in the leaching test of EDU SIER into the SGW and NaOH solution.

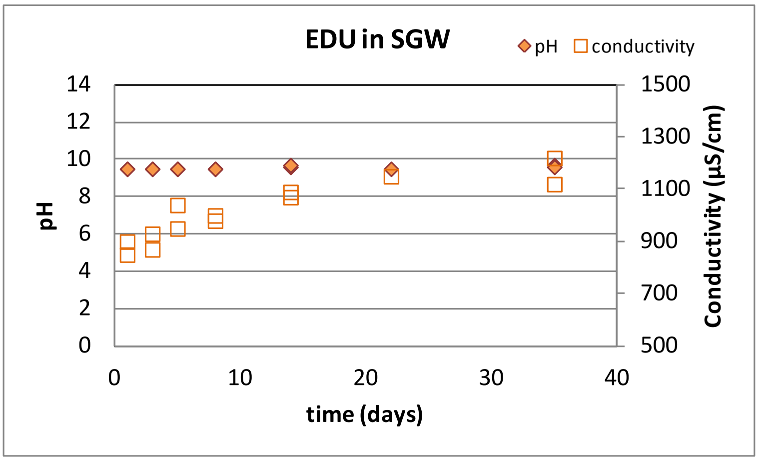


Figure 29. The pH and conductivity values of the leachate during the leaching test of EDU SIER from into the SGW.

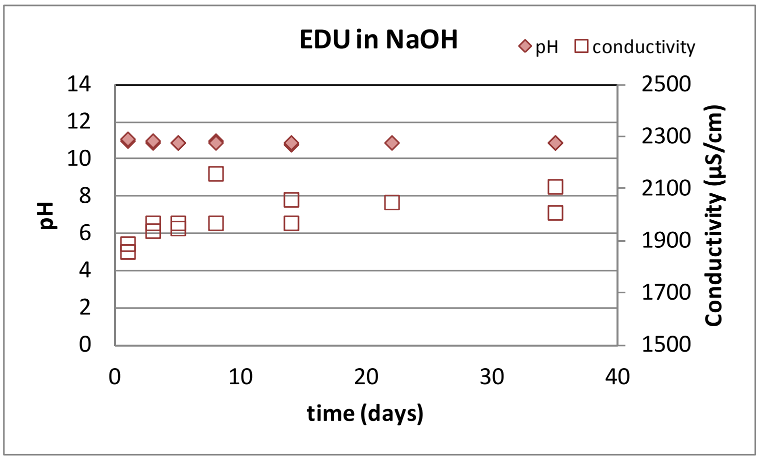


Figure 30. The pH and conductivity values of the leachate during the leaching test of EDU SIER into the NaOH solution.

5.4.2.2 ÚJV SIERs

In ÚJV SIERs leaching/desorption experiments relevant changes of electrical conductivity and pH values of the leachates were not observed, for both solutions NaOH and SGW (Figure 32 and 33). The calculated released fraction of ^{14}C activity gradually increases up to 1% during the first week of the test and further was constant on this level. This behaviour was observed for both leaching media (Figure 31).

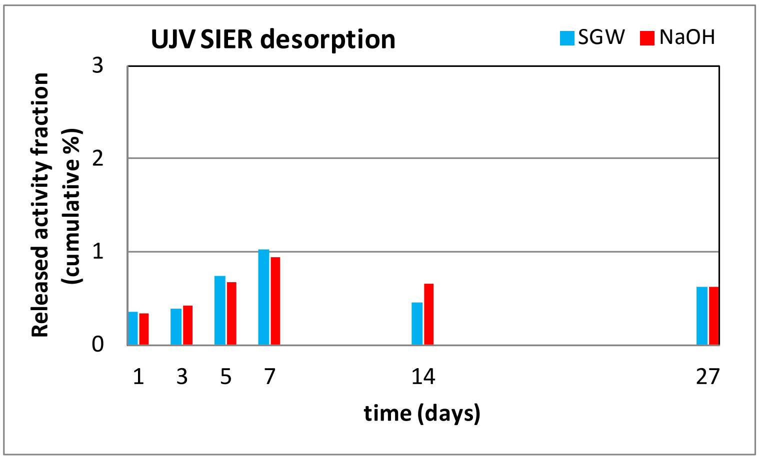


Figure 31. Released fraction of ^{14}C activity in the leaching test of ÚJV SIER into the SGW and NaOH solution.

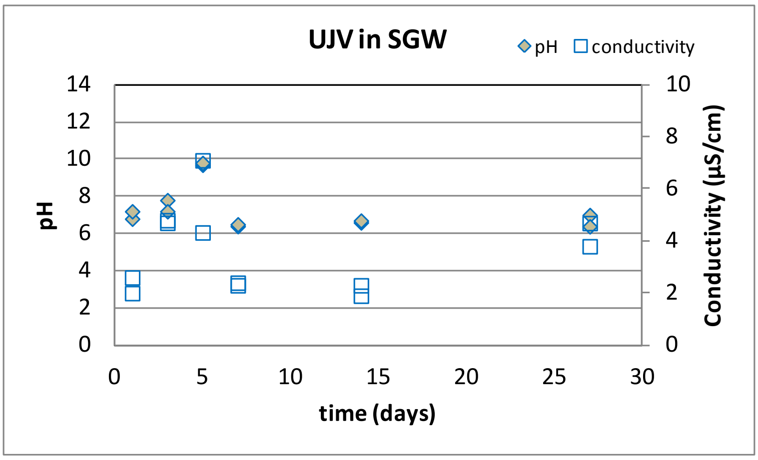


Figure 32. The pH and conductivity values of the leachate during the leaching test of ÚJV SIER into the SGW.

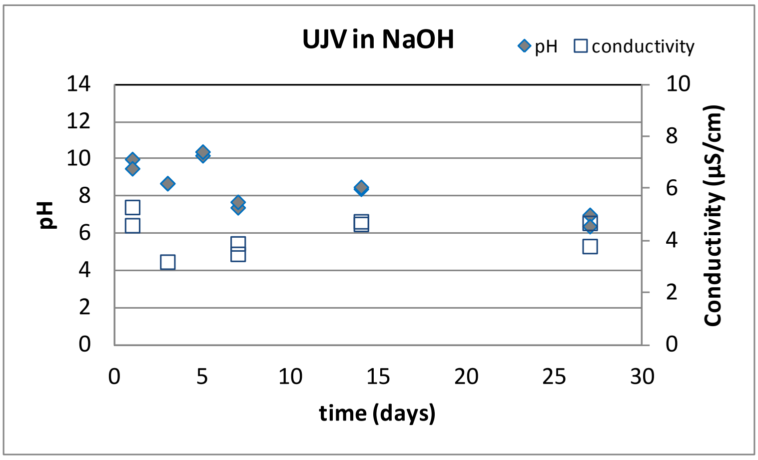


Figure 33. The pH and conductivity values of the leachate during the leaching test of ÚJV SIER into the NaOH solution.

5.4.3 Solidified samples leaching

Leaching tests of solidified SIERs matrix were performed in on artificial SIERs fixed in the cement. Two types of ^{14}C tracers (bicarbonate and acetate) were used for resins saturation and three types of leaching media were applied (distilled water, SGW and sodium hydroxide solution).

5.4.3.1 Solidified bicarbonate saturated resins

The first test of solidified artificial SIERs leaching was performed on specimens prepared from ^{14}C bicarbonate saturated resins. The test was performed for three months' time period by leaching the specimens into the distilled water. The leaching liquid volume/surface area ratio = 10 was applied in this experiment. Diffusivity coefficients were calculated for leached amounts of the tracer in every leaching interval. Negligible release of ^{14}C was observed during the whole duration of the leaching experiment. From all data obtained and calculated in this test the leachability index L_i = 12.2 was calculated.

Table 22. Diffusivity coefficient and leachability index values calculated from first leaching test of solidified artificial SIER saturated by ^{14}C bicarbonate.

bicarbonate	**distilled water**	
time (days)	**D ($cm^2.s^{-1}$)**	**L_i**
0.5	$1.5\ 10^{-13}$	12.2
3	$1.5\ 10^{-13}$	
4	$5.8\ 10^{-12}$	
5	$5.5\ 10^{-12}$	
6	$5.9\ 10^{-12}$	
7	$7.0\ 10^{-12}$	
14	$7.0\ 10^{-15}$	
30	$5.8\ 10^{-13}$	
60	$1.3\ 10^{-13}$	
90	$4.2\ 10^{-13}$	

The second set of leaching tests on artificial SIERs samples saturated by ^{14}C bicarbonate was performed for time period of 160 days by leaching the specimens into the distilled water, SGW and NaOH solution. The leachate volume/surface area ratio = 5 was applied. As shown in Table 23 the values of calculated diffusion coefficient are very low, which confirmed almost no release of ^{14}C tracer from testing specimens. The leachability indexes were calculated: 13.2 at leaching in to distilled water, 12.1 at leaching into SGW and 13.3 at leaching into the NaOH solution. As it is shown in Figure 34 the ^{14}C activity in leachates in all tests is on the background/blank level. It is a reason of relatively large variance of calculated diffusion coefficients, because of big uncertainties of activity measurements at this very low activity levels.

Table 23. Diffusivity coefficient and leachability index values calculated from leaching test of solidified artificial SIER saturated by ^{14}C bicarbonate.

Bicarbonate	distilled water		SGW		0.02M NaOH	
time (days)	D ($cm^2.s^{-1}$)	L_i	D ($cm^2.s^{-1}$)	L_i	D ($cm^2.s^{-1}$)	L_i
0.25	$2.4\ 10^{-13}$	13.2	$1.7\ 10^{-12}$	12.1	$3.3\ 10^{-13}$	13.3
1	$1.9\ 10^{-16}$		$3.1\ 10^{-13}$		$2.7\ 10^{-14}$	
2	$8.7\ 10^{-14}$		$2.1\ 10^{-12}$		$4.3\ 10^{-15}$	
5	$1.9\ 10^{-13}$		$2.0\ 10^{-13}$		$2.2\ 10^{-14}$	
6	$2.5\ 10^{-12}$		$6.9\ 10^{-13}$		$1.3\ 10^{-12}$	
7	$1.2\ 10^{-12}$		$3.3\ 10^{-12}$		$2.4\ 10^{-13}$	
8	$5.6\ 10^{-15}$		$3.2\ 10^{-12}$		$1.4\ 10^{-13}$	
9	$2.3\ 10^{-13}$		$3.3\ 10^{-12}$		$3.1\ 10^{-13}$	
10	$6.3\ 10^{-14}$		$7.0\ 10^{-12}$		$1.6\ 10^{-14}$	
20	$2.7\ 10^{-15}$		$2.8\ 10^{-14}$		$1.7\ 10^{-15}$	
29	$2.0\ 10^{-15}$		$1.6\ 10^{-13}$		$2.0\ 10^{-15}$	
91	$5.8\ 10^{-13}$		$7.8\ 10^{-13}$		$6.2\ 10^{-15}$	
160	$3.0\ 10^{-13}$		$6.4\ 10^{-13}$		$2.6\ 10^{-12}$	

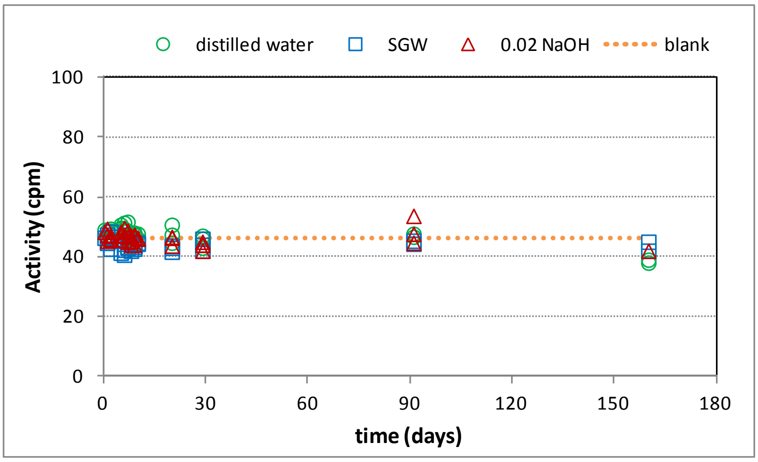


Figure 34. Activity of ^{14}C in leachates sampled from experiments of solidified bicarbonate saturated resin.

5.4.3.2 *Solidified acetate saturated resins*

In the first set of leaching tests on artificial SIERs samples saturated by ^{14}C acetate, experiments were performed for time period of 124 days by leaching the specimens into the distilled water, SGW, and NaOH solution. The leachate volume/surface area ratio = 5 was applied to increase the ^{14}C activity/concentration values in the leachates. Two types of artificial SIERs saturated by acetate tracer were used in tests, the Cl^- form and OH^- form of the resin. From the obtained data the diffusivity coefficients were calculated for leached activity of the tracer for every leaching interval. Negligible release of ^{14}C over the whole duration of the leaching experiment was observed. In experiments with Cl$^-$ form of artificial SIER, leachability index L_i = 11.5, 11.3, and 10.9 were calculated when distilled water, SGW, and 0.02 M sodium hydroxide solution were used as leaching media respectively (see Table 24). The ^{14}C activity in leachates in all tests was a little higher or on the background/blank level. Some slightly decreasing trend of ^{14}C activity in the leachates can be observed during the increasing time period of leaching, see Figure 35, but there is still a large variance in obtained experimental data.

In experiments with OH$^-$ form of artificial SIER leachability index L_i = 11.2, 10.7, and 12.1 were calculated when distilled water, SGW, and 0.02 M sodium hydroxide solution were used as leaching media, respectively (see Table 25). Also in these tests the ^{14}C activity in leachates was a little higher or on the background/blank level. The same case of slightly decreasing trend of ^{14}C activity in the leachates can be observed, but there is still a large variance in obtained experimental data, see Figure 36.

Table 24. Diffusivity coefficient and leachability index values calculated from leaching test of solidified artificial SIER in Cl form saturated by ^{14}C acetate, V/S ratio = 5.

acetate/Cl form	**distilled water**		**SGW**		**0.02M NaOH**	
time (days)	**D (cm^2.s^{-1})**	**Li**	**D (cm^2.s^{-1})**	**Li**	**D (cm^2.s^{-1})**	**Li**
1	$2.0\ 10^{-12}$	11.5	$3.1\ 10^{-12}$	11.3	$2.3\ 10^{-10}$	10.9
2	$3.7\ 10^{-10}$		$3.5\ 10^{-13}$		$2.7\ 10^{-9}$	
3	$4.5\ 10^{-9}$		$6.6\ 10^{-12}$		$2.6\ 10^{-13}$	
6	$1.3\ 10^{-14}$		$7.3\ 10^{-13}$		$2.2\ 10^{-12}$	
7	$6.9\ 10^{-13}$		$1.4\ 10^{-11}$		$3.9\ 10^{-13}$	
8	$2.0\ 10^{-11}$		$1.5\ 10^{-9}$		$1.3\ 10^{-9}$	
15	$8.9\ 10^{-11}$		$7.1\ 10^{-12}$		$6.1\ 10^{-11}$	
21	$1.8\ 10^{-10}$		$2.1\ 10^{-10}$		$8.5\ 10^{-13}$	
27	$7.1\ 10^{-14}$		$8.2\ 10^{-12}$		$3.6\ 10^{-13}$	
33	$3.5\ 10^{-13}$		$1.7\ 10^{-11}$		$2.1\ 10^{-10}$	
61	$1.4\ 10^{-13}$		$1.5\ 10^{-12}$		$1.4\ 10^{-11}$	
97	$7.5\ 10^{-11}$		$3.2\ 10^{-14}$		$2.3\ 10^{-13}$	
124	$4.0\ 10^{-15}$		$2.7\ 10^{-12}$		$1.5\ 10^{-10}$	

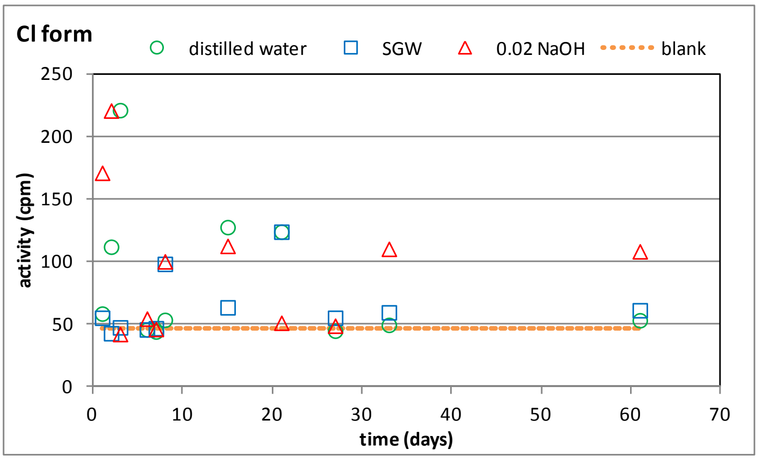


Figure 35. Activity of ^{14}C in leachates sampled from experiments of solidified acetate saturated resin (Cl form), V/S ratio = 5.

Table 25. Diffusivity coefficient and leachability index values calculated from leaching test of solidified artificial SIER in OH form saturated by ^{14}C acetate, V/S ratio = 5.

acetate/OH form	distilled water		SGW		0.02M NaOH	
time (days)	D ($cm^2.s^{-1}$)	Li	D ($cm^2.s^{-1}$)	Li	D ($cm^2.s^{-1}$)	Li
1	$1.2\ 10^{-12}$	11.2	$6.2\ 10^{-12}$	10.7	$2.9\ 10^{-10}$	12.1
2	$1.6\ 10^{-13}$		$2.3\ 10^{-9}$		$1.6\ 10^{-13}$	
3	$6.5\ 10^{-10}$		$3.8\ 10^{-9}$		$2.6\ 10^{-13}$	
6	$1.6\ 10^{-10}$		$1.0\ 10^{-12}$		$1.2\ 10^{-12}$	
7	$1.4\ 10^{-10}$		$2.4\ 10^{-10}$		$3.9\ 10^{-13}$	
8	$1.4\ 10^{-9}$		$1.6\ 10^{-9}$		$1.6\ 10^{-9}$	
15	$7.4\ 10^{-13}$		$9.3\ 10^{-11}$		$2.4\ 10^{-14}$	
21	$4.5\ 10^{-12}$		$1.3\ 10^{-14}$		$1.8\ 10^{-10}$	
27	$2.2\ 10^{-10}$		$2.4\ 10^{-10}$		$1.8\ 10^{-14}$	
33	$2.2\ 10^{-14}$		$3.1\ 10^{-10}$		$2.2\ 10^{-14}$	
61	$1.6\ 10^{-15}$		$2.0\ 10^{-11}$		$3.5\ 10^{-15}$	
97	$1.0\ 10^{-13}$		$1.0\ 10^{-14}$		$2.4\ 10^{-12}$	
124	$1.4\ 10^{-9}$		$8.2\ 10^{-14}$		$2.6\ 10^{-13}$	

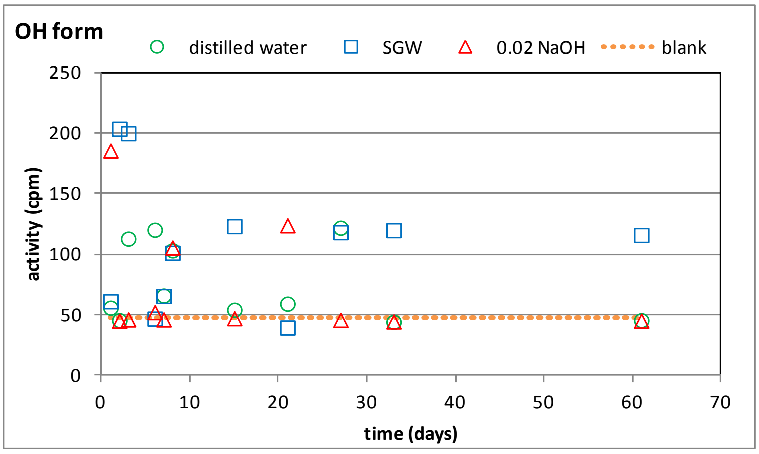


Figure 36. Activity of ^{14}C in leachates sampled from experiments of solidified acetate saturated resin (OH form), V/S ratio = 5.

In the second set of leaching tests on artificial SIERs samples saturated by ^{14}C acetate, experiments were performed for time period of 124 days by leaching the specimens into the distilled water, SGW, and 0.02 M NaOH solution. The leachate volume/surface area ratio was changed to the value = 2.2 to try to ensure the increase of ^{14}C activity/concentration values in the leachates. Two types of artificial SIERs saturated by acetate tracer were used in tests, the Cl^- form and OH^- form of the resin. Also in this set of leaching tests negligible release of ^{14}C tracer during the whole duration of the leaching experiment was observed. In experiments with Cl^- form of artificial SIER, leachability index L_i = 11.1, 10.5, and 11.0 were calculated when distilled water, SGW, and 0.02 M sodium hydroxide solution were used as leaching media, respectively (see Table 26). Also in these tests with lowered V/S ratio the ^{14}C activities were close the background/blank level in measured leachates. The slightly decreasing trend of ^{14}C activity in the leachates can be observed more clearly than in previous tests with V/S ratio = 5, but there is still a large variance in obtained experimental data, see Figure 37.

In experiments with OH^- form of artificial SIER leachability index L_i = 11.1, 11.2, and 11.6 were calculated when distilled water, SGW, and 0.02 M NaOH solution were used as leaching media, respectively (see Table 27). In these tests with lowered V/S ratio the ^{14}C activities were also close or a little above the background/blank level in measured leachates. The slightly decreasing trend of ^{14}C activity in the leachates can be again observed more clearly than in previous tests with V/S ratio = 5, but still there is a large variance in obtained experimental data (Figure 38).

Table 26. Diffusivity coefficient and leachability index values calculated from leaching test of solidified artificial SIER in Cl form saturated by ^{14}C acetate, V/S ratio = 2.2.

acetate/Cl form	distilled water		SGW		0.02M NaOH	
time (days)	**D ($cm^2.s^{-1}$)**	**Li**	**D ($cm^2.s^{-1}$)**	**Li**	**D ($cm^2.s^{-1}$)**	**Li**
1	4.5 10^{-12}		4.2 10^{-12}		9.1 10^{-12}	
2	2.4 10^{-9}		7.4 10^{-11}		7.3 10^{-10}	
3	1.6 10^{-10}		1.1 10^{-9}		1.3 10^{-9}	
6	1.6 10^{-11}		1.5 10^{-11}		3.3 10^{-12}	
7	1.9 10^{-10}		4.4 10^{-11}		7.3 10^{-12}	
8	2.1 10^{-9}		1.7 10^{-9}		1.2 10^{-10}	
15	2.2 10^{-10}	11.1	1.7 10^{-12}	10.5	5.9 10^{-11}	11.0
21	3.3 10^{-13}		1.6 10^{-10}		1.2 10^{-13}	
27	1.9 10^{-11}		7.1 10^{-12}		7.1 10^{-14}	
33	1.6 10^{-12}		2.4 10^{-10}		1.1 10^{-11}	
61	1.0 10^{-13}		1.9 10^{-11}		8.6 10^{-13}	
97	1.6 10^{-13}		8.0 10^{-12}		4.0 10^{-12}	
124	4.0 10^{-15}		4.4 10^{-13}		7.6 10^{-12}	

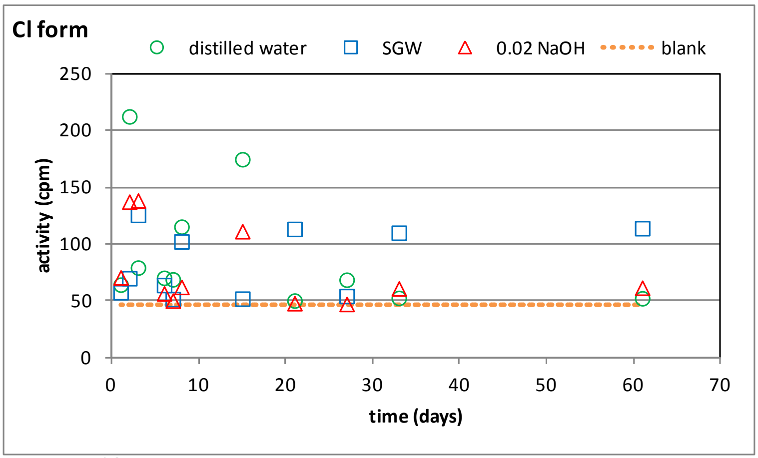


Figure 37. Activity of ^{14}C in leachates sampled from experiments of solidified acetate saturated resin (Cl form), V/S ratio = 2.2.

Table 27. Diffusivity coefficient and leachability index values calculated from leaching test of solidified artificial SIER in OH form saturated by ^{14}C acetate, V/S ratio = 2.2.

acetate/OH form	distilled water		SGW		0.02M NaOH	
time (days)	D (cm^2.s^{-1})	Li	D (cm^2.s^{-1})	Li	D (cm^2.s^{-1})	Li
1	$8.6\ 10^{-11}$		$1.3\ 10^{-10}$		$5.2\ 10^{-12}$	
2	$1.4\ 10^{-12}$		$2.0\ 10^{-11}$		$9.5\ 10^{-10}$	
3	$3.7\ 10^{-12}$		$5.6\ 10^{-11}$		$1.2\ 10^{-10}$	
6	$1.6\ 10^{-10}$		$1.7\ 10^{-10}$		$1.6\ 10^{-10}$	
7	$6.2\ 10^{-12}$		$7.1\ 10^{-8}$		$1.6\ 10^{-12}$	
8	$1.7\ 10^{-9}$		$2.0\ 10^{-13}$		$4.5\ 10^{-13}$	
15	$9.1\ 10^{-11}$	11.1	$1.3\ 10^{-11}$	11.2	$7.3\ 10^{-11}$	11.6
21	$2.0\ 10^{-10}$		$1.1\ 10^{-12}$		$2.6\ 10^{-12}$	
27	$4.0\ 10^{-14}$		$2.0\ 10^{-10}$		$4.0\ 10^{-12}$	
33	$1.6\ 10^{-12}$		$5.0\ 10^{-14}$		$2.2\ 10^{-14}$	
61	$6.6\ 10^{-14}$		$3.9\ 10^{-14}$		$6.3\ 10^{-15}$	
97	$9.6\ 10^{-13}$		$1.6\ 10^{-15}$		$1.4\ 10^{-13}$	
124	$2.0\ 10^{-12}$		$3.1\ 10^{-11}$		$2.6\ 10^{-13}$	

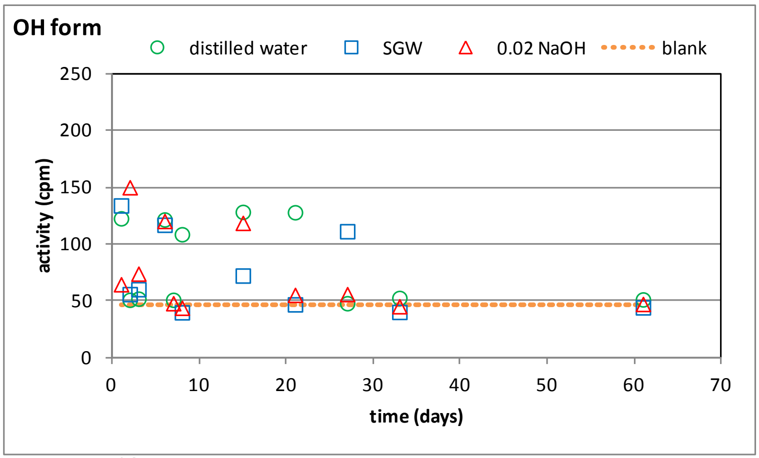


Figure 38. Activity of ^{14}C in leachates sampled from ÚJV experiments of solidified acetate saturated resin (OH$^-$ form), V/S ratio = 2.2.

In all experiments and obtained results the relatively large variance of calculated diffusion coefficients is caused by uncertainties of activity measurements at this very low activity levels. The leaching of carbonate ions is limited by solubility of calcite ($CaCO_3$), which is formed in presence of Ca^{2+} from cement matrix and interactions with carbonate anions. Due to this phenomenon no significant release of inorganic form of ^{14}C was observed. Minimal or no release of acetate tracer was observed in all leaching experiments, even though calcium acetate solids are more soluble than calcium carbonate [SEIDELL, 1940; ROBIE AND HEMINGWAY, 1995]. It can be concluded that strong adsorption of acetate tracer on the studied resins and fixation in the cement matrix does not allow any significant release of this tracer. One can remind that anions in general, and conjugated bases of the organic acid in particular, can be adsorbed in cementitious phases [POINTEAU *et al.*, 2006; POINTEAU *et al.*, 2008]. In all tests it was shown, that the release of ^{14}C species is minimal, close to the detection limits, no matter what type of artificial SIER or V/S ratio was used and what type of leaching medium was applied.

6 Conclusions

In the framework of WP4, different experiments were performed by each partner related to each SIERs national management strategy. The main objectives were first to assess the ^{14}C content and the fraction of organic compound containing ^{14}C, and second when possible, to assess leaching behaviour in disposal conditions. It led to direct desorption studies of SIERs in different conditions for each partner (NaOH, LiOH) and to leaching experiments for ÚJV and RATEN-ICN — alkaline and/or synthetic granitic water conditions. Participants have used their own samples representative of the SIERs coming from different reactors: SIERs from PWR reactors for CEA-EDF and ÚJV, SIERs from CANDU reactors for RATEN-ICN, SIERs from light water experimental reactor for ÚJV. No common samples were used. The different experiments performed by each partner are presented in Table 28.

Table 28. Summary of performed experiments and types of used SIERs.

	SIERs from commercial reactors		**Virgin IER spiked with ^{14}C**
	Non conditioned	**Conditioned**	**Conditioned**
Leaching experiment	RATEN-ICN, ÚJV	none	ÚJV
Desorption experiment	CEA-EDF	none	none

Performed experiments show, on the one hand, that the samples are heterogeneous because they correspond to mixtures of different purification circuits and, on the other hand, that new analytical methodologies have to be developed. In conclusion, further measures are needed to allow a statistical approach and to obtain significant results on the evaluation of the ^{14}C source term (inventory and speciation).

From the experiments on solidified resins, it was shown, that no or a negligible amount of ^{14}C was leached in any type of leaching/desorption test of SIERs. In leaching tests of laboratory prepared cemented resins, the release of organic form (acetate) was not observed, probably due to acetate adsorption on cementitious phases. The release of inorganic forms of ^{14}C (carbonates, bicarbonates) was not observed and is probably limited due to the presence of calcium ions by solubility of calcite.

The obtained results also showed that absorption of ^{14}C on fresh resins is temperature dependent. At temperature of 50 °C the ^{14}C absorption percentage slightly decrease compared to fresh resin (from ~99% to ~96%), but temperature of 80°C generates an important decrease of the ^{14}C absorption percentage (to ~63%). The detailed results of performed work of each institution are described in following sections.

6.1 *CEA*

In the framework of Task 4.3, experimental desorption tests were performed 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 hydro-soluble organic compounds. Desorption tests were performed with 10^{-3} and 1 M LiOH aqueous solutions. A 1 M LiOH solution is needed to achieve a nearly complete desorption of ^{14}C. In that case, an apparent loss of ^{14}C is evidenced. The solutions have been transferred for analyses by LRMO to have a first identification of the nature of the organic molecules.

The observed carbon mass balance is around 50 $mg_C.L^{-1}$. Around 12% of carbon mass balance is identified. The only organic compound identified in resin desorption solutions, glycolate, is identified in very low concentration, around 1% of total organic carbon. No amine derivate is detected and ammonium is quantified in very low concentration by ionic chromatography. So these observations can confirm that no or very little chemical degradation coming from resin polymer or functional groups occurs under these conditions. However, an organic contamination in concentrated LiOH at 1 M (solution used for resins desorption) makes difficult the characterization of organic molecules coming only from resins desorption.

The representativeness of the sampling and also the conservation over time – including time between discharge from reactor and sampling, shipment, and storage time before analyses – is although questioned. The EDF SIERs coming from different circuits of PWRs were sampled and analysed after different storage delays – such as 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.

6.1 *FZJ*

Direct examination of the suspension water and FZJ SIERs from BWR behaviour in static leaching experiments showed a very small or undetectable ^{14}C activity in the gas and liquid phase, probably due to preliminary release of a fraction of ^{14}C occurred in the interim storage in contact with air, even though some fraction of ^{14}C was still bound to the SIERs. Any disturbances in the system´s equilibrium is likely to result in a release of radionuclides, depending also on the selectivity of the specific compounds.

A speciation of the releases in solution by means of HPLC revealed the presence of small amounts of formic acid for FZJ-A SIERs, particularly when a regeneration of the resins takes place, in line with the results reported in RIZZO *et al.* [2017]. The pre-conditioning drying process experienced by FZJ-B SIERs influenced most probably the releases in solution, since no formic acid was detected in the leachates.

A further development to quantify the total amount of organic ^{14}C released in solution could imply a separation of the leachate from the SIERs and an evaluation of the organic/inorganic fractions with *e.g.* the methods reported by MAGNUSSON *et al.* [2008]. A further speciation of the compounds released in solution would require dedicated analytical methods, since the release of several species could be expected, both in ionic and non-ionic form, possibly arising also from the resins' degradation.

Gaseous releases from SIERs in cementitious conditions are caused by a transient/permanent decrease in the pH of the alkaline solution, depending on the molarity/volume of the solution, on the SIERs/solution ratio, and on the saturation of SIERs. The pH drop is caused most probably by H^+ ions released during the ion-exchange reaction of SIERs and alkaline solution. The phenomenon is observed locally also with solutions of higher molarity.

6.2 RATEN-ICN

Two sub-samples (unconditioned) from the SIERs transferred from Cernavoda NPP were used to evaluate the ^{14}C desorption in alkaline solution. These samples contain around 3.37×10^4 Bq.g^{-1} of ^{14}C, mostly as inorganic form (around 93%).

The experiments performed show that around 79% from the total ^{14}C present in the SIERs sample used for desorption tests was released as dissolved species, mostly in inorganic form, and around 7% as inorganic ^{14}C gaseous species. No organic ^{14}C released in gas phase was measured. At the end of desorption test the residual ^{14}C activity in the resin sample was less than 9% from the initial activity.

Around 6% from the initial ^{14}C activity in the SIER samples used in desorption tests was not found either as dissolved species and inorganic gas species, or as residual on the SIER sample after desorption test. This amount could be due to the inherent experimental errors — the uncertainty of this kind of test was estimated to be 20% — but could also represent the ^{14}C released in gas phase as organic species. But, since the no organic ^{14}C released in gas was measured this is only a hypothesis and further experiments need to be carried out to have a conclusion on organic ^{14}C release in gas phase.

The experiments carried out to evaluate the influence of ion exchange thermal degradation on ^{14}C uptake show that temperatures higher than 80°C produce an important decrease of the ^{14}C uptake on IER, while temperature of 50°C only slightly decrease the ^{14}C uptake.

6.3 *ÚJV*

In leaching/desorption tests performed in ÚJV laboratories, real SIERs samples from Dukovany NPP (PWR) and ÚJV Group research reactor were studied. Very low release of ^{14}C into the leaching/desorption media (SGW, and 0.02 NaOH solution) was observed. After one month of interaction the cumulative released fraction of ^{14}C activity was evaluated. Following values were calculated: 2% for EDU SIERs and 1% for ÚJV SIERs.

Because of low ^{14}C activity in real SIERs, the laboratory-prepared artificial SIERs were prepared. Amberlite resin in Cl^- and OH^- form was saturated by organic and inorganic form of ^{14}C tracer (bicarbonate and acetate). The artificial SIERs were used for solidification into the cement matrix and preparation of solidified SIERs specimens.

Solidified SIERs were tested by leaching method based on ANSI/ANS [2003] methodology. Cylindrical specimens were leached into the distilled water, synthetic granitic water, and 0.02 M sodium hydroxide solution. From experimental data diffusion coefficients and leachability indexes were calculated. In all experiments and obtained results the relatively large variance of calculated diffusion coefficients is caused by uncertainties of activity measurements at these very low activity levels. In all tests it was shown that the release of ^{14}C species is minimal, close to the detection limits, no matter what type of artificial SIER or V/S ratio was used and what type of leaching medium was applied.

6.4 *General comments*

A general conclusion on the matter of SIERs is a difficult task to tackle, knowing that in most cases, the SIERs samples provided were coming from various places in the purification systems, and mixed altogether. Even if the national programs for the SIERs handling are different, some general comments can be made.

It seems confirmed that more than 90% of ^{14}C occurs in BWRs under inorganic form, *i.e.* ions from the carbonate system [RIZZO *et al.*, 2017]. For PWRs the situation seem less clear but the analyses from the resins sampled in Swedish reactors and resins provided by EDF seem to indicate that 20-30% of ^{14}C occurs under organic form. Up to now only formic acid is detected in the case of BWRs.

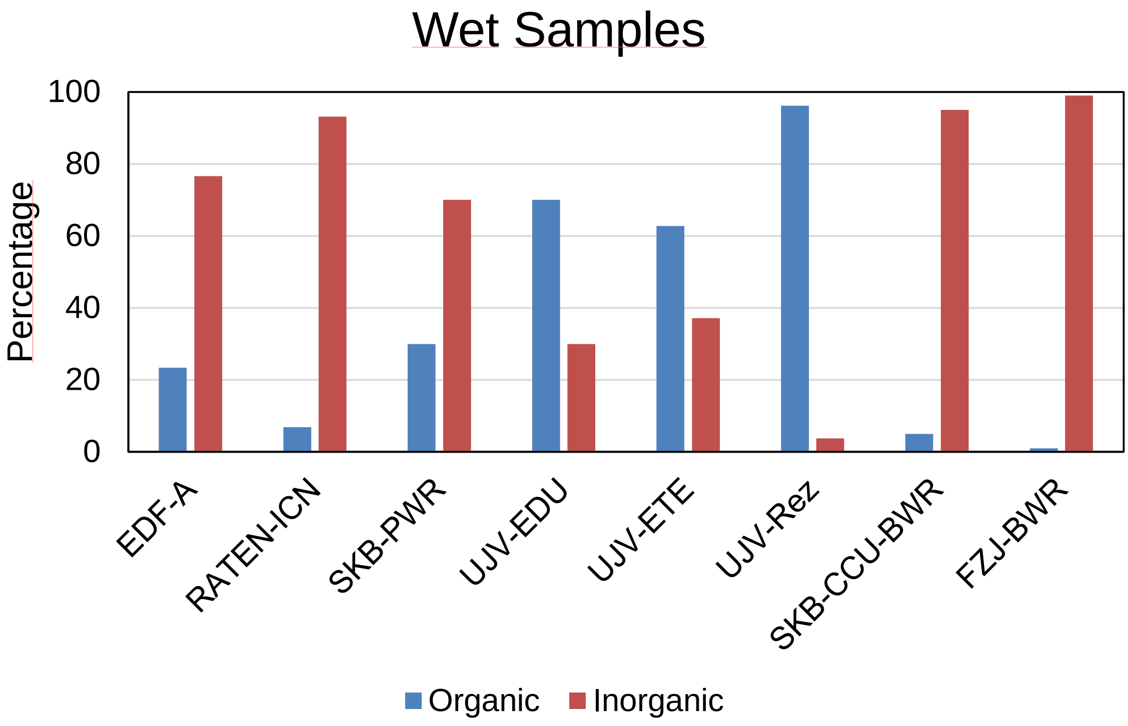


Figure 39. Organic/Inorganic percentage for sample — from results in RIZZO *et al.* [2017].

Concerning the release of ^{14}C under alkaline conditions, which should occur under cementitious environment, a concentration of at least 0.1 M of alkaline hydroxide seems necessary. But the immobilization of ^{14}C seems efficient when the SIERs are cemented either due to adsorption of organic acids for the organic species, or precipitation of carbonate ions for inorganic species.

The assessment of the ^{14}C source term and release from SIERs is heavily dependent on the national strategies of electricity production and SIERs waste handling. From the contrasting results that were obtained during the course of WP4 it seems that a reassessment of the analytical strategies for ^{14}C determination in SIERs should be necessary. A better understanding of ^{14}C bearing molecules’ formation in the different compartments of reactors purification systems is desirable.

References

ADR 2013. European Agreement Concerning the International Carriage of Dangerous Goods by Road. *United Nations Economic Commission for Europe*. Available from http://www.unece.org/trans/danger/publi/adr/adr2013/13contentse.html.

AHN, H. J., SONG, B. C., SOHN, S. C., LEE, M. H., SONG, K. AND JEE, K. Y. 2013. Application of a wet oxidation method for the quantification of ^{3}H and ^{14}C in low-level radwastes. *Applied Radiation and Isotopes*, Vol. 81, 62-66. http://dx.doi.org/10.1016/j.apradiso.2013.03.059.

AITTOLA, J.-P., CHYSSLER, J. AND RINGBERG, H. 1982. Thermal stability of ion-exchange resins. *Studsvik Energiteknik AB*, 1982-01-13. Available from http://www.iaea.org/inis/collection/NCLCollectionStore/_Public/13/703/13703734.pdf.

ANSI/ANS 2003 Measurement of the leachability of solidified low-level radioactive wastes by a short-term test procedure. Available from http://www.ans.org/store/item-240249/.

BARRON, R. E. AND FRITZ, J. S. 1984. Effect of functional group structure on the selectivity of low-capacity anion exchangers for monovalent anions. *Journal of Chromatography A*, Vol. 284, 13-25. http://dx.doi.org/10.1016/S0021-9673(01)87798-0.

BUCUR, C., COMTE, J., LEGAND, S., RIZZATO, C., RIZZO, A., VEČERNÍK, P. AND REILLER, P. E. 2015. 2nd Annual Progress Report on WP4 – 2015 – (D4.3). *Carbon-14 Source Term (CAST) Project, N° 604779*, CAST - D4.3. Available from http://www.projectcast.eu/cms-file/get/iFileId/2513.

BUCUR, C., RIZZATO, C. AND SHCHERBINA, N. 2017. Final Report on gaseous release of C-14 from BWR and CANDU Spent Ion Exchange Resins (D4.7). *Carbon-14 Source Term (CAST) Project, N° 604779*, CAST - D4.7. Available from http://www.projectcast.eu/cms-file/get/iFileId/2584.

COMTE, J., BUCUR, C., RIZZATO, C., RIZZO, A., KÄLLSTRÖM, K., VEČERNÍK, P. AND REILLER, P. E. 2017. 3rd Annual Progress Report on WP4 – 2016 – (D4.4). *Carbon-14 Source Term (CAST) Project, N° 604779*, CAST - D4.4. Available from http://www.projectcast.eu/cms-file/get/iFileId/2548.

DOW 2016. Ion Exchange Resins Selectivity. *DOW Chemical*, Form No 177-01755. Available from http://www.dow.com/scripts/litorder.asp?filepath=liquidseps/pdfs/noreg/177-01755.pdf.

DUVAL, D. L. AND FRITZ, J. S. 1984. Coated anion-exchange resins for ion chromatography. *Journal of Chromatography A*, Vol. 295, 89-101. http://dx.doi.org/10.1016/S0021-9673(01)87601-9.

HAVLOVÁ, V., HOLEČEK, J., VEJSADA, J., VEČERNÍK, P. AND ČERVINKA, R. 2010. Příprava syntetické podzemní vody pro laboratorní experimentální práce. *Ministry of Industry and Trade of the Czech Republic*, FR-TI1/367. In Czech.

LEGAND, S., BOUYER, C., CASANOVA, F., LEBEAU, D. AND LAMOUROUX, C. 2014. Uranium carbide dissolution in nitric acid: speciation of organic compounds. *Journal of Radioanalytical and Nuclear Chemistry,* Vol. 302, 27-39. http://dx.doi.org/10.1007/s10967-014-3409-2.

MAGNUSSON, Å., STENSTRÖM, K. AND ARONSSON, P. O. 2008. ^{14}C in spent ion-exchange resins and process water from nuclear reactors: a method for quantitative determination of organic and inorganic fractions. *Journal of Radioanalytical and Nuclear Chemistry,* Vol. 275, 261-273. http://dx.doi.org/10.1007/s10967-007-7035-0.

PARK, S. C., CHO, H. R., LEE, J. H., YANG, H. Y. AND YANG, O. B. 2014. A study on adsorption and desorption behaviors of ^{14}C from a mixed bed resin. *Nuclear Engineering and Technology,* Vol. 46, 847-856. http://dx.doi.org/10.5516/Net.06.2014.088.

PLANCQUE, G., AMEKRAZ, B., MOULIN, V., TOULHOAT, P. AND MOULIN, C. 2001. Molecular structure of fulvic acids by electrospray with quadrupole time-of-flight mass spectrometry. *Rapid Communications in Mass Spectrometry,* Vol. 15, 827-835. http://dx.doi.org/10.1002/rcm.307.

POINTEAU, I., HAINOS, D., COREAU, N. AND REILLER, P. 2006. Effect of organics on selenite uptake by cementitious materials. *Waste Management,* Vol. 26, 733-740. http://dx.doi.org/10.1016/j.wasman.2006.01.026.

POINTEAU, I., COREAU, N. AND REILLER, P. E. 2008. Uptake of anionic radionuclides onto degraded cement pastes and competing effect of organic ligands. *Radiochimica Acta,* Vol. 96, 367-374. http://dx.doi.org/10.1524/ract.2008.1503

REILLER, P. E., BUCUR, C., COMTE, J., HEISBOURG, G., LEBEAU, D., RIZZATO, C., RIZZO, A. AND VEČERNÍK, P. 2014. Annual Progress Report on WP4 – 2014 – (D4.2). *Carbon-14 Source Term (CAST) Project, N° 604779,* CAST - D4.2. Available from http://www.projectcast.eu/cms-file/get/iFileId/2492.

RIZZATO, C., RIZZO, A., HEISBOURG, G., VEČERNÍK, P., BUCUR, C., COMTE, J., LEBEAU, D. AND REILLER, P. E. 2014. State of the Art Review on Sample Choice, Analytical Techniques and Current Knowledge of Release from Spent Ion-Exchange Resins (D4.1). *Carbon-14 Source Term (CAST) Project, N° 604779,* CAST - D4.1. Available from http://www.projectcast.eu/cms-file/get/iFileId/2503.

RIZZATO, C. in prep. Spent Ion-Exchange Resins arising from BWRs: ^{14}C speciation, release and effects of gamma-radiation. PhD Thesis. Rheinisch-Westfälische Technische Hochschule Aachen.

RIZZO, A., BUCUR, C., COMTE, J., KÄLLSTRÖM, K., RIZZATO, C., VEČERNÍK, P. AND REILLER, P. E. 2017. Final Report on the Estimation of the Source Term and Speciation (D4.5). *Carbon-14 Source Term (CAST) Project, N° 604779,* CAST - D4.5. Available from http://www.projectcast.eu/cms-file/get/iFileId/2587.

ROBIE, R. A. AND HEMINGWAY, B. S. 1995. Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 bar (10^5 Pascal) Pressure and at Higher Temperatures. *US Geological Survey,* US Geological Survey Bulletin 2131. Available from http://pubs.usgs.gov/bul/2131/report.pdf.

SEIDELL, A. 1940 *Solubilities of Inorganic and Metal Organic Compounds. A Compilation of Quantitative Solubility Data from the Periodical Litterature* (New York, NY, USA: D. Van Nostrand Company, Inc). Available from http://archive.org/details/solubilitiesino04seidgoog.

VAN LOON, L. R. AND HUMMEL, W. 1995. The Radiolytic and Chemical Degradation of Organic Ion Exchange Resins under Alkaline Conditions: Effect on Radionuclide Speciation. *Paul Scherrer Institut*, PSI Bericht 95-13. Available from http://www.iaea.org/inis/collection/NCLCollectionStore/_Public/27/010/27010434.pdf.

WIELAND, E., TITS, J., SPIELER, P. AND DOBLER, J. 1998. Interaction of Eu(III) and Th(IV) with sulfate-resisting Portland cement. *Material Research Society Proceedings*, Vol. 506, 573-578.