^{14}C CONTENT IN CANDU SPENT ION EXCHANGE RESINS AND ITS RELEASE UNDER ALKALINE CONDITIONS

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ABSTRACT. The total ^{14}C content and its speciation (inorganic/organic) were measured in spent ion exchange resins (SIERs) received from Cernavoda Nuclear Power Plant (NPP). Also, ^{14}C release from SIERs was investigated by desorption tests carried out in alkaline solution relevant for cementitious environment disposal. The method used for total ^{14}C measurement consists of combustion in oxygen-rich atmosphere, while for speciation measurements, both in SIERs and in desorption solutions, an analytical method based on acid stripping and wet oxidation was applied. Around 97% from the total ^{14}C inventory measured on the Cernavoda SIERs (33.7 kBq/g) was found to be in inorganic form and only 7% as organic ^{14}C. Under alkaline conditions, ^{14}C could be released both as gaseous and as soluble species: from the total ^{14}C present in the SIERs samples around 7% was released as inorganic ^{14}C in the gas phase and 79% as dissolved species (mainly as inorganic ^{14}C). These percentages were obtained for unconditioned SIERs in NaOH solution. The SIERs will be immobilized in a suitable matrix for disposal, and the presence of Ca ions dissolved in cement pore water favor precipitation of ^{14}C and consequently the amount of ^{14}C released from disposal area should be lower.

KEYWORDS: CANDU, inorganic and organic ^{14}C, spent ion exchange resins.

INTRODUCTION

In Romania, two CANDU 600 (CANada Deuterium Uranium) reactors are currently in operation at the Cernavoda site, and two more CANDU units are foreseen to be commenced in the future. Due to its long half-life ($T_{1/2}$ = 5730 yr), high mobility in groundwater system, easy incorporation into humans via the food-chain, and high inventory in radioactive waste generated from Cernavoda Nuclear Power Plant (NPP) operation, ^{14}C is a radionuclide of concern for radioactive waste management, both in the predisposal activities as well as for final disposal.

^{14}C is generated mainly by neutron activation of stable nitrogen—^{14}N, oxygen—^{17}O and, to a lesser extent, stable carbon isotope—^{13}C. In nuclear reactors, ^{14}C is produced in the fuel, from core structural materials, and in reactor coolant, due to the presence of the stable parent isotopes that are activated by the neutrons generated from nuclear fission reactions occurring in the fuel (Yim and Caron 2006).

Since CANDU reactors use heavy water (D_2O) both as moderator and as coolant, more ^{14}C is generated in this type of reactors due to the large amount of D_2O having higher isotopic abundance in ^{17}O compared to the light water (0.055% in D_2O and 0.037% in H_2O), but also to the higher average thermal neutron flux in CANDU reactors (10^{14} n cm^{-2} s^{-1} compared to 10^{13} n cm^2 s^{-1} in light water reactors).

From the total ^{14}C generated in a CANDU reactor, more than 95% is generated in moderator system (MOD), around 1.3% in the primary heat transport system (PHTS), 3.37% in the fuel, and 0.13% in the annulus gas (IAEA 2002). Most of the ^{14}C generated in MOD and PHTS is retained in

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the ion exchange resins (IERs) used to purify the heavy water from these circuits. When the criteria thresholds are reached in a circuit, spent ion exchange resins (SIERs) are discharged in form of slurry (under a flow of light water) and transferred to the storage vaults designed to store the SIERs generated during the life of Cernavoda NPP. At Cernavoda NPP, the SIERs are stored in different concrete vaults depending on their origin: SIERs originating from non-fuel contact systems (systems that are not coming in contact with the fuel, i.e. MOD, liquid zone control, etc.) are stored separately to the SIERs generated in fuel contact systems (i.e. PHTS, spent fuel cooling pool, etc.).

The chemical form under which ^{14}C is fixed within or adsorbed to the IERs is highly related to the chemical condition of the reactor. The heavy water in CANDU MOD system has low temperature and pressure (~60°C and essentially atmospheric pressure) and it is highly purified; the only chemicals added to the system are those used as neutron poisons for excess reactivity control or to guarantee reactor shut-down (typically, gadolinium nitrate and/or boric acid). The pH of the heavy water in MOD is kept slightly acidic and it is not purposely deaerated; if necessary oxygen may be added to ensure the recombination of deuterium generated by radiolysis (Cook and Lister 2014). Due to the above described chemical conditions prevailing in the MOD system of the CANDU reactor, the ^{14}C, generated mainly by neutron activation of ^{17}O, would be predominantly as ^{14}CO$_2$ and carbonate species dissolved in D$_2$O (IAEA 2002). These species are easily fixed on the IERs (around 91.43 % of the ^{14}C generated in MOD is retained on the IERs) and only a limited amount of ^{14}C is released to the atmosphere through the ventilation system of the moderator cover gas system (IAEA 2002). Consequently, the main radioactive waste stream containing ^{14}C consists of SIERs generated in MOD purification system. Even for the MOD SIERs, it is recognized that the ^{14}C content is highly dependent on the column operating history. For example, the resins used for normal moderator purification usually contain high levels of ^{14}C, while the resins used for moderator reactivity control contain low levels of ^{14}C.

Unlike the MOD, the heavy water in the PHTS system has an alkaline pH (~10.5) and the water is deaerated to maintain the dissolved oxygen concentrations below 0.01 mg/kg (Cook and Lister 2014). Under these reducing conditions, in the PHTS less oxidized ^{14}C species could be generated, i.e. end-product ^{14}CH$_4$. But as mentioned above, in PHTS only a small fraction of ^{14}C is generated.

The different release pathways for ^{14}C in gaseous or dissolved forms and the lack of knowledge of its speciation in both phases results in high uncertainty in its potential contribution to the total dose that could be associated with a radionuclide release from a radioactive waste disposal facility. The travel time of ^{14}C from such a facility to the biosphere 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 the chemical speciation (organic and inorganic ^{14}C species have different sorption in the geosphere). For these reasons, not only the total ^{14}C inventory in SIERs but also its speciation are important for a safety assessment of disposal facility containing SIERs.

The information on ^{14}C content and speciation in CANDU SIERs is scarce, and available data are those from the measurements carried out on SIERs generated from CANDU reactors in operation in Canada and South Korea. Based on available data for CANDU reactors from Canada, the specific activity of ^{14}C in the SIERs originating from the MOD is ranging between 0.05 and 213 Ci/m^3, with an average value of 71 Ci/m^3, while in the SIERs from PHTS the ^{14}C specific activity is between 0.24 and 6.7 Ci/m^3, with an average of 3.34 Ci/m^3 (Miller et al. 1997). Results obtained by Park et al. (2008) on SIERs from CANDU reactors from Korea, and by Moir et al. (1994) on two moderator SIERs from the CANDU reactor Bruce A in Canada, show that more than 92% of the ^{14}C activity in SIERs is retained in anionic resins under inorganic form (Park et al. 2008). A minor fraction of ^{14}C containing species has been measured

in the cation exchange resins, after their separation from a mixed bed (Moir et al. 1994; Park et al. 2008), probably under the form of metal carbonate (Moir et al. 1994).

Within the CArbon-14 Source Term (CAST) project (Scourse and Williams 2014), Work Package 4 was particularly dedicated to the identification of the source term of ^{14}C within SIERs and to the speciation of the possible released ^{14}C bearing molecules. In this paper, experimental data for inorganic and organic ^{14}C content in a SIERs sample from Cernavoda NPP are reported. Also, to get an insight on potential ^{14}C form and species (inorganic and organic) released from SIERs in cementitious environment characteristic to the SIERs disposal, results on ^{14}C desorption in alkaline conditions are also presented.
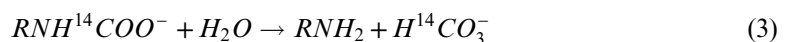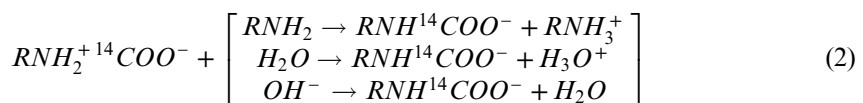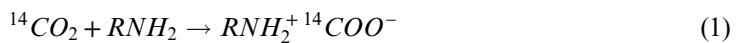
MATERIALS AND METHODS

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 as fuel contact and non-fuel contact resins and stored in separated vaults. No SIER samplings from the Cernavoda storage vaults were performed and no real measurements on Cernavoda SIERs were performed before the beginning of the CAST project. During maintenance, beads of spent resins were collected from the strainers of the purification systems and stored in drums in Cernavoda storage facility. Such a SIER sample (in form resin beads in heavy water) originating from purification systems of MOD and of PHTS from Unit 1 of Cernavoda NPP was transferred to RATEN ICN laboratory in 2015 to be used in the experimental programme developed under CAST project. To decrease the tritium content and 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.

Method Used for Total ^{14}C Measurement

For total ^{14}C measurement in SIERs, a non-catalytic combustion by the flame oxidation method was used. By this method, the resin samples are combusted in an oxygen-enriched atmosphere with a continuous flow of oxygen using sample oxidizer Model 307 by Perki-nElmer. By sample combustion in this system any hydrogen and carbon is oxidized to H_2O and CO_2, respectively. The H_2O resulting from the combustion process is condensed in a cooled coil, washed into a counting vial where it is mixed with LSC cocktail (MonophaseS) and the resulting vial is ready for tritium counting by liquid scintillation counting (LSC).

Since the carbon dioxide readily reacts with compounds containing amines (RNH_2, with R representing the organic radical, an organic substituent known as "side chain"), the Carbo-Sorb® E was chosen to absorb the CO_2 released during combustion process. The adsorption reaction of carbon dioxide can be described as follows (Ahn et al. 2013):

$$^{14}CO_2 + RNH_2 \rightarrow RNH_2^{+\,14}COO^- \tag{1}$$

$$RNH_2^{+\,14}COO^- + \begin{bmatrix} RNH_2 \rightarrow RNH^{14}COO^- + RNH_3^+ \\ H_2O \rightarrow RNH^{14}COO^- + H_3O^+ \\ OH^- \rightarrow RNH^{14}COO^- + H_2O \end{bmatrix} \tag{2}$$

$$RNH^{14}COO^- + H_2O \rightarrow RNH_2 + H^{14}CO_3^- \tag{3}$$

As shown in the above equations, the amine contained by the Carbo-Sorb E® solution (RNH_2) reacts with ^{14}C-labeled carbon dioxide to form a zwitterion, which reacts with H_2O to form a stable carbonate compound (Equation 3) that is mixed with Perma-fluor® E + directly in the counting vial to be counted by LSC for ^{14}C measurement.

At the end of the combustion process, two separate samples, one for ^{14}C measurement and one for ^{3}H measurement, are trapped at ambient temperature minimizing the cross-contamination. [14]C and ^{3}H measurements were achieved using a Tri-Carb® analyzer Model 3110 TR. The major problem encountered in LSC measurements is chemiluminescence and photo-luminescence (phenomena characteristic of an excitation of the cocktail either during sample preparation or storage). The standard method of avoiding this problem is to use a cocktail which is known to be resistant to chemiluminescence as well as to allow the chemiluminescence to decay in the dark before counting. For these reasons, even the LSC cocktails used are resistant to chemiluminescence, all samples were kept few hours in dark before counting.

Method Used for [14]C Speciation Measurement

As ^{14}C is a pure β-emitter (with a fairly low energy compared with the β energy emissions of the other radionuclides) it belongs to the category of difficult-to-measure radionuclides. For ^{14}C measurement by LSC, the ^{14}C has to be separated and purified by other potential interfering radionuclides (such as ^{3}H, [129]I, ^{137}Cs etc.) to get accurate results.

The analytical method used for inorganic and organic ^{14}C measurement in SIERs samples consists of a sequential extraction of inorganic 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 setup used for release and separation of inorganic and organic ^{14}C is schematically presented in Figure 1. It consists of a reaction vessel, a separatory funnel, a nitrogen supply and a vacuum pump, two gas washing lines with a catalytic furnace between them. An Erlenmayer flask (300 mL) with a three-hole rubber stopper (two for gas and separatory
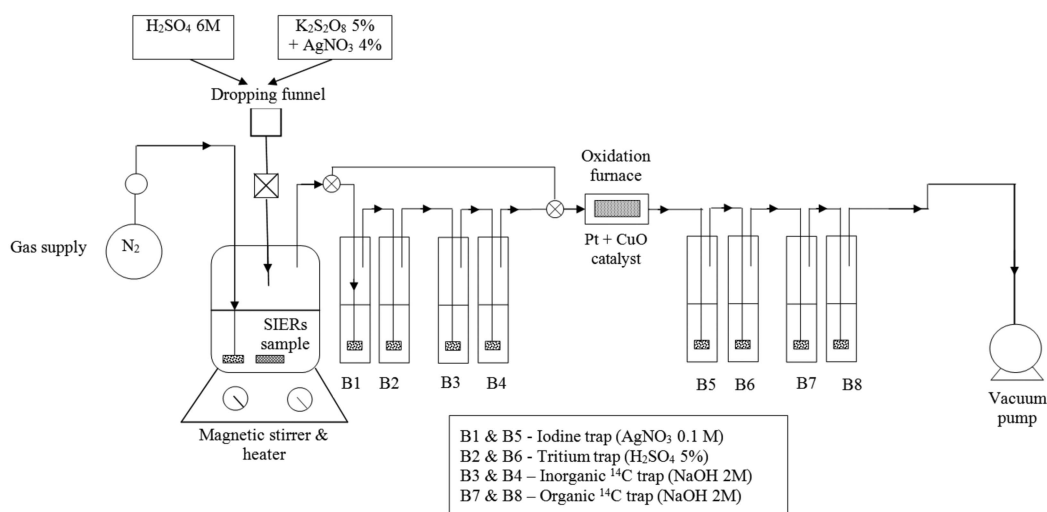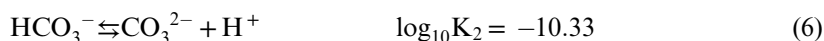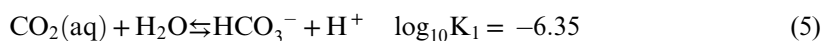

Figure 1   Experimental setup for separation of inorganic and organic [14]C.

funnel inlets and one for gas outlet) was used as reaction vessel and a tap-water cooling loop, made of copper tubing that fits the outer side of the Erlenmeyer flask ensured the vapor condensation. The reaction vessel was placed on a heater with magnetic stirring.

To ensure that no gases escape from the system, all dissolution and wet oxidation experiments were carried out at 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 (controlled by a flow meter).

Since SIERs could contain, besides ^{14}C, also tritium, iodine, and other beta emitters that interfere with ^{14}C measurement by LSC, the gas washing lines consist of iodine traps, placed both before and after the catalytic furnace, with silver nitrate ($AgNO_3$), slightly acidic trap with sulphuric acid (5% H_2SO_4) for tritium and other potential interfering radionuclides and four alkaline traps (two placed before the catalytic furnace and two after it) with 2M sodium hydroxide (NaOH).
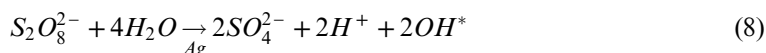
The possible inorganic ^{14}C species in equilibrium are described by the following equilibria (Guillaumont et al. 2003):
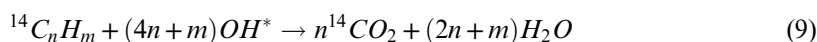
$$CO_2(g) \leftrightharpoons CO_2(aq) \qquad\qquad \log_{10}k_h = -1.47 \tag{4}$$

$$CO_2(aq) + H_2O \leftrightharpoons HCO_3^- + H^+ \quad \log_{10}K_1 = -6.35 \tag{5}$$

$$HCO_3^- \leftrightharpoons CO_3^{2-} + H^+ \qquad\qquad \log_{10}K_2 = -10.33 \tag{6}$$

Carbonates CO_3^{2-}, bicarbonates HCO_3^-, and dissolved $CO_2(aq)$ equilibria can be easily shifted by weak acids towards gaseous carbon dioxide. The inorganic ^{14}C is released during an acid stripping step resulting mainly in the release of $^{14}CO_2$ and the gases are carried by the carrier gas through the first gas washing line (Figure 1). If any ^{14}C is released as ^{14}CO or other organic molecules, the flow passes through the scrubbing bottles of the first gas washing line, and further through the catalytic furnace, where ^{14}CO and other ^{14}C-bearing organic molecules are oxidized to $^{14}CO_2$, and are 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-way valves placed before the first scrubbing bottle and the fourth one.

Since organic compounds have higher bounding energies between atoms, they are decomposed by strong oxidants such as potassium persulphate ($K_2S_2O_8$). The presence of a catalyzer such as silver nitrate ($AgNO_3$) enhances the decomposition of the organic compounds and also the iodine precipitation as AgI. 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-labeled organic compounds decomposition is based on the $OH^{(*)}$ radicals and can be expressed by the following equations (Ahn et al. 2013):

$$K_2S_2O_8 \xrightarrow{H_2o} 2K^+ + S_2O_8^{2-} \tag{7}$$

$$S_2O_8^{2-} + 4H_2O \underset{Ag}{\rightarrow} 2SO_4^{2-} + 2H^+ + 2OH^* \tag{8}$$

$$^{14}C_nH_m + (4n+m)OH^* \rightarrow n^{14}CO_2 + (2n+m)H_2O \qquad (9)$$

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 carrier gas through a catalytic furnace where it is oxidized to CO_2, which is afterwards absorbed in the scrubbing bottles of the second gas washing line (Figure 1).

The ^{14}C activity in the alkaline traps, as well as the ^{3}H activity in solutions sampled from the acid scrubbing bottles, was measured by LSC. 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 1:10. All samples were kept in darkness overnight before their counting to allow for the chemiluminescence decay.

Aliquots from the reaction vessel solution, as well as from all scrubbing bottles were sampled for gamma measurements using an HPGe ORTEC detector and digiDart analyzer for spectra acquisition and Gamma Vision software for radionuclides quantification. The spectrometer was calibrated in energy and efficiency using a standard liquid source containing ^{60}Co, ^{137}Cs, ^{241}Am, ^{152}Eu in 20 mL glass vials and the same geometry was used for all gamma measurements. Depending on the radioactivity content, each sample was counted for more than 4 hours.

^{14}C Desorption in Alkaline Conditions

Investigations of the SIERs' behavior in alkaline solution (NaOH 0.1 M, with pH ~ 13), as a proxy to cementitious conditions, were carried out by means of desorption tests on two sub-samples from Cernavoda SIERs. Two parallel tests (Test #1 and Test #2) were performed with 0.4 g of SIERs in contact with 40 mL of NaOH 0.1 M (liquid to solid ratio of 0.01 g.mL^{-1}), in borosilicate glass bottles with polyketone (PK) lids adapted to allow N_2 introduction in the desorption vessels and outgas washing through the two gas washing lines of the experimental setup presented in Figure 1. To assess the inorganic and organic ^{14}C release in gas phase during desorption tests, scrubbing bottles with smaller volume were used as alkaline traps: two with 3 mL of NaOH 2M (B3 and B7) and two with 15 mL NaOH 2M (B4 and B8).

Desorption tests were performed at room temperature (23 ± 3°C) in semi-dynamic conditions: 5 mL of desorption solution was sampled at each time step, and 5 mL of fresh NaOH was added. Desorption 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 desorption solution, at each sampling time, N_2 gas was purged in the space above the liquid level and outgases were washed through the gas bubblers. 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.

The inorganic and organic ^{14}C measurements in desorption solutions sampled during the tests were achieved using a similar procedure as that described for ^{14}C speciation measurement in SIERs.

RESULTS AND DISCUSSION

Total ^{14}C Measurements

To optimize the combustion method described above for total ^{14}C measurements, preliminary tests were carried out in controlled conditions using samples of ion exchange resin (IRN 150, similar with the mixed bed resin used in the purification circuits of Cernavoda NPP) labeled with the radionuclides of interest: ^{14}C (inorganic form as sodium carbonate/bicarbonate, and organic form as sodium acetate), ^{3}H, ^{60}Co, ^{137}Cs, ^{241}Am, and ^{152}Eu. By these tests, recovery yields, reproducibility of the results, and memory effect of the methods were evaluated. After these preliminary combustion tests, it was concluded that the complete resin combustion is achieved within 3 minutes for 0.15 g of resin mixed with 0.5 mL of combustade (an agent that enhance the combustion process).

The ^{14}C recovery obtained in these combustion tests was ranging between 93.8% and 99.9%, with an average of 97.5% and standard deviation of 1.24, proving the good reproducibility of the results. The memory effect was less than 0.04% and no gamma emitters were identified either in the counting vial for ^{14}C measurement or in the ^{3}H one.

Before analyzing the spent resins by combustion, a mass of SIERs sample received from Cernavoda was filtered to remove the excess of water. After filtration, the water content of the resin sample was 60.10% (calculated based on mass loss at 105°C, using a thermo balance). From this sample, 5 subsamples of around 0.15 g were prepared for total ^{14}C measurement by combustion and other 5 subsamples were used for inorganic and organic ^{14}C measurements by acid stripping/wet oxidation method. The values obtained for total ^{14}C specific activity in the analyzed SIERs samples are reported in Table 1. After combustion, no other beta-gamma emitters were identified in the ^{14}C vials.

The experimental results obtained for these samples indicate that the SIERs sample transferred from Cernavoda NPP has a ^{14}C content of 36.5kBq/g, corresponding to around 7 Ci/m^3 (assuming a bulk density of 0.71 g/mL for wet resin). This activity is lower than the reported values for MOD SIERs and more closed to the values reported for PHTS resins (Miller et al. 1997), but as it was mentioned earlier the available SIERs sample is a mixture of resin beads collected during maintenance activities and it is not representative for the SIERs generated in MOD or PHTS. The total ^{14}C was measured to confirm the recovery of the method used for ^{14}C speciation measurements rather than to have representative total ^{14}C content in SIERs generated at Cernavoda NPP.

Table 1   The total ^{14}C content in Cernavoda SIERs.

Sample ID	SIERs mass* (g)	^{14}C activity (Bq/g)
CANDU 1	0.149	3.82 10^4
CANDU 2	0.149	3.38 10^4
CANDU 3	0.154	3.91 10^4
CANDU 4	0.153	3.65 10^4
CANDU 5	0.152	3.48 10^4
Average		(3.65 ± 0.22) 10^4

*Wet mass.

^{14}C Speciation Measurements

To optimize the experimental conditions and chemicals used for inorganic and organic ^{14}C measurements, a series of acid stripping/wet oxidation tests were carried out in controlled conditions, using liquid solutions with known activities for the radionuclides of interest (^{14}C in inorganic form as sodium carbonate/bicarbonate and organic forms as sodium acetate and lauric acid, ^{3}H, ^{129}I, ^{60}Co, ^{137}Cs, ^{241}Am and ^{152}Eu) as well as ion exchange resin labeled with the same radionuclides.

By these tests the ^{14}C recovery, the reproducibility of the results and the efficiency of the acid stripping/wet oxidation method to distinguish between inorganic and organic ^{14}C species were evaluated. The results show that by this analytical method good recovery and efficient purification are obtained:

- inorganic ^{14}C recovery: between 95% and 99%, with an average value of 97% and standard deviation of 1.46;

- organic ^{14}C recovery: between 94% and 98%, with an average value of 96% and standard deviation of 1.55;

- no other emitters were identified in the solutions sampled from alkaline gas washing bottles.

An average memory effect of less than 1% was observed (no washing step was performed between the recovery step and the memory one).

To account for the uncertainty associated to this analytical method, six identical tests were carried out using ion exchange resin (IRN 150) labeled with the above-mentioned radionuclides. The standard deviation of the results of these tests was less than 15%, proving the good reproducibility of the results. The experimental conditions chosen for the inorganic and organic ^{14}C measurement in CANDU SIERs are presented in Table 2.

From the same filtered SIERs prepared for total ^{14}C measurement, five subsamples of 1 g each were used to measure the inorganic and organic ^{14}C content in experimental conditions summarized in Table 2. Both filtered spent resin samples and the excess water were analyzed. The experimental results obtained for inorganic and organic ^{14}C are presented in Table 3.

The total ^{14}C content in the analyzed SIERs samples are quite close to the value determined by combustion, demonstrating the good recovery of the acid stripping/wet oxidation method. The analysis of the excess water shows that it contains no inorganic ^{14}C and only 4.42 Bq/mL of organic ^{14}C (representing only 0.01% from the ^{14}C on the spent resin).

Table 2   Parameters for inorganic and organic ^{14}C measurement in CANDU SIERs.

Resin mass	1 g
Mass of the carbon carrier	0.2 g
Carrier gas flow	60–80 mL/min
Stripping acid	20 mL of H_2SO_4 6M
Oxidation reagents	10 mL $K_2S_2O_8$ 5% + 4 mL $AgNO_3$ 4%
Alkaline trapping solution	50 mL of NaOH 2M
Gas flushing during acid stripping	1 hr
No. of wet oxidation cycles	3
Gas flushing during wet oxidation	1 hr / each cycle

Table 3 Inorganic and organic ^{14}C content in Cernavoda SIERs.

SIERs #	Bq/g in wet SIERs ($\omega = 60.10\%$)			% from the total ^{14}C	
	Inorganic ^{14}C	Organic ^{14}C	Total ^{14}C	Inorganic ^{14}C	Organic ^{14}C
CANDU 6	$(2.99 \pm 0.59)\ 10^4$	$(3.44 \pm 0.69)\ 10^3$	$(3.33 \pm 0.66)\ 10^4$	89.68 ± 17.94	10.32 ± 2.06
CANDU 7	$(3.04 \pm 0.61)\ 10^4$	$(1.88 \pm 0.37)\ 10^3$	$(3.23 \pm 0.65)\ 10^4$	94.18 ± 18.84	5.82 ± 1.16
CANDU 8	$(3.27 \pm 0.65)\ 10^4$	$(2.04 \pm 0.41)\ 10^3$	$(3.47 \pm 0.69)\ 10^4$	94.12 ± 18.82	5.88 ± 1.18
CANDU 9	$(3.25 \pm 0.65)\ 10^4$	$(2.00 \pm 0.44)\ 10^3$	$(3.45 \pm 0.69)\ 10^4$	94.19 ± 18.84	5.81 ± 1.16
CANDU 10	$(3.17 \pm 0.63)\ 10^4$	$(2.18 \pm 0.46)\ 10^3$	$(3.39 \pm 0.68)\ 10^4$	93.56 ± 18.71	6.44 ± 1.29
Weighted average	$(3.14 \pm 0.13)\ 10^4$	$(2.13 \pm 0.50)\ 10^3$	$(3.37 \pm 0.10)\ 10^4$	93.08 ± 2.01	6.30 ± 1.46

Regarding the partition between mineral and organic species, the results obtained show that the ^{14}C in the analyzed SIERs is predominantly in inorganic form and only less than 7% from the measured ^{14}C is present in organic form. Since the main source of the analyzed SIERs is the moderator purification system, and in the CANDU moderator the major chemical form of ^{14}C is as bicarbonate, the chemical form of ^{14}C absorbed on the resin is also mostly bicarbonate ($H^{14}CO_3^-$).

Even though these results were not obtained on a representative SIER sample for the spent resins that will be disposed of (either in a surface disposal facility or in a geological one), data obtained are similar to those reported by Park et. al. (2008), who found that more than 92% of the ^{14}C activity concentration is as inorganic ^{14}C.

^{14}C release under Alkaline Conditions

Desorption experiments with Cernavoda SIERs demonstrated that the highest fraction of ^{14}C is released as dissolved species, presumably as carbonate. Equilibrium in the solution is reached within the first 2 days (Figure 2), whereas the equilibrium level of inorganic ^{14}C released into the gas phase was instantly achieved and did not change until the end of experiment (ca. 200 days).

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 4. As can be seen, 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.

Based on these data, cumulative ^{14}C release, as well as the release rate, were calculated and are presented in Figure 3.

From the total ^{14}C present in the SIERs sample used for desorption test, around 7% was released as inorganic ^{14}C in the gas phase, around 79% as dissolved species and 8% was found as residual in the SIERs sample after desorption. Around 94% of ^{14}C content in the SIER sample was recovered at the end of desorption test. The remaining ca. 6% was not found either as dissolved species or inorganic gas species, or as residual on the SIER sample after desorption test, and could represent an unaccounted for ^{14}C fraction of instantly released $^{14}CO_2$. No organic ^{14}C released in gas phase was measured during these tests. Gaseous releases from SIERs in cementitious conditions are caused by a transient/permanent decrease in the pH of the
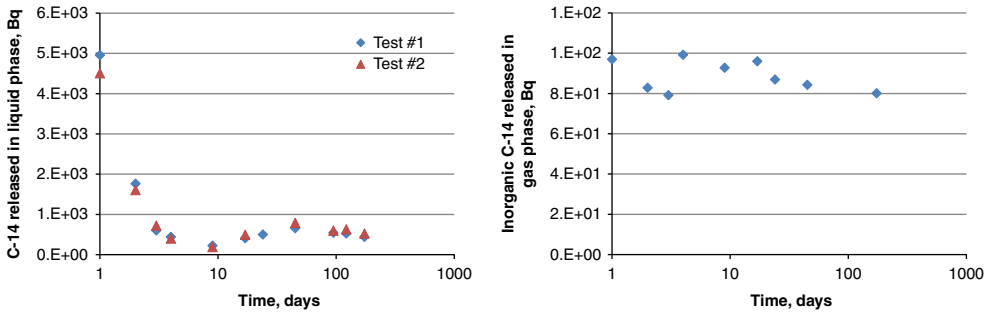
Figure 2   The kinetic of ^{14}C released into the solution (left) and gas phase (right).

Table 4   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%)	2.71×10^2 (8.09%)	80.04
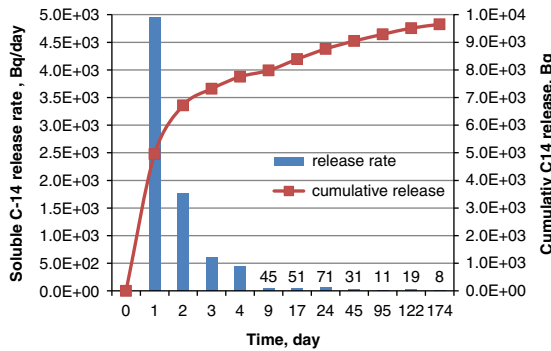
Figure 3   Differential and cumulative release of ^{14}C in liquid phase.

alkaline solution, most probably due to H^+ ions released during the ion-exchange reaction of SIERs and alkaline solution (Bucur et al. 2017).

These results should nevertheless be further mitigated in view of the composition of actual cement pore water, which contains high concentration of dissolved calcium, and the possible precipitation of calcite (Berner 1992; Pointeau et al. 2008).

In the Cernavoda spent ion exchange resins, the major part of ^{14}C is retained as inorganic form, in complete agreement with the literature data, and only less than 7% from the measured ^{14}C on a SIERs sample is present inorganic form.

The total ^{14}C content obtained by acid stripping/wet oxidation is quite close to the value determined by combustion, demonstrating the good recovery of the acid stripping/wet oxidation method. Moreover, the acid stripping/wet oxidation method allows measurement of other radionuclides in SIERs (i.e. tritium, iodine, and gamma emitters) and consequently could be used in addition to other separation techniques for a complete SIERs radiochemical characterization.

In alkaline conditions, ^{14}C is released from SIERs both as gaseous and soluble species, predominantly as inorganic soluble species (~79%) and only a small fraction (~7%) as inorganic gaseous species. But in real conditions, SIERs will be conditioned in a suitable matrix (i.e. cement or polymer) and the percent of ^{14}C released as soluble species shall be much lower. Furthermore, the presence of dissolved Ca in cement pore water will favor the ^{14}C precipitation and consequently the decrease of dissolved ^{14}C released from the disposal area.

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