14C IN RADIOACTIVE WASTE FOR DECOMMISSIONING OF THE IGNAلينA NUCLEAR POWER PLANT

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ABSTRACT. Radiocarbon is one of the most significant radionuclides affecting the safety margins of near-surface repositories for the disposal of low- and intermediate-level, short-lived radioactive waste, arising from the operation and decommissioning of nuclear power plants (NPPs). One of the goals of the present study was to characterize radioactive waste from Ignalina NPP (Lithuania) (storage tanks TW18B01 and TW11B03) from the spent ion-exchange resins/perlite stream to determine the 14C-specific activity of inorganic and organic carbon compounds. The approach applied is based on classical radiochemical separation methods, including acid-stripping techniques and wet oxidation with subsequent catalytic combustion. The suitability of the method for 14C-specific activity determination in ion-exchange resin samples with a minimum detectable activity of 0.5 Bq/g by liquid scintillation counting (LSC) was demonstrated. The extraction efficiency of inorganic and organic carbon compounds based on model samples with known 14C activity was estimated. The fraction of 14C associated with organic compounds ranged from 42% to 63% for storage tank TW18B01 and from 30% to 63% for storage tank TW11B03. The specific activity of inorganic 14C was estimated as 12.6 Bq/g with a relative standard deviation (RSD) of 29% for storage tank TW18B01, and 177.5 Bq/g with a RSD of 35% for storage tank TW11B03. Based on volume and density data, the total 14C activity for radioactive waste stored in tanks TW18B01 and TW11B03 was estimated as 3.59E + 10 Bq (±32%) and 4.15E + 11 Bq (±28%), respectively.

INTRODUCTION

Radiocarbon activity and its variation in the environment depend on many 14C sources, including: cosmogenic production (Libby 1946; Raen et al. 1968), emissions via the Suess effect (Fairhall and Young 1970), numerous atmospheric nuclear weapons tests, and CO2 uptake by the oceans and biosphere (Hertelendi and Csongor 1982). 14C is also artificially produced in all types of nuclear reactors by neutron-induced reactions on isotopes of carbon, nitrogen, and oxygen present in the fuel, cladding, coolant, moderator, and structural materials of reactors (NCRP 1985; IAEA 2004). A fraction of the generated 14C is released continuously during normal operation of nuclear power plants (NPPs), mainly in 2 chemical forms: oxidized, i.e. carbon dioxide (CO2), and reduced, which is mostly in the form of CH4 (Levin et al. 1988). For all types of reactors, except pressurized-water reactors (PWRs), most of the gaseous releases of 14C are in the form of 14CO2 (IAEA 2004).

The 2 reactor units of the Ignalina NPP (INPP) in Lithuania were put into operation in December 1983 and August 1987, respectively. Both units, Unit 1 and Unit 2, are RBMK-1500 reactors (Almenas et al. 1998). The RBMK reactor is a graphite-moderated, boiling-water channel-type reactor. Its principle method of electricity generation is the same as for boiling-water reactors (BWRs). Under the obligations of the European Union Accession Treaty, Lithuania was required to shut down units 1 and 2 of the INPP and to decommission them as soon as possible. Unit 1 was shut down in December 2004 and Unit 2 in December 2009.

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In 2002, the government of Lithuania approved the adoption of the “immediate dismantling” strategy for the decommissioning of INPP. A key component of this decommissioning strategy is to dispose of operating and decommissioning waste in a near-surface repository (NSR). In Lithuania, the intermediate-level radioactive waste (ILRW) produced during operation and decommissioning of the INPP mainly consists of the ion-exchange resins, perlite, and sediments accumulated from 1) the purification system of the circulating water and 2) the bottom of the sewage water treatment evaporator (LEI 2010). Spent ion-exchange resins comprise the most important inventory of $^{14}\text{C}$ (LEI 2010).

$^{14}\text{C}$ is considered to be one of the more difficult-to-measure nuclides (pure beta emitters) due to the presence of other radionuclides in a sample. $^{14}\text{C}$ is rarely measured in the process media of nuclear reactors on a routine basis (even in gaseous releases from nuclear plants), even though equipment for monitoring $^{14}\text{C}$ in gaseous releases is commercially available. However, releases of gaseous $^{14}\text{C}$ from INPP to the environment during normal operations resulted in the largest dose fraction when compared to all other radionuclides from gaseous releases (Nedveckaite et al. 2000).

Based on the scaling factor method, a preliminary inventory of $^{14}\text{C}$ for NSR with capacity for disposal of approximately 100,000 m$^3$ of waste was evaluated to be $1.43 \times 10^{13}$ Bq (Lukauskas et al. 2006; Plukis et al. 2008). Similar $^{14}\text{C}$ inventory ratings were evaluated for NSRs in other countries: Japan, Rokkasho-Mura disposal facility, first 40,000 m$^3$, maximal inventory of $3.37 \times 10^{12}$; Spain, El Cabril disposal facility, maximum permissible activity of $2.00 \times 10^{13}$ Bq (IAEA 2004).

Because $^{14}\text{C}$ is a long-lived and mobile radionuclide (specifically in its organic form) in the environment, and due to its large inventory in INPP NSR, our main focus was to quantitatively evaluate the $^{14}\text{C}$ activity concentrations (activities) in both the organic and inorganic forms in the spent ion-exchange resins and perlite mixture. The aim of the study was to demonstrate good applicability of the carbon separation method for characterization of the unconditioned spent ion-exchange resins. The basic principles of $^{14}\text{C}$ extraction from liquid and solid samples are reviewed in Salonen and Snellman (1985), Veres et al. (1995), and Magnusson (2007). Classical radiochemical separation methods, including acid-stripping techniques and wet oxidation with subsequent catalytic combustion, were used for extraction of organic and inorganic fractions of $^{14}\text{C}$ in a single sample as described in Magnusson and Stenström (2005). In order to evaluate radiochemical recovery of $^{14}\text{C}$ in separation procedures, model samples with known activity of $^{14}\text{C}$ tracers in inorganic and organic forms were produced from inactive ion-exchange resins. The model samples were decomposed by the same methods as active samples of spent ion-exchange resins and the perlite mixture from INPP. The $^{14}\text{C}$ activity of model samples and waste samples was measured by LSC in the same manner.

**EXPERIMENTAL**

**Materials**

A significant part of the spent ion-exchange resins and perlite mixture originated from the operation of the circulating water-purification system are stored in radioactive waste storage tanks TW18B01 and TW11B03 of INPP. These ion-exchange resins consist of a cationite and anionite mixture. Cationite is a styrene and divinylbenzene copolymer, able to exchange cations in water solutions. Anionite is produced by chloromethylation of co-polymer with divinylbenzene with further amination with trimethylamine. Perlite has been used at INPP for water purification and is included in the waste concentrates.

The radioactive waste from the resin/perlite treatment stream is mixed with Portland cement and the homogenous mixture is filled into 200-L drums at the cementation facility of the INPP in accordance with the established procedure. The waste is treated according to the following proportions:
the amount of granulated and powder-like ion-exchange resins and filter-perlite was within the range of 14.3–22.5% of dry mass; the content of salts, the amount of Portland cement, and additive of bentonite were within the range of 1.7–2.3% (dry mass), from 42% to 54% (dry mass) and from 4.2% to 5.4% (dry mass), respectively. The amount of water was within the range 21.6–31.8% (mass). Bentonite clay from the Chakasko deposit in Russia was used as an additive. Portland cement CEM II/A-L 42.5N (MA) was used as waste binder and was applied in compliance with European Standard EN 197-1.

Filling of waste storage tank TW18B01 began at the beginning of INPP’s operation and was finished in 1999. For a few years, it had the status of temporary storage and since March 2006, the radioactive waste has begun to solidify at the cementation facility. The waste from this storage tank was taken for analysis on 3 November 2011 from the depth at which wastes were stored approximately in 1990, according to operational records of INPP staff.

At present, the new spent ion-exchange resins from INPP are stored in tank TW11B03. Tank TW11B03 is not prepared for the final mixing and cementation of wastes. The wastes for analysis were taken from this tank on 14 November 2011 from the depth at which wastes were stored approximately in 2006, according to INPP operational staff records.

The samples of ion-exchange resins attributed to storage tank TW11B03 were taken for analysis with a manual sampler. The samples of ion-exchange resins attributed to storage tank TW18B01 from the technological line before cementation, and then the cemented compound sample before 200-L drum filling, were also taken for analysis. According to the cementation protocol, the contents of the investigated waste-storage drum attributed to tank TW18B01 were 159.4 kg of raw waste and 149.0 kg of cement and bentonite. Taking into account the mass of the waste package and using a stationary gamma-spectrometer station (in situ) by operator staff measuring activities of gamma-emitting radionuclides in a drum, the specific activities were $3.37 \times 10^3$ ($\pm 74$), $1.79 \times 10^2$ ($\pm 12$), and $1.44 \times 10^4$ ($\pm 520$) Bq/g for $^{60}$Co, $^{134}$Cs, and $^{137}$Cs, respectively.

For comparison, 1 sample of cemented spent resins from the same waste package before $^{14}$C extraction was analyzed at the INPP laboratory using a gamma spectrometer. There was a good agreement between the results of both gamma in situ and laboratory tests. These results were used for the initial prediction of $^{14}$C activity by applying the scaling factor method (Plukis et al. 2008). The predicted activities of $^{14}$C$_{\text{total}}$ were 240 Bq/g for cemented waste and 490 Bq/g for initial raw waste attributed to the particular drum based on this model.

A standard $^{14}$C solution in the form of Na$_2$CO$_3$ (chemical concentrations 5 g/L, specific activity 199.2 Bq/g ($\pm 2\%$), standard type ERX, Czech Metrology Institute, No 111011-531012, reporting date 15 November 2011) was used for calculating $^{14}$C counting efficiency. This solution was also used for estimating the extraction efficiency of $^{14}$C for the inorganic fraction. A solution of organic $^{14}$C was used for estimating the extraction efficiency of $^{14}$C in the organic form. The specific activity of $^{14}$C in this solution was 166.5 Bq/g ($\pm 1.5\%$). This was prepared from the initial $^{14}$C solid organic compound ([U-$^{14}$C]-Sucrose, C$_{12}$H$_{22}$O$_{11}$, molecular weight 366.51, activity 1.67 kBq [$\pm 1\%$], reporting date August 2009, Amersham International No 1210-123), which can be related to NIST SRM No 4222.C.

Mixtures of simulated ion-exchange resin matrix, containing known amounts of inorganic and organic $^{14}$C, were produced at the laboratory for a recovery test with raw resins. The activity of the initial solution containing a known amount of introduced $^{14}$C was 245 Bq/g ($\pm 1.8\%$) and 2400 Bq/g ($\pm 5\%$) for Na$_2$CO$_3$ and C$_6$H$_{12}$O$_6$, respectively.
Radiochemical Carbon Extraction Experiment

The most commonly applied physico-chemical processes leading to converting the carbon compounds to CO₂ are either combustion or acidification. The carbon extraction method is based on acid-stripping techniques and wet oxidation with subsequent catalytic combustion (Salonen and Snellman 1985; Magnusson and Stenström 2005; Hou 2005; Magnusson 2007; Motiejunas et al. 2012) with different modifications. For the majority of spent ion-exchange resins and perlite mixture samples, the combination of acid stripping and wet oxidation allowed separate extractions of the organic and inorganic carbon from a single sample (Figure 1).

The fraction of inorganic carbon was obtained by magnetic stirring of 1 g of the sample in 20 mL of H₂SO₄ (6M) during 1 hr without heating (route C_{inorg}, Figure 1). CO₂ containing ¹⁴C was absorbed in a pair of alkali gas washing traps (absorbers), each filled with 100 mL of 2M NaOH. The fraction of organic carbon was extracted from the remaining compounds by adding a strong oxidant (20 mL 5% K₂S₂O₈ and 4 mL 4% AgNO₃) and magnetic stirring for 1 hr at 100–120 °C (route C_{org}, Figure 1). The procedure was repeated 3 times for the organic fraction. Released CO₂ was collected in the second pair of absorbers. A catalytic furnace with CuO and Pt (at 750 °C) was introduced between the 2 sets of absorbers in order to ensure the oxidation of reduced carbon compounds. A more detailed description is presented in Magnusson (2007).

The remaining fraction of inorganic ¹⁴C (from the carbonates and CO₂) in the first pair of absorbers was separated from the fraction of organic ¹⁴C (from hydrocarbons, organic acids, and other organic compounds), which was collected in the second pair of absorbers. Tritium and other contaminants were trapped in a flask with slightly acidified water located behind the reaction vessel. Carbon sorption tests were performed with 4 g of raw ion-exchange resin samples and 4-mL solutions of ¹⁴C in the organic and inorganic forms, respectively. The solutions were filtered after 2 days’ exposure and carbon activity for each filtrate was measured.

Measurements

A liquid scintillation analyzer Tri-Carb® 3170TR/SL was used to measure the activities of extracted ¹⁴C. Four mL of solution samples were taken from the ¹⁴C absorbers with 100 mL of 2M NaOH.
Some 16 mL of scintillation cocktail Optiphase HiSafe® 3 was added to each solution sample. The resulting aqueous solution (20 mL) gives an average counting efficiency of 93.9 ± 0.9% for the $^{14}$C counting region of 4–105 keV. A 20-min counting time was sufficient to achieve negligible radio-metric uncertainty.

The impact of the quenching effect on the results has been evaluated using the spectral index of sample (SIS) and the transformed spectral index of external standard (tSIE) (Passo and Kuko 1994). tSIE more accurately expresses the quenching effect in the sample, which is derived using the external $^{133}$Ba source. $^{14}$C activity in the sample can even be determined when tSIE varies from 10 (heavily quenched sample) to 1000 (unquenched sample). The tSIE values for the samples of the analyzed ion-exchange resins, for the background and blank samples and $^{14}$C standard, vary within a very narrow interval (Figure 2). For this reason, the $^{14}$C counting efficiency for all samples was determined directly from the data of background and $^{14}$C standard counts per minute (CPM) without applying quenching correction because this would not affect the results.

### RESULTS AND DISCUSSION

Before recovery tests of $^{14}$C, sorption tests on raw ion-exchange resin samples with introduced organic and inorganic $^{14}$C were implemented. Approximately 7% and 20% of the initial amount of inorganic and organic $^{14}$C, respectively, were found in the solution after exposition. The results indicate good retention properties of the raw ion-exchange resins mixture.

Thirteen raw ion-exchange resin samples with added $^{14}$C in Na$_2^{14}$CO$_3$, [U-$^{14}$C]-sucrose forms or a mixture of both were analyzed for a recovery test, and ~40 determinations of $^{14}$C activity were carried out using the LSC method. Nine recovery tests were performed and the recovery efficiency of inorganic carbon compounds was obtained at 93%, with one of the organic compounds at 85% on average (Table 1). For the obtained recovery rate, a minimum detectable activity of $^{14}$C using the LSC system for ion-exchange resin samples can easily be reached at the level of 0.1–0.5 Bq/g. The observed amount of organic $^{14}$C recovered was lower in comparison to the amount of inorganic $^{14}$C. This could be due to the effect of bacterial growth, which can potentially convert some organic carbon into inorganic forms, or due to the production of anions from microbes, which can displace the $^{14}$C from resins (Yim and Caron 2006).

Five subsamples each from 2 samples of the spent ion-exchange resins/perlite mixture from storage tanks TW18B01 and TW11B03 of INPP were investigated at the INPP laboratory using the system setup presented here (Figure 1). Approximately 40 determinations of $^{14}$C-specific activity were done. Full and reliable experiments were performed with 3 subsamples taken from storage tank...
TW18B01 (Sample IDs 2, 3, and 5 in Table 2) and with 4 subsamples taken from storage tank TW11B03 (Sample IDs 1A, 7, 9, and 10 in Table 3).

Table 1 The results of recovery tests of $^{14}$C ($^{14}$C in Na$_2^{14}$CO$_3$ and [U-$^{14}$C]-sucrose) with acid stripping and wet oxidation and CO$_2$ absorbing in alkali gas washing absorbers (inactive ion-exchange resins treated).$^a$

<table>
<thead>
<tr>
<th>Weight (g)</th>
<th>$^{14}$C added</th>
<th>$^{14}$C inorganic (Bq)</th>
<th>$^{14}$C organic (Bq)</th>
<th>$^{14}$C recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Form</td>
<td>Bq</td>
<td>Mean ± SD</td>
<td>Mean ± SD</td>
</tr>
<tr>
<td>0.9074</td>
<td>Na$_2$CO$_3$</td>
<td>195.2</td>
<td>188.1 ± 9.4</td>
<td>&lt;</td>
</tr>
<tr>
<td>1.2150</td>
<td>Na$_2$CO$_3$</td>
<td>167.9</td>
<td>146.5 ± 7.3</td>
<td>&lt;</td>
</tr>
<tr>
<td>1.2650</td>
<td>Organic</td>
<td>168.1</td>
<td>&lt;</td>
<td>141.0 ± 7.0</td>
</tr>
<tr>
<td>1.0869</td>
<td>Na$_2$CO$_3$ and organic</td>
<td>103.0 and 149.8</td>
<td>91.2 ± 4.6</td>
<td>131.3 ± 6.6</td>
</tr>
<tr>
<td>1.1025</td>
<td>Organic</td>
<td>77.2</td>
<td>&lt;</td>
<td>67.1 ± 3.4</td>
</tr>
<tr>
<td>1.0060</td>
<td>Na$_2$CO$_3$</td>
<td>105.1</td>
<td>97.4 ± 4.9</td>
<td>&lt;</td>
</tr>
<tr>
<td>1.0050</td>
<td>Organic</td>
<td>48.2</td>
<td>&lt;</td>
<td>41.4 ± 2.1</td>
</tr>
<tr>
<td>1.2805</td>
<td>Na$_2$CO$_3$</td>
<td>86.0</td>
<td>82.1 ± 4.1</td>
<td>&lt;</td>
</tr>
<tr>
<td>1.2807</td>
<td>Na$_2$CO$_3$ and organic</td>
<td>118.8 and 70.0</td>
<td>114.5 ± 5.7</td>
<td>61.8 ± 3.1</td>
</tr>
</tbody>
</table>

$^a$< does not differ from blank samples.

Table 2 Analytical results of spent ion-exchange resins from storage tank TW18B01.

<table>
<thead>
<tr>
<th>Sample nr</th>
<th>Weight (g)</th>
<th>$^{14}$C$_{\text{inorg}}$ (Bq/g) Mean ± SD</th>
<th>$^{14}$C$_{\text{org}}$ (Bq/g) Mean ± SD</th>
<th>$^{14}$C$_{\Sigma}$ (Bq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.132</td>
<td>11.2 ± 0.6</td>
<td>18.9 ± 0.8</td>
<td>30.1</td>
</tr>
<tr>
<td>2</td>
<td>1.125</td>
<td>16.8 ± 0.8</td>
<td>12.2 ± 0.6</td>
<td>29.0</td>
</tr>
<tr>
<td>5</td>
<td>1.185</td>
<td>9.8 ± 0.6</td>
<td>9.6 ± 0.6</td>
<td>19.0</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>12.6 ± 0.3</td>
<td>13.6 ± 0.3</td>
<td>26.0</td>
</tr>
<tr>
<td>RSD (%)</td>
<td></td>
<td>29</td>
<td>35</td>
<td>23</td>
</tr>
</tbody>
</table>

Table 3 Analytical results of spent ion-exchange resins from storage tank TW11B03.

<table>
<thead>
<tr>
<th>Sample nr</th>
<th>Weight (g)</th>
<th>$^{14}$C$_{\text{inorg}}$ (Bq/g) Mean ± SD</th>
<th>$^{14}$C$_{\text{org}}$ (Bq/g) Mean ± SD</th>
<th>$^{14}$C$_{\Sigma}$ (Bq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>0.503</td>
<td>139.3 ± 3.2</td>
<td>77.7 ± 2.2</td>
<td>217</td>
</tr>
<tr>
<td>7</td>
<td>0.918</td>
<td>202.7 ± 2.7</td>
<td>110.9 ± 2.0</td>
<td>314</td>
</tr>
<tr>
<td>9</td>
<td>0.875</td>
<td>115.1 ± 2.1</td>
<td>196.3 ± 2.6</td>
<td>311</td>
</tr>
<tr>
<td>10</td>
<td>0.732</td>
<td>252.9 ± 3.4</td>
<td>109.4 ± 2.2</td>
<td>362</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td>177.5 ± 12.6</td>
<td>123.6 ± 4.1</td>
<td>301.0</td>
</tr>
<tr>
<td>RSD (%)</td>
<td></td>
<td>35</td>
<td>41</td>
<td>20</td>
</tr>
</tbody>
</table>

The mean value of total $^{14}$C-specific activity is 26 and 301 Bq/g wet weight in the spent ion-exchange resin samples from storage tanks TW18B01 and TW11B03, respectively. The measured levels of $^{14}$C are lower than the expected values derived using the nuclide scaling factor method (Plukis et al. 2008). The significant $^{14}$C activity difference between these samples is due to the time the tanks were filled (TW18B01 starting in 1983, TW11B03 starting in 1996) and the different initial liquid radioactive waste sources.
The fraction of $^{14}$C associated with organic compounds ranged from 42% to 63% for storage tank TW18B01 and from 30% to 63% for storage tank TW11B03. The specific activity of inorganic $^{14}$C was estimated as 12.6 Bq/g with a relative standard deviation (RSD) of 29% for storage tank TW18B01 and 177.5 Bq/g with RSD of 35% for storage tank TW11B03. The specific activity of organic $^{14}$C was estimated at 13.6 Bq/g with RSD of 35% for tank TW18B01 and 123.6 Bq/g with RSD of 41% for tank TW11B03. Based on volume and density data, the total $^{14}$C activity was estimated as $3.59 \times 10^8$ Bq ($\pm 32\%$) and $4.15 \times 10^9$ Bq ($\pm 28\%$) for radioactive waste stored in tanks TW18B01 and TW11B03, respectively.

CONCLUSION

The performed study demonstrates good applicability of the carbon-separation method based on acid stripping and wet oxidation for characterization of unconditioned ion-exchange resins (recovery of inorganic carbon 93%, recovery of organic carbon 85%) from the Ignalina Nuclear Power Plant (INPP). This is the first systematic attempt to measure the content of $^{14}$C associated with different chemical forms in waste from INPP.

The total $^{14}$C-specific activity in the spent ion-exchange resins from radioactive waste storage tanks TW18B01 and TW11B03 of INPP is 26 and 301 Bq/g wet weight, accordingly. The fraction of $^{14}$C associated with organic compounds for both storage tanks is rather variable and was between 42% and 63% for storage tank TW18B01 and 30% to 63% for storage tank TW11B03. The data obtained will be used in future assessments as a basis for realistic estimates of the $^{14}$C inventory in the Lithuanian near-surface repository, as well as to reduce the level of conservatism applied in the safety assessment.

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