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Final Report on gaseous release of C-14 from BWR and CANDU Spent Ion Exchange Resins (D4.7)

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

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

For more information, please visit the CAST website at:

<http://www.projectcast.eu>

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Final Report on gaseous release of C-14 from BWR and CANDU Spent Ion Exchange Resins (D4.7)

Executive Summary

Two CAST partners, FZJ and RATEN ICN, carried out experimental programmes under Task 4.3 to evaluate the gaseous release of ^{14}C from the BWR and CANDU SIERs in chemical conditions relevant to storage and/or disposal (cementitious environment).

Two BWR SIERs samples (named FZJ-A and FZJ-B) and one CANDU SIER sample were used in the experimental programmes carried out at FZJ and RATEN ICN, respectively. The generation of gases from BWR SIERs (FZJ-A/B) during storage was investigated in different experimental conditions (temperature, atmosphere) and the organic/inorganic ^{14}C released has been measured. An on-line approach was chosen to study the kinetic of ^{14}C release from BWR resins in cementitious environment (simulated cement pore-water) and to investigate the pH variations in the cement pore-water in contact with SIERs.

The inorganic ^{14}C gaseous release ($^{14}\text{CO}_2$) from CANDU SIER was assessed during the desorption tests carried out in semi-dynamic conditions and alkaline solution (NaOH 0.1M). The PP lids of the glass bottles used in the experiments were adapted to allow the N_2 purging in the space above the liquid level and the outgas washing through gas bubblers filled with alkaline solution (NaOH 2M).

No detectable ^{14}C activity in the gas phase was found from the storage experiments carried out for FZJ-A sample and a relatively fast equilibrium of the gas phase (less than 20 days) was observed in the storage experiments on FZJ-B samples. The total ^{14}C activity (related to the anion-exchange fraction) measured in gas phase during storage of FZJ-B sample in air in a closed system was between 0.6% and 1% at room temperature and between 0.6% and 3% at 50°C.

Gaseous releases from SIERs in cementitious conditions are caused by a transient/permanent decrease in the pH of the alkaline solution caused most probably by H⁺ ions released during the ion-exchange reaction of SIERs and alkaline solution.

The ¹⁴C release in gas phase in cementitious conditions was around 10% of the total ¹⁴C content of BWR SIERs, measured exclusively as inorganic ¹⁴C. From CANDU SIER, around 7% of the total ¹⁴C content was released as inorganic gas.

No organic ¹⁴C was measured in gas phase either for BWR or for CANDU SIERs. Further tests are needed to allow a statistical approach to obtain significant results on the assessment of ¹⁴C gaseous release from BWR and CANDU SIERs in disposal relevant conditions (cementitious environment).

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1 Introduction

In several reference cases of disposal systems, ^{14}C is one of the most important contributors to the dose. Due to the long half-life (5,730 years), the ^{14}C travel time to the biosphere is a main contributor to uncertainty. This is affected by both the physical form of ^{14}C (*e.g.* due to the potential migration of gaseous ^{14}C with bulk gas) and chemical speciation (*e.g.* the form of dissolved species will determine sorption behaviour from groundwater).

Ion exchange resins (IERS) are widely used in nuclear facilities for the purification of liquid processes or waste streams and represent an important waste streams for all NPPs irrespective of the reactor type. Exhausted (spent) ion-exchange resins are referred as SIERS.

In Germany, different management strategies are applied to SIERS originating from BWRs. In some cases, water is removed either by vacuum, heating or by filtration. SIERS are then stored in standard 200 litre drums in intermediate storages. In other cases, SIERS are stored in big vessels, waiting for a reprocessing with *e.g.* acid aimed to remove ^{14}C (that will be retained through alkaline solutions). In other cases, LLW SIERS are burned to reduce the waste volume. Containment for intermediate storage or final disposal like GNS Gusscontainer[®] Type VI or MOSAIK[®] II have been developed. A common waste management strategy is, however, still missing. The final disposal of SIERS (ILW/LLW with negligible heat generation) should take place in the deep geological repository “Konrad”, a former iron ore mine in the Lower Saxony region. SIERS should meet, however, the requirements for the final disposal related *e.g.* to quality control of waste packages, activity limitations, volatility of ^{14}C , accident analysis.

In Romania, the SIERS generated from the two operational CANDU units are segregated upon their generation systems (as non-fuel contact and fuel contact resins) and stored under water in concrete vaults lined with epoxy (200 m³ each). Due to the high ^{14}C inventory, the non-fuel contact resins (mainly from Moderator purification system) shall be disposed of in the future geological repository (foreseen to be operational in 2065) while the fuel-contact resins will be disposed of in a near surface repository (foreseen to be operational in 2023).

The experiments carried out under Task 4.3 of CAST WP4 were meant to achieve experimental data and evidences on gaseous release of ^{14}C from SIERs under storage and/or disposal relevant conditions.

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

2 Materials and Methods

2.1 SIERs sample used in experiments

BWR and CANDU SIERs were used in the experimental programme performed by FZJ and RATEN ICN to evaluate the ^{14}C gaseous release in storage and disposal relevant conditions.

Two BWR SIERs samples were used in the experimental programme carried out at FZJ (named FZJ-A and FZJ-B). The criteria applied by FZJ in selecting the BWR SIERs are reported in D4.1 [RIZZATO *et al.*, 2014]. Furthermore, a more detailed approach to the sample choice for every selected BWR SIERs is described in D4.4 [COMTE *et al.*, 2017].

In the case of FZJ-A, SIERs coming from the Condensate Clean-Up (CCU) System were 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 (powder resin) were collected and delivered to FZJ.

In the case of FZJ-B, SIERs 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 allow 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. Sampling of the gas phase from the storage drums was not feasible.

The CANDU SIERs were transferred at RATEN ICN from Unit 1 of Cernavoda NPP. The sample transferred is not representative from the all volume of SIERs generated from non-fuel contact systems of Cernavoda NPP since no SIERs sampling from the storage vaults was carried out up to now at Cernavoda NPP.

Some SIERs are collected during maintenance from the strainers situated on the inlet and outlet of the ion exchange resins (IER) columns of different purification systems. A sample of spent resins sampled from a storage drum containing mixed SIERs collected from strainers of the moderator (MOD) and Primary Heat Transport (PHTS) purification systems was transferred to RATEN ICN in 2015 to be used in the experimental programme carried out under CAST WP4.

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 resins) and IRN 78 (strong base anion-exchange resin).

The systems from where these SIERs were collected contain heavy water that after almost 19 years of operation has a high ^3H 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.

2.2 Analytical techniques

2.2.1 Radiological characterization

The radiological characterization of FZJ-A/B and Cernavoda SIERs was performed by gamma spectrometry (HPGe), total combustion and inorganic/organic ^{14}C partitioning. More details about the inorganic and organic ^{14}C determination in BWR and CANDU SIERs are reported in D.4.1 [RIZZATO *et al.*, 2014] and D4.5 [RIZZO *et al.*, 2017], respectively.

2.2.2 Analytical development

Analytical development to lower the detection limits for the ^{14}C -speciation/quantification in solution and in the gas phase has been performed in FZJ, with a particular effort put in the validation of the equipment implied for the gas phase analyses.

In detail, the conversion efficiency of organic compounds in the catalyser has been investigated with reference gases (CO , H_2 , CH_4) at different gas flows, using the experimental set-up presented in Figure 1. A sample of calibration gases (extra pure and certified) has been loaded in a sample cylinder at a well-defined pressure. After the background stabilization of the quadrupole mass-spectrometer under argon, a by-pass allows the flowing of the sample through the catalyser. The resulting gas composition was analysed by MS and the conversion efficiency has been calculated. The experiments have been performed with the catalyser at room temperature and at 750°C , in order to have a reliable comparison of the results. The catalyser was regenerated after each experiment.

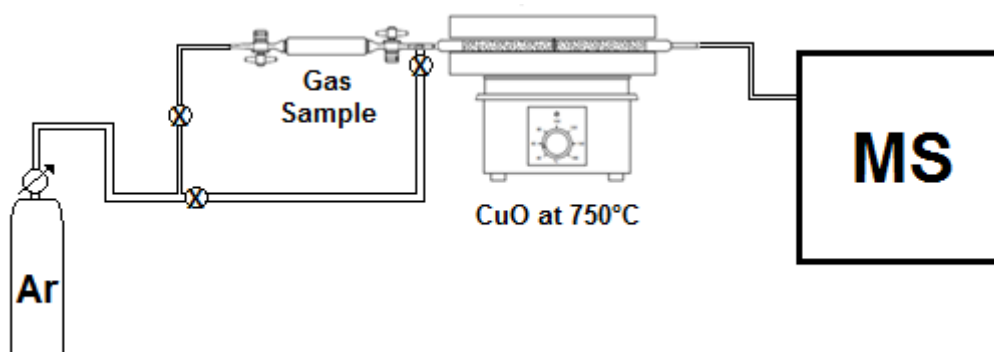


Figure 1. Experimental set-up for testing the conversion efficiency of the CuO catalyser.

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

catalyser) showed an efficient conversion of the gases at different partial pressures (concentrations).

The sequence of washing bottles for the radioanalytical analyses of ^{14}C released in the gas phase has been successfully optimized, allowing a lower dilution of the ^{14}C activity and an optimal volume for the ^3H and ^{14}C absorption. In particular, miniaturized washing bottles (Figure 2) have been developed and tested, with a reduced volume and, accordingly, a reduced dilution of the activity – see D4.3 [BUCUR *et al.*, 2015].

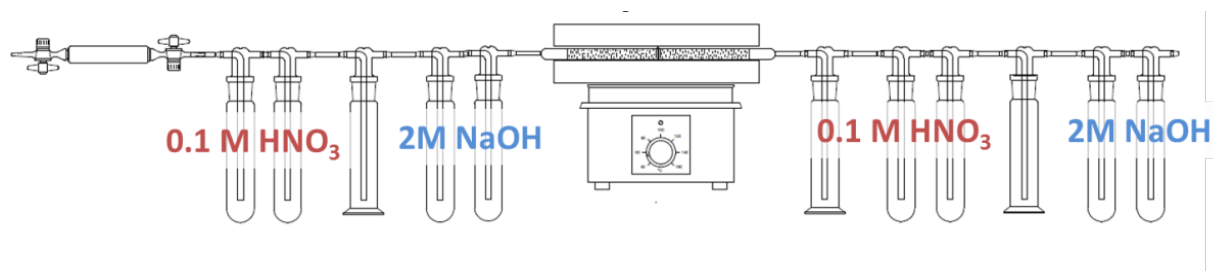


Figure 2. Experimental setup for the analysis of ^{14}C in FZJ, with a catalyser to convert HT to HTO, CO to CO_2 and organics to CO_2 .

The employment of $\text{CuO-Pt/Al}_2\text{O}_3$, initially considered, has been abandoned due to the activity retention (memory effect) experienced during leaching tests on graphite. Only CuO has been employed for the catalyser. The washing bottles, positioned after the catalyser, are intended for absorbing the newly-formed HTO (tritiated water) and $^{14}\text{CO}_2$.

A similar analytical method was also used at RATEN ICN for inorganic and organic ^{14}C measurements, but with larger gas washing bottles (15, 25 and 50 ml, depending on ^{14}C activity in the respective experiment) and $\text{CuO-Pt/Al}_2\text{O}_3$ as the catalyser [RIZZO *et al.*, 2017].

2.3 Generation of gases from BWR SIERs during storage

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

The ^{14}C release kinetics were investigated with small samples (about 1,5 g), stored in 15 ml vials furnished with a double access/valve to allow the exchange of the whole gas phase during analysis (see Figure 3).



Figure 3. Example of vial used for the storage experiments of small FZJA/B samples

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

2.4 Release of ^{14}C from BWR and CANDU SIERs at high pH

Of particular interest for the final disposal is the conditioning of SIERs in cement. For this reason, the ^{14}C gaseous release in alkaline conditions simulating the cementitious environment was evaluated for both BWR and CANDU SIERs.

NaOH + KOH solution was used in the experiments carried out on BWR SIERs and NaOH solution in the experiments performed on CANDU SIERs.

Small samples of FZJ-B were prepared in 15 ml air-tight vials with cement pore water to study the kinetics of ^{14}C release from SIERs in cementitious conditions. Such a strategy was however abandoned, since an evolution of gas was observed during sample preparation. Therefore, an on-line measurement with the equipment represented in Figure 2 was performed. A sample of about 1 g was loaded in the reactor vessel and 10 mL of cement pore water (0.114 M NaOH, 0.18 M KOH) was added. The washing bottles were exchanged every 24 hours and new solution was added to the sample at every step, until the activity in the washing bottle solutions was below the detection limit of the LSC.

A similar 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 (1g SIERs and 10ml 0.1 N NaOH) and on the equilibrium pH value at different ionic strengths of the alkaline solution.

For CANDU SIER, the inorganic ^{14}C gaseous release was evaluated during desorption tests carried out in aerobic conditions, using two sub-samples from the SIERs received from Cernavoda NPP, in alkaline solution (NaOH 0.1 M, with pH of 12.5).

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 PP lids that were adapted to allow N_2 purging in the desorption vessels and outgas washing through alkaline gas washing bottles (Figure 4) to absorb the inorganic ^{14}C . Desorption tests were performed at room temperature ($23\pm 3^\circ\text{C}$), for solid to liquid ratio of 0.01 g/ml (0.4 g of SIER + 40 ml of NaOH solution), in semi-dynamic conditions: 5 ml of leachant were sampled at each time step and 5 ml of fresh NaOH were added. The leachant 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 phase was measured but also the residual ^{14}C activity in the SIER sample subject to desorption test.



Figure 4. The glass vessels adapted for desorption tests.

Before sampling the leachant solution, at each sampling time N_2 gas was purged in the space above the liquid level and the outgases were washed through gas bubblers using a similar experimental set-up as those reported in Figure 2.

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 the alkaline bubblers, the nitrogen gas was introduced through both parallel desorption vessels at the same time. To get the amount of gaseous ^{14}C released from one vessel, the amount measured in the alkaline solutions from the gas bubblers was divided by two assuming the ^{14}C released in gas phase was equal from the two parallel tests.

The ^{14}C measurements were achieved by liquid scintillation counting (LSC), using a Tri-Carb[®] analyser Model 3110 TR using Hionic Fluor as liquid scintillation cocktail. The ratio between sample and scintillation cocktail was 1 to 10. All samples were kept in darkness over night before counting.

3 Results and discussion

3.1 Radiological characterization of BWR and CANDU SIERS

The most relevant radionuclides retained in FZJ-A/B are reported in Table 1. From data reported in Table 1 one can observe that all samples show the same order of magnitude in the ^{14}C content, except for sample FZJB-2.

Table 1. Radionuclide inventory of the investigated samples.

Sample	Age (y)	Total ^{14}C [Bq/g]	^{60}Co [Bq/g]	^{137}Cs [Bq/g]	^{134}Cs [Bq/g]	^{54}Mn [Bq/g]
FZJA	-	1906 ± 256	360.7 ± 10.8	72.0 ± 3.6	4.75 ± 0.48	17.6 ± 1.2
FZJB-1	9.2	3166*	455.3 ± 13.7	240.5 ± 13.7	< 0.1	< 0.1
FZJB-2	12	553*	138.1 ± 4.1	276.5 ± 8.3	0.80 ± 0.16	< 0.1
FZJB-3	16.8	2202*	4220 ± 127	1880 ± 56.4	< 0.1	< 0.1
FZJB-4	17.2	4680*	144.5 ± 4.3	548.3 ± 16.5	< 0.1	< 0.1

*values with poor statistics

A correlation of the ^{14}C activity with the ^{60}Co activity, as performed in the past (the so-called scaling factor), is not performed here since the formation mechanisms of the two radionuclides are completely different and not correlated. However, a self-irradiation effect of the SIERS, due to the retained gamma-emitters, cannot be excluded a priori. The gamma activities of all samples are however limited and the self-irradiation dose that occurred during interim storage and during the experimental work is expected to be very small. A comparison of the activities of samples FZJB1-4 reveals a partial agreement with the adopted selection criteria reported in D4.1 [RIZZATO *et al.*, 2014]. In particular, samples FZJB-1 and FZJB-4 show the same order of magnitude in the ^{14}C and ^{60}Co activities, while FZJB-3 is characterized by a significantly higher gamma activity (one order of magnitude higher). On the contrary, sample FZJB-2 shows very low ^{14}C activity compared to the other samples. This could be due to a depleted anion-exchange fraction in the mixed resins (anion + cation) or to a non-representative sampling. The determination of ^{14}C in all FZJ-B samples

is, however, affected by poor statistics, since a complete analysis of inorganic + organic fraction implied experimental time frames up to 15 days/sample.

The initial concentration activities of the main radionuclides in the CANDU SIER sample used for desorption tests are reported in Table 2.

Table 2. The initial radionuclide content in CANDU SIER sample.

Radionuclide	Activity, Bq/g in wet SIERS ($\omega = 60.10\%$)
Total ^{14}C	$(3.37 \pm 0.12) 10^4$
Inorganic ^{14}C	$(3.14 \pm 0.15) 10^4$ (93.18%)
Organic ^{14}C	$(2.31 \pm 0.86) 10^3$ (6.85%)
^3H	$(1.43 \pm 0.49) 10^5$
^{137}Cs	$(1.72 \pm 0.07) 10^4$
^{60}Co	$(9.78 \pm 2.25) 10^2$
^{134}Cs	$(3.48 \pm 0.16) 10^2$
^{54}Mn	18.4 ± 1.17

The radionuclides inventory reported in Table 2 for CANDU SIER represent the average values of measurements carried out on 5 sub-samples from the SIER transferred from Cernavoda NPP [RIZZO *et al.*, 2017].

As it can be observed from data presented in Tables 1 and Table 2, the CANDU SIER sample contains an initial ^{14}C inventory with more than one order of magnitude higher than BWR SIER samples. Also, the concentration activities of the other gamma radionuclides are much higher in CANDU SIER samples than in BWR SIER samples.

3.2 Generation of gases from BWR SIERS during storage

Experiments on samples FZJ-A resulted in undetectable – or close to the LSC detection limit, *i.e.* <0.1 Bq/sample – releases of ^{14}C in the gas phase in all cases.

Low releases could be explained by the fact that FZJ-A samples were stored in a (probably) open system in the NPP, so a depletion of ^{14}C could have already occurred by isotope-exchange and/or ion-exchange with the atmospheric air. However, analyses on the FZJ-A SIERS revealed nevertheless consistent ^{14}C activities, mainly in inorganic form. This fact seems to contradict the measured values, considering that an isotope exchange and an ion-

exchange process with air (CO_2) could take place. A possible explanation could be linked to the number of groups interacting with the counter-ions, leading to a more stable CO_3^{2-} ion bound to the resin against a less stable HCO_3^- ion. However, such an hypothesis should be proven.

Storage experiments of FZJ-B samples were carried out in presence of small amounts of water (*ca.* 12%), retained in the resins as received, at room temperature and 50°C , in air. Storage experiments in vacuum were also performed.

^{14}C was measured exclusively in the third washing bottle (see Figure 2) in all cases of storage in air, therefore SIERs released detectable amounts of $^{14}\text{CO}_2$ in the gas phase during storage. Analyses of the samples stored at room temperature in air revealed activities in the gas phase ranging from 0.6 to 1.0% of the total ^{14}C . Results are reported in Figure 5. One can notice that most values are comparable. Only one point from FZJB-2 results is out of the trend, probably due to heterogeneous sampling.

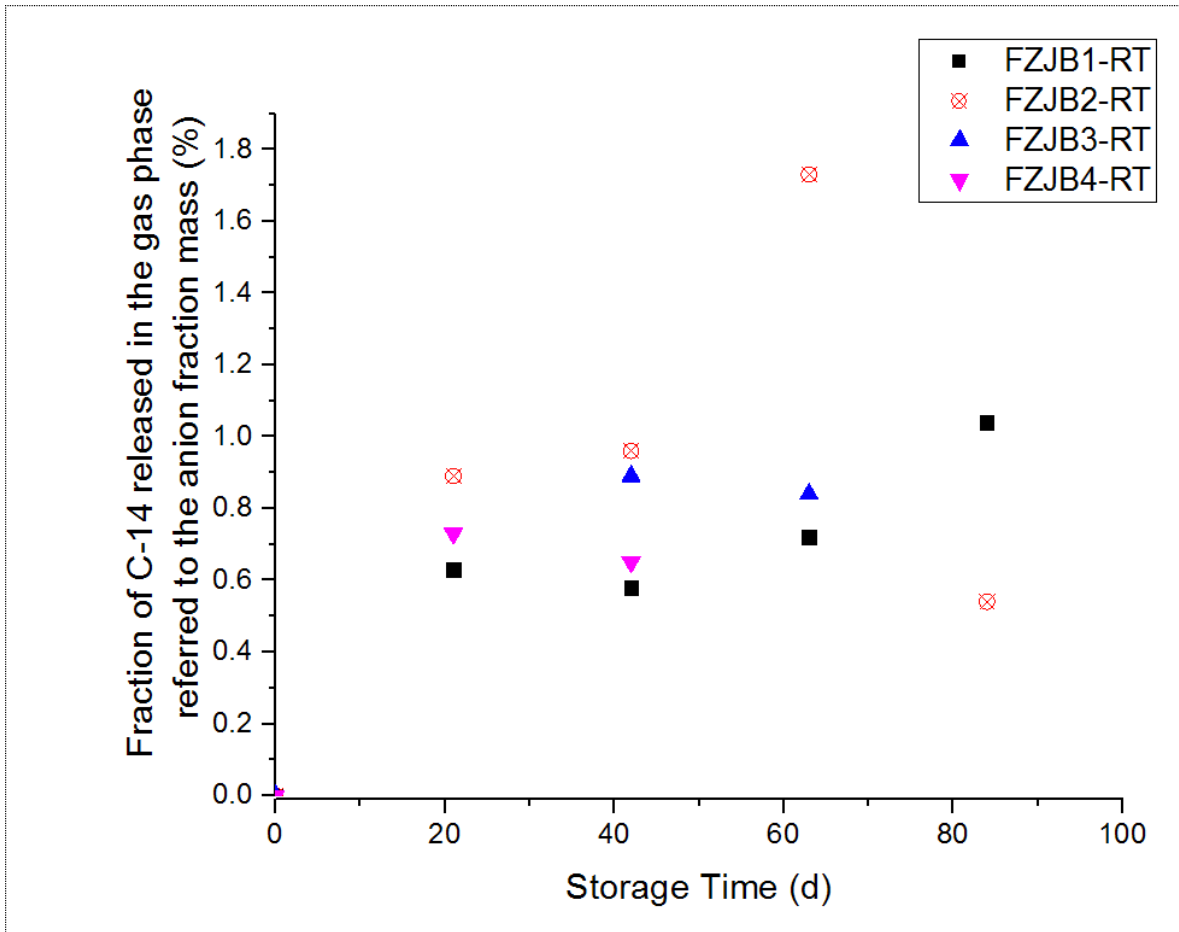


Figure 5. Release of ^{14}C in the gas phase in air at room temperature at different time intervals.

At 50°C in air, FZJ-B samples showed, in general, similar results, with slightly higher releases in some cases, with 0.6% to 3.0 % of the total ^{14}C in the gas phase (see Figure 6). However, one can notice that most results from FZJB-2 are out of the trend.

All values graphically represented in Figure 5 and Figure 6 are reported with reference to the dry anion-exchange fraction of the mixed resin regenerated in a reference ionic form, assuming that ^{14}C is mainly retained here. Results on the determination of the anion- and cation-exchange fractions will be reported in detail in RIZZATO [in prep.].

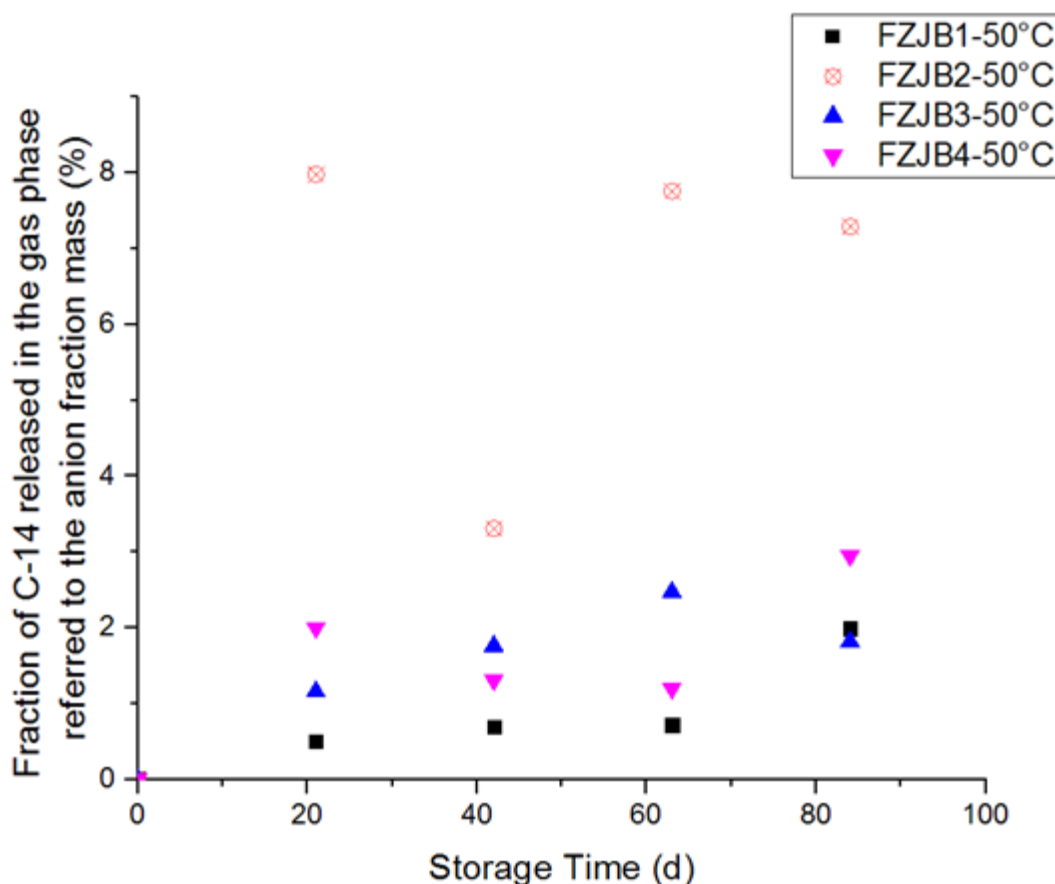


Figure 6. Release of ^{14}C in the gas phase in air at 50°C at different time intervals.

Storage experiments were performed also with FZJ-B samples under vacuum. After vacuum was established in the vial containing approx. 1.5 g of sample, analyses of the gas phase were performed similarly to the previous case. All samples revealed no activity release in the gas phase.

The interpretation of the above-reported results, considering a possible deviation due to sample inhomogeneity, points to the direction of a relatively fast equilibrium of the SIERS stored in a closed system (less than 20 days) in the presence of air. Storage experiments at 50°C revealed higher releases in some cases, probably due to the enhanced kinetics and a possible slow temperature-related degradation of the SIERS. Releases from one sample (FZJ-B) were in most cases anomalous with respect to the overall trend. This is probably due to poor statistics in the determination of the total ^{14}C , with an evaluation performed on a non-representative sample (poor in ^{14}C) or due to an erroneous anion-to-cation fraction of the mixed resin before employment in the BWR.

The ageing effect and the self-irradiation effect do not seem to be relevant for the investigated samples. However, SIERs arising from *e.g.* PWR are expected to retain considerable amounts of gamma-emitters, therefore such a conclusion may not be applied to SIERs from different reactor types.

Ion-exchange cannot take place in absence of water. Therefore, a vacuum drying of the resins and the absence of any humidity and gases in contact with the waste hindered any releases in the gas phase. This could result in a possible strategy for intermediate storage of SIERs. It is reasonable to expect, however, problems related to the volatility of the powder SIERs. Additionally, the contact of dry resins with (humid) air would lead to a release of ^{14}C . In any case, the degradation induced by self-irradiation would not be hindered, since all gamma-emitters would be still present in the waste. A selective separation of most ^{14}C could be a reasonable and feasible solution for managing SIERs, accomplishing possibly a de-classification of the waste from ILW to LLW. The generation of secondary waste should be, however, minimized.

No organic ^{14}C was observed in the gas phase. This observation could not exclude, however, the presence of volatile organics in small amounts, since the small samples here investigated were retaining few Bq of organic ^{14}C in total, probably resulting in released activities below the detection limits.

In conclusion, in presence of air the main release mechanism leading to the release of ^{14}C in the gas phase seems to be – in the short-term – ion-exchange and/or isotope exchange with the atmospheric CO_2 . At enhanced temperatures, faster exchange kinetics is likely to take place, accompanied by a slow degradation of the resins, in particular the anion-exchange fraction. Finally, self-irradiation of SIERs seems not to be relevant for the investigated samples, but cannot be excluded in general. More details on the argument will be reported in RIZZATO [in prep.].

3.3 Release of ^{14}C from SIERs at high pH

On-line analyses of the gas phase resulting from FZJB SIERs in contact with cement pore water revealed a consistent release of ^{14}C in few hours. The washing bottles were exchanged

every 24 hours and the solution was analysed at every step. In addition, 10 ml cement pore water was added every 24 hours. Results are showed in Figure 7.

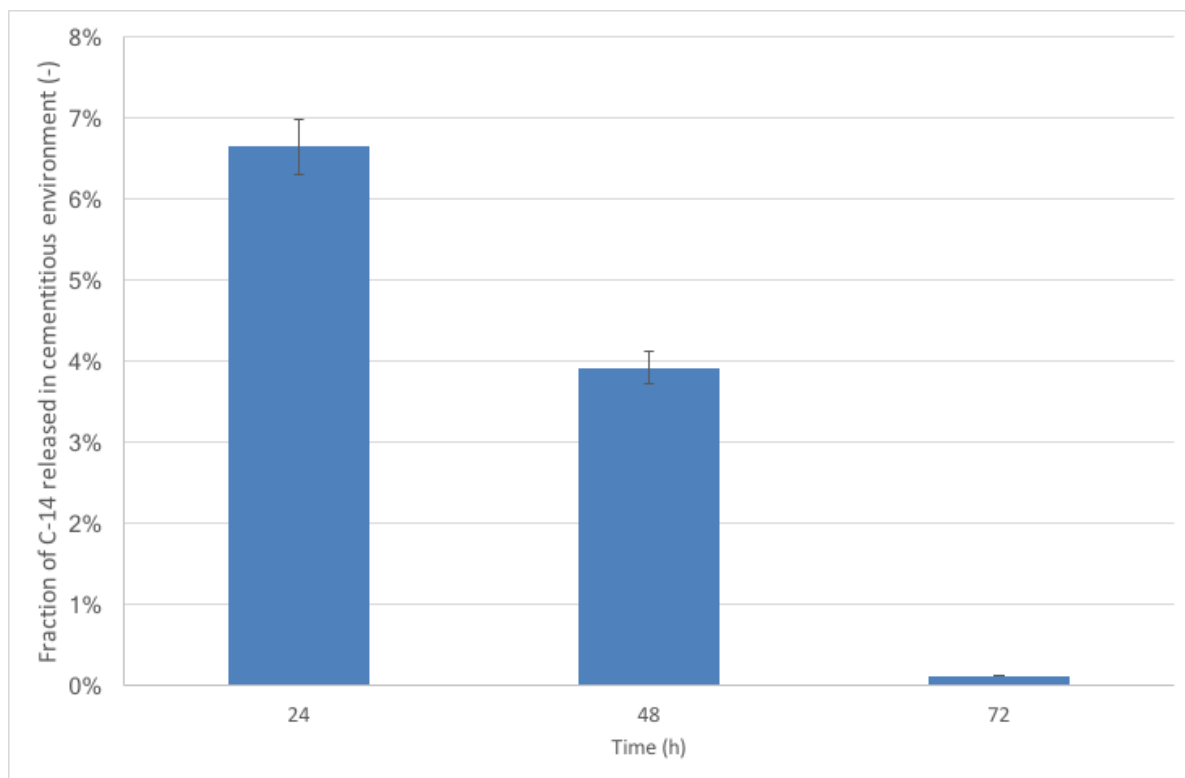


Figure 7. On-line release of inorganic ^{14}C from FZJB-2 SIERS in contact with cement pore water. Values referred to the total sample's mass as delivered.

^{14}C was retained exclusively in the third washing bottle (see Figure 2), therefore the gaseous releases from SIERS in a high pH environment were indicated to be in form of $^{14}\text{CO}_2$ (no organic ^{14}C was detected). This seems to be a contradiction, since at high pH no CO_2 should be in gas form, but in carbonate form (non-volatile). A possible explanation of the observed results could arise from the nature of the SIERS. They are, in fact, mixed anion- and cation-exchange resins. 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 touch with the solution, cations like Na^+ or K^+ (relatively big compared to the anions $-\text{OH}$) 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 $-\text{H}$ 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 (-SO₃H) in solution due to a degradation of the resin. Measurements of the residual cation-exchange capacity of SIERS seem to disprove this hypothesis – more details in RIZZATO [in prep.].

The experimental data obtained for ¹⁴C release (both as inorganic gas and as dissolved species) during desorption tests carried out on CANDU SIERS in NaOH 0.1 M are reported in Table 3.

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

Table 3. The row data measured in desorption tests.

Time, days	Inorganic ¹⁴C released in gas*, Bq	Total ¹⁴C measured in solution, Bq
1	96.83 (1.92%)	4.96 10 ³ (98.08%)
2	82.75 (1.34%)	6.10 10 ³ (98.66%)
3	79.02 (1.31%)	5.93 10 ³ (98.69%)
4	99.10 (1.73%)	5.63 10 ³ (98.27%)
9	92.70 (1.85%)	4.93 10 ³ (98.15%)
17	95.91 (1.99%)	4.72 10 ³ (98.01%)
24	86.80 (2.02%)	4.22 10 ³ (97.98%)
45	84.16 (1.90%)	4.35 10 ³ (98.10%)

174	80.04 (1.91%)	$3.35 \cdot 10^3$ (98.09%)
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* these values were measured in the alkaline solution from the gas washing bottles used to wash the outgas from the desorption vessels before their opening to sample the desorption solution and represent only the inorganic ^{14}C released as gas phase.

The most part of ^{14}C released as dissolved species was released in the first 2 days (Figure 8), while the amount of inorganic ^{14}C released in gas phase is almost constant.

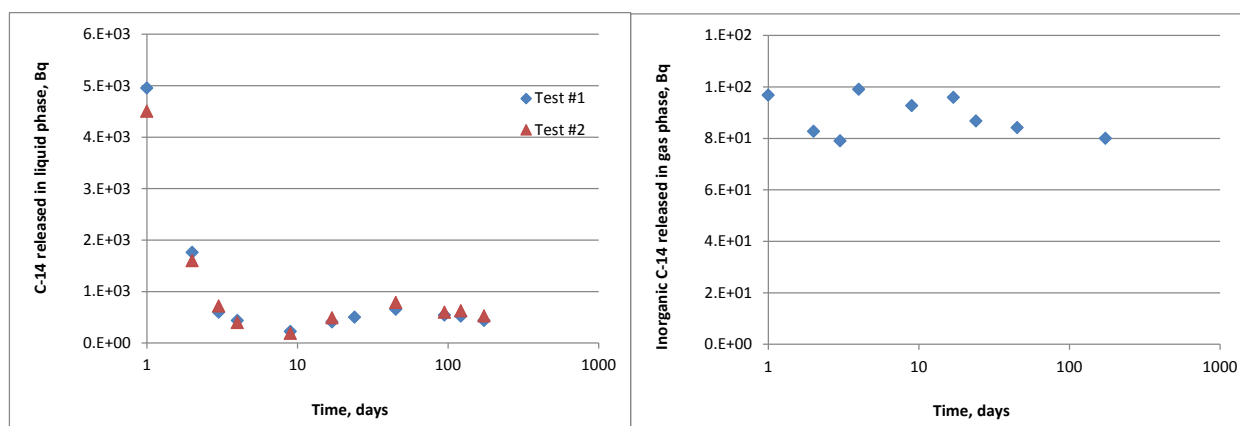


Figure 8. The ^{14}C released during desorption tests in liquid (left) and gas phase (right).

The global inventory of the ^{14}C in different phases of the desorption tests is presented in Table 4.

Table 4. 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	$1.35 \cdot 10^4$	-
	Inorganic ^{14}C	$1.26 \cdot 10^4$	-
	Organic ^{14}C	$9.24 \cdot 10^2$	-
Residual ^{14}C in SIER sample at the end of desorption test	Total ^{14}C	$1.12 \cdot 10^3$	8.30
	Inorganic ^{14}C	$9.66 \cdot 10^2$	7.67
	Organic ^{14}C	$1.52 \cdot 10^2$	16.45
^{14}C cumulative release in solution		$1.06 \cdot 10^4$	78.52
Inorganic ^{14}C cumulative release in gas phase		980.03	7.26
Total ^{14}C measured at the end of		$1.27 \cdot 10^4$	94.07

desorption tests (in liquid, gas and residual on the SIERs)		
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Data presented in Table 4 show that, from the total ^{14}C present in the SIERs sample used for desorption test, around 7% was released as inorganic ^{14}C in gas phase and around 79% as dissolved species. Around 94% of ^{14}C content in the SIER sample was recovered at the end of desorption test. The remaining ~ 6% was not found either as dissolved species and inorganic gas species, or as residual on the SIER sample after desorption test, and could represent the ^{14}C released in gas phase as organic species. However, since no organic ^{14}C in gas phase was measured, this is only an hypothesis and further experiments need to be carried out to have a conclusion on organic ^{14}C release in gas phase.

Two experiments were performed by FZJ to clarify the mechanism leading to the release of $^{14}\text{CO}_2$ in alkaline conditions. A first one consisted in mixing 1 g FZJB 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 FZJB samples), with pH values down to 7.3, a value low enough to allow the presence of gaseous CO_2 .

A second experiment, more detailed, consisted on mixing 1 g of FZJB SIERs with increasing amounts of alkaline solution (XOH , with $\text{X}=\text{K}, \text{Na}$), at a well-defined molarity. The pH was then measured after several minutes, allowing the system to equilibrate. Results are shown in Figure 9, 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 seems to be confirmed. A more detailed description of the mechanism would require additional investigations. Considering the experimental conditions, however, and taking into account a cementation process of the SIERs, the number of anions present in the cement mixture would be much higher than the ones employed here.

A final 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 10), but the solution had enough OH⁻ ions to avoid any release of gases.

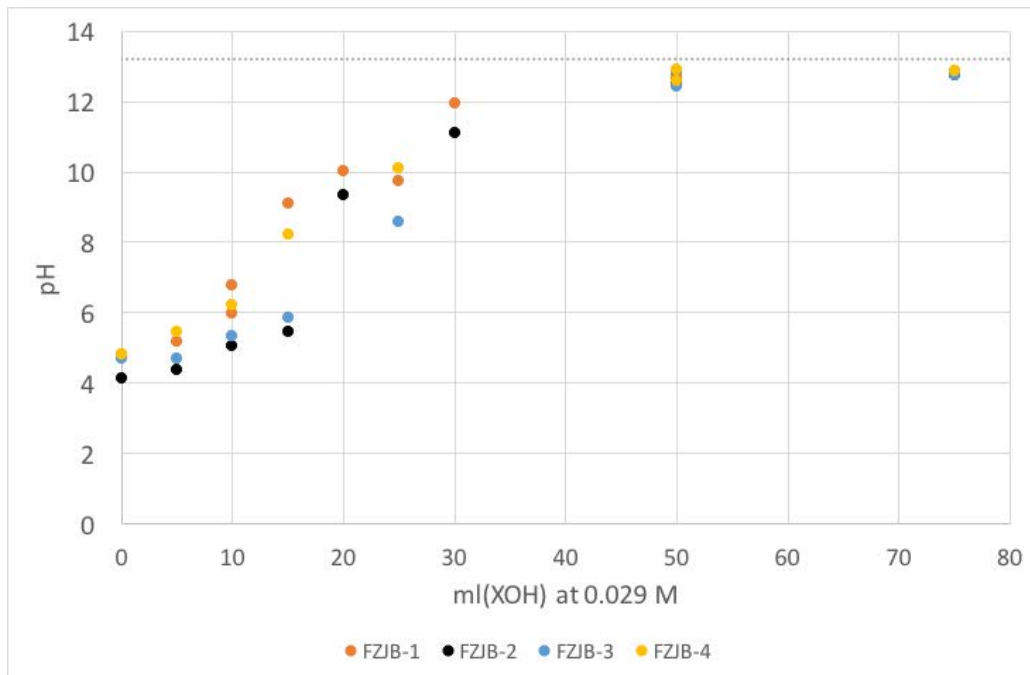


Figure 9. Static pH values of the solution in function of the equivalent volume in contact with FZJB SIERs. The initial point relates to the pH of deionised water in contact with SIERs.

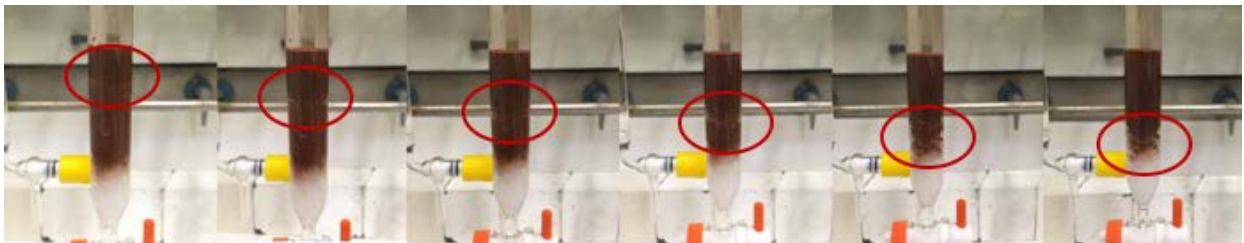


Figure 10. Evolution of gas at the reaction front of the alkaline solution in contact with SIERs.

In Figure 10 one can observe the evolution of the reaction front going through the resins, accompanied by the gas bubbles.

3.4 Uncertainties

SIERs arising from BWR (CCU) are ion-exchangers in powder form, composed of an anion- and a cation-exchange fraction mixed together with a flocculation media. Considering the principle of work, the activity and radionuclide inventory of SIERs is dependent on the position of the sample in the exchange bed; a sample that is representative of a whole batch would imply a large amount of SIERs. In the case of FZJA, SIERs from

CCU were collected in the same vessel after every discharge. Since SIERS were mixed several times, the collected samples could be considered as representative for the whole lifetime of the reactor. FZJB SIERS were collected separately for every batch. In this case, a few grams of sample could possibly not be representative for the whole amount (tens of kilograms per batch). A solution would be a statistical approach, with small samples, or the analysis of large samples. In the present study, due to laboratory limitations, only small samples could be collected and analysed. In the case of FZJA, a statistical approach was possible, thanks to the sufficient amount of samples collected. However, the determination of total ^{14}C of FZJB samples is recognised as being affected by poor statistics, since the reported values were obtained by single (time-consuming) measurement. Therefore, the reported ^{14}C activity associated with FZJB samples should be considered as indicative only. In particular, sample FZJB-2 shows a relatively low amount of ^{14}C , compared to the other samples. This fact could highlight a non-representative sampling or an erroneous mixture of the resins in the batch before employment in the reactor. This (probably erroneous) evaluation of total ^{14}C in sample FZJB-2 is reflected in the calculations of the relative gaseous releases from the same sample.

Data on the ^{14}C releases from FZJB in the gas phase during storage shows, however, a common trend. Even considering statistical deviations and sample heterogeneity, the results are pointing towards the conclusion that a relatively fast equilibrium of ^{14}C takes place in the gas phase.

Concerning the measurements of ^{14}C activity in the gas phase, a conservative uncertainty of *ca.* 5% could be assumed. The fraction of ^{14}C released in the gas phase related to the dry anion fraction mass in a reference ionic form is affected by *ca.* 15% uncertainty, related to the determination of the anion/cation fraction and due to uncertainty propagation in the calculations.

The pH values are affected by a ± 0.2 uncertainty.

An important factor to consider for the comparison of values from different laboratories and/or reactors is the reference mass used for the calculation of *e.g.* specific activity or specific release. In fact, all SIERS are characterized by the presence of water, with amounts

depending on many factors (type of resin, ionic form, cross-linking, etc.). A standard reference, *e.g.* dry weight and reference ionic form, must be taken into account for comparison.

On-line releases in the gas phase at high pH were obtained only from one sample, to verify the effective release of ^{14}C in alkaline conditions. Such values should not be taken as a reference, since there are many influencing factors inducing the ^{14}C release, *e.g.* amount of SIERs, molarity and volume of solution, different anion/cation fractions, etc.

The CANDU SIER sample used for the evaluation of gaseous ^{14}C release (inorganic) is not representative for the all SIERs generated from the purification systems of Cernavoda MOD and PHT systems. This is due to the fact that up to now no sampling campaign from the storage tanks has been carried out and the resin used in this experimental programme was collected during maintenance operations. This CANDU SIER sample seems to be quite homogeneous since the radiological analyses carried out on 5 sub-samples (of 1 g each) generated very similar radioactivity content (both for ^{14}C and for the main gamma emitters).

The uncertainty of ^{14}C measurement by LSC was around 7%. A covering uncertainty of 10% should be considered for the values reported in Tables 3 and 4 regarding the ^{14}C measurement in the desorption tests carried out on CANDU SIER.

4 Conclusions

Experiments reported herein using FZJA SIERS resulted in no detectable ^{14}C activity in the gas phase, probably due to the interim storage in contact with air. Even though ^{14}C was still present in the resins, no releases were measured. A possible explanation of the phenomenon could be linked to the nature of ^{14}C bound to the resin. In particular, HCO_3^- ions, bound to one functional group, are believed to be less stable than CO_3^{2-} ions, bound to two functional groups.

Experiments using FZJ-B SIERS resulted in a relatively fast equilibrium of the gas phase (less than 20 days), taking into account statistical deviations and sample heterogeneity. Only one sample produced results that were anomalous with respect to all other samples, probably due to an erroneous determination of the total ^{14}C or to a heterogeneous sample. The ^{14}C activity released in the gas phase (air), related to the dry anion-exchange fraction in a reference ionic form, was indicated to be 0.6-1.0% at room temperature and 0.6-3.0% at 50°C. The ^{14}C present was shown to be inorganic in all cases. However, the possibility that small organic fractions were present cannot be excluded.

The main mechanism leading to the release of ^{14}C in the gas phase during storage in air seems to be – in the short-term – ion-exchange and/or isotope exchange, with equilibrium values dependent on the total ^{14}C activity of the sample and on the volume of gas available. At enhanced temperature (50°C) in air, faster exchange kinetics are likely to take place, accompanied by a slow degradation of the resins, in particular the anion-exchange fraction. Self-irradiation of SIERS seems not to be relevant for the investigated samples, but cannot be excluded in general. Ageing effects on the investigated samples do not seem to influence the release of ^{14}C . More details on the argument will be reported in RIZZATO [in prep.].

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 amount/mixture, 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 also with high molarity solutions, in a local way.

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 $3.37 \cdot 10^4$ Bq/g of ^{14}C , mostly as inorganic form (around 93%). The experiments carried out indicated that around 7% from the total ^{14}C present in the SIERs sample used for desorption tests was released as inorganic ^{14}C gaseous species and around 79% was as dissolved species (mostly in inorganic form). Organic ^{14}C released in gas phase was not measured, but it could be the case that 6% of the initial ^{14}C activity in the SIER samples, which was not found either as dissolved species and inorganic gas species or as residual on the SIER sample after desorption test, could represent ^{14}C released in the gas phase as organic species. However, since organic ^{14}C released as gas was not measured in this study, this hypothesis should be subsequently verified. Further tests are needed to allow a statistical approach to be followed, to obtain statistically-significant results on the assessment of ^{14}C gaseous release from CANDU SIERs in disposal relevant conditions (cementitious environment).

A comparison of the results obtained by FZJ/RATEN ICN on the ^{14}C released from SIERs at high pH, reveals consistent conclusions. Although SIERs generated from different reactors and cleaning circuits could not result in comparable releases, because of the variation in relevant features and processes, the basic mechanisms related to ^{14}C release have, however, been identified. Releases of inorganic ^{14}C have been confirmed, even at high pH, with a relatively fast equilibrium reached in a closed system. A decrease of pH in the alkaline solution in contact with SIERs causes the release of gaseous $^{14}\text{CO}_2$, a phenomenon that could be also be transient depending on the amount/molarity of the solution and on the amount/mixture/saturation of the SIERs. The generation of small amounts of gaseous organic ^{14}C could not be excluded, due to the limited sensitivity of the equipment used.

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