Open Chem., 2015; 13: 177–186

RAD2014 & SEERAS

Open Access

Jonas Mažeika*, Galina Lujanienė, Rimantas Petrošius, Nadežda Oryšaka, Sergej Ovčinikov

Preliminary evaluation of ^{14}C and ^{36}Cl in nuclear waste from Ignalina Nuclear Power Plant decommissioning

Abstract: On a first attempt, the determination of ^{14}C and ^{36}Cl activity concentrations in basic operational waste (spent ion-exchange resins and perlite mixture), in decommissioning waste (construction concrete, sand, stainless steel and serpentinite) and irradiated graphite from the Ignalina NPP has been performed. The samples for measurement of the specific activity of ^{14}C and ^{36}Cl were obtained from the selected places, where the highest values of the dose rate and the activity concentrations of gamma emitters were found. The performed study of the total ^{14}C and ^{36}Cl activity concentrations was based on estimated chemical forms of ^{14}C (inorganic and organic compounds) and ^{36}Cl as Cl- ion. The tested methods used in this study were found to be suitable for estimation of activity concentrations of measured radionuclides.

Keywords: ^{14}C, ^{36}Cl, ^{137}Cs, liquid scintillation counting, ion-exchange chromatography

DOI: 10.1515/chem-2015-0014

received February 28, 2014; accepted June 16, 2014.

1 Introduction

The two reactor units of the Ignalina Nuclear Power Plant (INPP), The two reactor units of the Ignalina Nuclear Power Plant (INPP), Unit 1 and Unit 2, were started operating in December 1983 and August 1987, respectively. Entering the European Union Lithuania was obligated to shut down Units 1 and 2 of the INPP and to decommission them as soon as possible. Unit 1 was shut down on December 31, 2004 and Unit 2 on December 31, 2009. The INPP was equipped with RBMK-1500 reactors (RBMK is a Russian acronym for Channelized Large Power Reactor). The ''1500'' refers to the designed electrical power expressed in Megawatts (MW). The designed thermal rating of RBMK-1500 reactors is 4800 MW with the nominal thermal power of 4250 MW, and the nominal electrical power of 1300 MW [1]. The RBMK reactors belong to the thermal neutron reactor category [1]. The graphite is used to moderate (slow down) the fast fission neutrons. This requires a large amount of graphite, so that the graphite stack of the reactor becomes its dominant component.

The expected inventory of future graphite waste is about 3600 tons of irradiated-graphite. Formation of activation products depends on the operational modes, origin and concentration of impurities in the graphite. The core of the reactor is housed in the 25 m deep, 21×21 m cross-section concrete vault. The core volume is dominated by a large cylindrical graphite stack. The stack can be visualized as a vertical cylinder, made up of 2488 graphite columns, constructed from various types of graphite blocks. The columns are made from high purity graphite GR-280 with a density of ~1700 kg m^{-3}. In order to improve heat transfer from the graphite stack, the central segment of the fuel channels is surrounded by the 20 mm high and 11.5 mm thick split GRP-2-125 grade graphite rings. These rings are arranged next to each other in such a manner that one is in contact with the channel, and the other with the graphite stack block. The graphite stack, including its hermetically sealed cavity, is called the sealed reactor space. This space was filled with a circulating helium-nitrogen mixture (about 10% nitrogen). Based on the immediate dismantling strategy, the design for dismantling of process channels and control protection system (CPS) channels is being developed at the INPP. The graphite rings and bushings will be separated and placed into 200-litre drums. The drums will be placed into reinforced concrete protective storage containers for

***Corresponding author: Jonas Mažeika**: Scientific Research Institute Nature Research Centre, Vilnius, 08412, Lithuania,
E-mail: mazeika@opalas.geo.lt
Rimantas Petrošius: Scientific Research Institute Nature Research Centre, Vilnius, 08412, Lithuania
Galina Lujanienė: Scientific Research Institute Nature Research Centre, Vilnius, 02300, Lithuania
Nadežda Oryšaka, Sergej Ovčinikov: Ignalina Nuclear Power Plant, Visaginas municipality, 31500, Lithuania

temporary storage (for the period of up to 50 years) in a Temporary Storage Building.

In 2002, the Government of Lithuania approved the adoption of the ''immediate dismantling'' strategy for decommissioning of both INPP units. A key component of this decommissioning strategy is to dispose low- and intermediate-level, short-lived radioactive waste (LILW), *i.e.*, operating and decommissioning, in a near-surface repository (NSR). One of the significant operating waste streams for disposal, containing highest specific activities of many radionuclides, is spent ion-exchange resins / perlite stream. As potential waste with big volume for NSR disposal a variety of decommissioning waste is considered. However, depending on the radiological characteristics of waste it can be attributed to different disposal options (NSR, landfill-type disposal or geological disposal facilities) or even free release. Based on the previously performed radiological characterization of the reactor building and equipment, several materials, *i.e.*, construction concrete, sand of reactor cylinder, stainless steel of numerous equipment and piping, serpentinite of the top metal structure were selected for further detailed analysis.

Carbon-14 was selected as the first radionuclide of interest. The long-lived (5730±40 years) and mobile in the environment ^{14}C has been recognized as one of the most important nuclides assessing the doses for future human generations arising from the INPP NSR due to its large inventory. Based on the scaling factor method [2,3], a preliminary inventory of ^{14}C for NSR with the capacity for disposal of approximately 100 000 m^3 of waste was evaluated as 1.43×10^{13} Bq. Chlorine-36, a radionuclide long-lived (301,000±2,000 years) and mobile in the environment, was selected as the second choice.

The irradiated-graphite as an exceptional kind of decommissioning waste was assumed to contain ^{14}C and ^{36}Cl as well. The specific activity of irradiated RBMK-1500 graphite evaluated by modeling is mainly determined by the specific activities of ^{14}C, ^{3}H, ^{60}Co, and ^{55}Fe; however, the presence of ^{36}Cl in graphite is also evident [4]. Activated graphite of INPP, of the long-lived ^{14}C is classified at present as the long-lived radioactive waste due to the high activity, up to 5×10^{5} Bq g^{-1} and it is foreseen for temporary storage for up to 50 years with later decision on final disposal options. The presence of other short-lived radionuclides and especially actinides may cause certain short or long term limitations for the packaging of spent graphite waste in the future. Based on calculations of graphite impurities activation, ^{14}C and tritium primarily contribute (3.91×10^{14} Bq and 2.19×10^{14} Bq, respectively) to the total activity of all the irradiated graphite constructions of the reactor [4]. It is the rough upper limit estimate, derived with an assumption that activation products were retained in the graphite.

Because ^{14}C and ^{36}Cl are significant radionuclides affecting the long-term safety margins of the near surface repository, and because the ^{14}C large and ^{36}Cl have uncertain inventory for INPP NSR, our main focus was to quantitatively evaluate the ^{14}C and ^{36}Cl activity concentrations in selected waste streams and materials produced during operation and decommissioning of the INPP. This was done, in order to support radioactive inventory framework for future safety assessments.

The aim of the study was to demonstrate applicability of determination methods of the ^{14}C and ^{36}Cl activity in different samples for characterization of the unconditioned operational and decommissioning waste of the INPP. The basic principles of waste sample decomposition, ^{14}C and ^{36}Cl separation, and purification procedures are reviewed [5-20]. The most common methods of the sample decomposition, including acid digestion, wet oxidation, and catalytic combustion, were used. In order to evaluate the radiochemical recovery of ^{14}C and ^{36}Cl in all separation procedures, model samples with the known activity of ^{14}C tracers in inorganic and organic forms and ^{36}Cl tracer in Cl^- form were produced. These were made from an inactive matrix similar to waste samples. The model samples were decomposed by the same methods as active samples of were selected from operational and decommissioning waste from the INPP. The ^{14}C and ^{36}Cl activity concentrations of model samples and waste samples were measured by liquid scintillation counting (LSC) in the same manner.

2 Experimental procedure

2.1 Main equipment and chemicals

For the combustion of valuable part of samples, oxidizer, model MTT – Carbon-14 – Tritium Furnace (Carbolite Limited, UK), was used. The Tri-Carb® 3170TR/SL (PerkinElmer Life and Analytical Sciences, USA) and Hidex 300SL (Hidex, Finland) liquid scintillation counters were used for measurement of ^{3}H, ^{14}C and ^{36}Cl. Some of the samples were assessed using gamma ray spectrometer with HPGe detector of GWL series GWL-120-15-LB-AWT (ORTEC, USA).

Optiphase HiSafe® 3 (PerkinElmer Inc.), Oxysolve C-400 (Zinsser Analytic), Oxysolve T (Zinsser Analytic), Aqualight Beta (Hidex) were used as absorption solution and scintillation cocktails.^{14}C standard solution (Czech

Metrology Institute) in chemical form of 5 g L^{-1} $Na_2{}^{14}CO_3$ was used as inorganic ^{14}C standard (combined standard uncertainty 2.0%). ^{3}H activity standard (Czech Metrology Institute) in form of THO was used as inorganic ^{3}H standard (combined standard uncertainty 1.6%). High DPM ^{14}C and High DPM ^{3}H capsules (Amersham Int.) in solid form, in which ^{14}C and ^{3}H exist as organic compounds [U-^{14}C]-Sucrose and D-[5-^{3}H(N)]-Glucose, respectively, were used as organic ^{14}C and ^{3}H standards (for both combined standard uncertainty 0.5%). ^{36}Cl standard solution (Czech Metrology Institute) in chemical form of 0.4 g L^{-1} $Na^{36}Cl$ was used as ^{36}Cl standard (combined standard uncertainty 1.0%). Other chemicals that were used were analytical reagents.

2.2 Sample selection and preparation

The significant part of spent ion-exchange resin and perlite mixture at INPP is stored in two tanks, TW18B01 and TW11B03. Initial radiological characterization evidenced that radionuclide inventory of two tanks was larger in tank TW11B03. For spent ion-exchange resin and perlite mixture characterization from tank TW11B03, five big volume samples (up to 500 mL) were taken from one-, two- or three- meters – level each, using manual sampler. After thorough mixing, five aliquots of 3-5 g from each sample were separated and dried at 70°C. ^{60}Co and ^{137}Cs activities were determined in all aliquots by gamma ray spectrometry. Two sub-samples with gamma-emitting nuclide activities of the minimum and maximum were rejected from each of three samples. The remaining three sub-samples of each of the three samples were mixed into one integrated sample and homogenized by mortar. For subsequent ^{14}C and ^{36}Cl determination, six sub-samples (replicates) of 1 g dry weight were separated.

In previous studies on the radiological characterization of Unit 1, a large collection of solid decommissioning waste samples was assembled and classified according to values of the dose rate and the activity concentrations of gamma emitters (reports are available from INPP). In this study, the archive of solid decommissioning waste samples of INPP was used and the samples for preliminary determination of the specific activity of ^{14}C and ^{36}Cl were selected from those places where the highest values of the dose rate and the activity concentrations of gamma emitters were found. At the same time, it is probable that in these samples the activity concentrations of ^{14}C and ^{36}Cl were highest. Location of some samples is shown in the schematic of the reactor structural elements (Fig. 1).

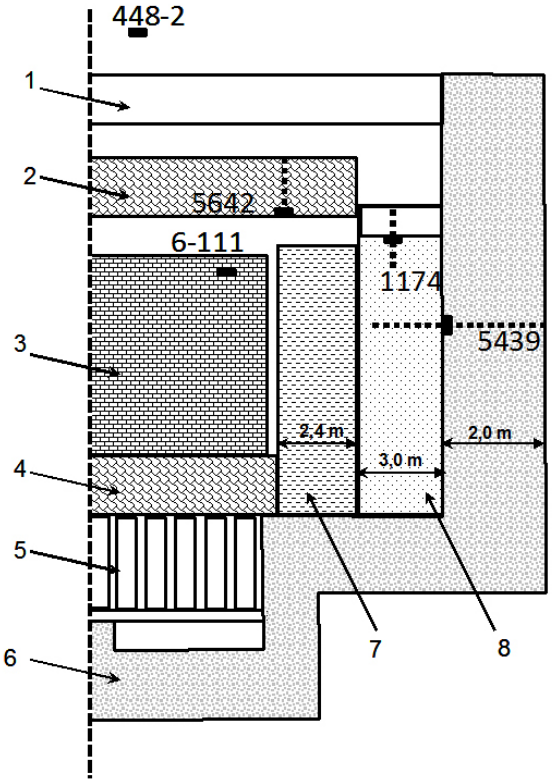

Figure 1: Simplified cross-section of the reactor vault with principal attributions of samples for ^{14}C and ^{36}Cl analysis: 1 – top cover, removable floor of the central hall, 2 – top metal structure filled with serpentinite, 3 – graphite stack (reactor), 4 – bottom metal structure, 5 – reactor support plates, 6 – concrete vault, 7 – annular water tank, 8 – sand cylinder [1] (modified from http://www.lei.lt/insc/sourcebook/).

Construction concrete sample (code 5439) was knocked out from drilling core in amount sufficient to prepare ten sub-samples of 2-5 g weight. A powder was made by mortar. Sand sample (code 1174) and serpentinite sample (code 5642) were taken from drilling core material stored in plastic bags in amount sufficient to prepare ten sub-samples of 2-5 g weight. Homogenization was made by mortar before sub-samples separation. The stainless steel sample (code 448-2) was a plate attributed to the separator-drum. From this stainless steel plate, rectangular plates with area of ~3 cm^2 and weight of ~3 g were cut.

The sample (code 6-111) of graphite GR-280 was selected from INPP archive of solid decommissioning waste samples and it was a segment of the reference bushing of the temperature channel. 5 g of sample was removed from ring and a fine powder was made into ten sub-samples of 0.02-0.2 g weight.

Table 1: Solutions for ^{3}H and ^{14}C analyses after sample digestion using a mixture of acids.

Bottle No	Absorption solution	Amount of solution taken for ^{3}H analysis	Amount of solution taken for ^{14}C analysis
1	100 mL 5% H_2SO_4	1-4 mL dilute to 10 mL by water + 10 mL of Aqualight Beta	-
2	50 mL 2 mol L^{-1} NaOH	-	4 mL + 16 mL of Optiphase HiSafe® 3
3	50 mL 2 mol L^{-1} NaOH	-	4 mL + 16 mL of Optiphase HiSafe® 3

2.3 Digestion by acids

For determination of the ^{14}C and ^{36}Cl activity concentration in samples of spent ion-exchange resins, solid waste and irradiated-graphite, methods similar to those reported in [9-15] were applied. They were based on the sample decomposition by acid digestion with certain modifications.

For digestion by mixed acids, the weighed sample was put into a three-neck flask connected to a digestion system, one washing bottle with diluted acid and two absorption bottles with an NaOH solution. A certain mixture of acids was then added to a separation funnel connected to the three-neck flask; the digestion solution was added to the sample flask from the funnel and nitrogen gas slowly bubbled through the solution under slight vacuum conditions. The sample was heated to 150-200°C for some time until clear solution for ion-exchange resins, stainless steel and graphite samples were obtained. Samples of spent ion-exchange resins (1.0-1.5 g) and irradiated-graphite (0.01-0.1 g) were decomposed by H_2SO_4:HNO_3:$HClO_4$ = 15:4:1, 20 mL, and stainless steel (1-3 g) – by HCl+HNO_3 = 3:1, 20 mL, while samples of concrete, sand and serpentinite were not completely decomposed. Samples of concrete (2-4 g), sand (2-4 g) and serpentinite (0.5-2 g) were partly decomposed by HCl+HNO_3 = 3:1, 30 mL. The washing bottles were filled with absorption solutions as follows: the first bottle contained 5% H_2SO_4, 100 mL, the second and third bottles were filled with 2 mol L^{-1} NaOH, 50 mL (Fig. 2, Table 1).

On completion of the sample decomposition (fully or partially), 4 mL-solution samples were taken from the ^{14}C absorbers with 50 mL of 2 mol L^{-1} NaOH. 16 mL of scintillation cocktail Optiphase HiSafe® 3 was added to each solution sample. Samples prepared in this way are suitable for the determination of ^{14}C without purification if activity concentrations of other interfering radionuclides, ^{36}Cl and ^{129}I, are considerably lower than those of ^{14}C. ^{3}H activity concentration in the sample can also be measured by taking the solutions from a three-neck flask and first bottle and by mixing them. To ensure analytical quality of ^{3}H determination, the neutralization and distillation of

Figure 2: Experimental setup.

mixed solution is required and it is due to the presence of other interfering radionuclides, especially ^{60}Co and ^{137}Cs, in mixed solution.

For further purification of ^{14}C, the remaining absorption solutions, 46 mL from each bottle, were combined and transferred to a similar system with a three-neck flask. The first washing bottle was filled with 5% H_2SO_4, 100 mL, the absorption solutions in the second and third bottles were 30 mL of CO_2 sorbing and scintillation cocktail mixture Oxysolve C-400. 20 mL 3 mol L^{-1} H_2SO_4 solution was added to the three-neckflask via separation funnel under conditions of slight vacuum and nitrogen flux. After 20-30 min., the absorption solutions were combined with Oxysolve C-400. From 60 mL of total solution 20 mL of Oxysolve C-400 was then transferred to a 20 ml LSC vial. In the absence of interfering radionuclides, particularly ^{36}Cl and ^{129}I, results of both 14C determinations within the uncertainty range should be very close to each other. It was a case for all studied samples due to significantly lower ^{36}Cl and ^{129}I activity concentrations compared to those of ^{14}C.

More than thirty modeled samples of different matrices (clear raw ion-exchange resin, materials analogous to solid waste and inactive graphite) 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 approximately 40 determinations

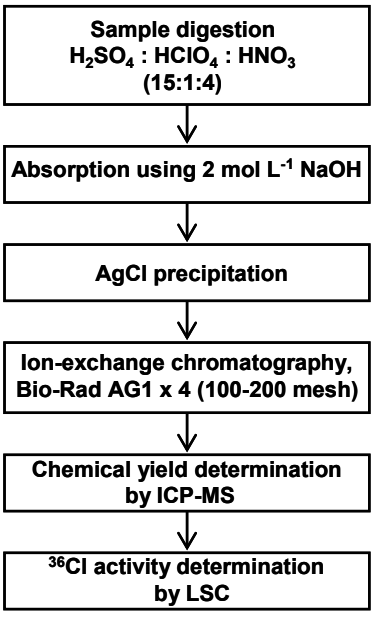

Figure 3: Analytical procedure for determination of ^{36}Cl in radioactive waste.

of ^{14}C activity was carried out using the LSC method. The recovery efficiency of inorganic carbon compounds was obtained at 93-100%, with one of the organic compounds at 85-95%. The extraction efficiency for total ^{14}C activity (inorganic and organic compounds) determination was assumed to be 97%.

Activity concentrations of ^{36}Cl in radioactive waste samples can be determined in a similar way as for ^{14}C using LSC techniques [16-19]. Digesting of radioactive waste samples can be performed using concentrated acids and acid mixtures as well as various modifications of the Fenton reaction and thermal destruction. Chlorine is released from the sample in HCl and Cl_2 chemical forms. After pre-concentration by NaOH solutions, ^{36}Cl can be isolated as AgCl and purified using ion-exchange chromatography.

A number of procedures have been tested to select a method to measure ^{36}Cl in the spent ion-exchange resins and irradiated-graphite [17-19]. Among them, are methods for decomposition of ion-exchange resins: a few Fenton reaction methods using H_2O_2 and Fe^{2+}, Fe^{3+}, Cu^{2+} ions as catalysts, mineral acids H_2SO_4, HCl, $HClO_4$, HNO_3 and their mixtures. The mixture of H_2SO_4, $HClO_4$ and HNO_3 was found to be most suitable for digesting (Fig. 3).

Water and 0.4 - 4 mol L^{-1} NaOH solutions were tested as absorption solutions. AgCl precipitation was used to separate ^{36}Cl from the matrix elements. Interfering radionuclides were removed by means of ion-exchange chromatography, Bio-Rad AG1 x 4 anion-exchange column (100 -200 mesh) was applied [18]. The chemical yield for real radioactive waste samples was determined by inductively coupled plasma mass spectrometry (ICP-MS). Thirteen modeled samples of different matrices (mostly raw ion-exchange resins and irradiated-graphite) with added ^{36}Cl in $Na^{36}Cl$ form were analyzed for a recovery test, and approximately 20 determinations of ^{36}Cl activity was carried out using the LSC method. The recovery efficiency of $^{36}Cl^-$ with modeled samples was obtained at 70-85%. The same or sometimes lower values of chemical yield were determined for each analyzed waste sample with added NaCl as carrier using ICP-MS technique.

2.4 Combustion using sample oxidizer

To further confirm the quality of determining the ^{14}C activity concentration in radioactive waste, some samples were decomposed using the Carbolite MTT oxidizer. Carbon and hydrogen of the sample are converted to gaseous CO_2 and H_2O vapor by catalytic combustion using the sample oxidizer, and when combusted at high temperature in a stream of O_2 gas. The resulting $^{14}CO_2$ and THO are bubbled through the absorption solutions. To avoid cross-contamination during determination of ^{14}C and ^{3}H in the radioactive waste samples, the following sequence of absorption solutions was used: bottle #1 – 30 mL of water vapor sorbing and scintillation cocktail Oxysolve T mixture, bottle #2 – 40 mL of 5% H_2SO_4, bottles #3 and #4 – 30 mL of CO_2 sorbing and scintillation cocktail Oxysolve C-400 mixture (Table 2).

From bottle #1 20 mL of solution was transferred to a 20 mL LSC vial for ^{3}H measurement. From bottle #2 1-4 mL of solution was diluted to 10 mL by deionized water and transferred to a 20 mL LSC vial and 10 mL of scintillation cocktail Aqualight Beta for ^{3}H measurement was added. From bottles #3 and #4 20 mL was transferred to two 20 mL LSC vials for ^{14}C measurement.

Based on many samples from different matrices (clear raw ion-exchange resin, materials analogous to solid waste and inactive graphite) with added ^{3}H and ^{14}C, the tracer solutions recovery percentages of ^{3}H and ^{14}C by the method of oxidizer were 80 ± 5% (2 σ) and 87 ± 7% (2 σ), respectively.

2.5 Measurement of ^{14}C and ^{36}Cl by liquid scintillation counter

^{14}C and ^{36}Cl (in some samples ^{3}H as well) activities were measured by Tri-Carb® 3170TR/SL and Hidex 300 SL liquid scintillation analyzers by setting corresponding energy windows. Depending on sample activity, the

Table 2: Solutions for ^{3}H and ^{14}C analysis after sample decomposition using oxidizer.

Bottle No	Absorption solution	Amount of solution taken for ^{3}H analysis	Amount of solution taken for ^{14}C analysis
1	30 mL of Oxysolve T	20 mL	-
2	40 mL of 5% H_2SO_4	1-4 mL dilute to 10 mL by water + 10 mL of Aqualight Beta	-
3	30 mL of Oxysolve C-400	-	20 mL
4	30 mL of Oxysolve C-400	-	20 mL

sample and the control were counted for a sufficient period of time with several cycles, in order to reach similar radiometric uncertainties with both analyzers. The averages of 3-6 cyclic measurements were calculated. The quench level for radionuclides was measured by tSIE (transformed spectral index of external standard) method for Tri-Carb® 3170TR/SL and TDCR (triple to double coincidence ratio) method for Hidex 300 SL and the counting efficiency was calculated using standards at different quench level.

The minimum detectable activities (MDA) of ^{14}C depending on sample material and weight, analyzer and counting time were similar for both (acid digestion and oxidizer) methods and varied in range 0.05-0.6 Bq g^{-1}. The minimum detectable activity of ^{36}Cl for ion-exchange resins, irradiated-graphite and other samples was in the range of 0.02-0.05 Bq g^{-1}.

3 Results and discussion

The normal operation of a nuclear reactor produces various radionuclides by fission within the fuel or by neutron activation in the structural materials and component systems of the reactor. The escape of these radionuclides from the reactor and its auxiliary process systems during the operation time generates a variety of solid, liquid and gaseous radioactive waste. Classification of radioactive waste for nuclear facilities decommissioning purposes requires that the content of different radioactive nuclides and their generation routes are known as the decommissioning and dismantling activities of the reactors will involve handling and disposing of a big amount of operational and decommissioning waste.

Major ^{14}C producing neutron activation reactions in NPP reactors are [21-25]: (a) the $^{14}N(n, p)^{14}C$ reaction with a very high thermal neutron capture cross-section (1.82 barn (1 barn = 10^{-24} cm^2)); (b) the $^{17}O(n, \alpha)^{14}C$ reaction with a high thermal neutron capture cross-section (0.24 barn); (c) the $^{13}C(n, \gamma)^{14}C$ reaction with a low cross-section (0.9×10^{-3} barn); (d) the $^{15}N(n, d)^{14}C$ reaction with a very low cross-section (2.5×10^{-7} barn); (e) the $^{16}O(n, ^{3}He)^{14}C$ reaction with a very low cross-section (5.0×10^{-8} barn).

Most of ^{14}C is produced in nuclear power reactors by $^{14}N(n, p)^{14}C$ reactions with nitrogen in fuels, moderators and coolants as a primary impurity, by $^{17}O(n, \alpha)^{14}C$ reactions in oxide fuels, moderators and coolants, and by $^{13}C(n, \gamma)^{14}C$ reactions in graphite moderators. Reactions (a) (b) and (c) are the most important contributors to ^{14}C production in thermal reactors. ^{14}C is also a ternary fission product, but the amount produced in this way is negligible. The substrate atoms for the activation reactions (*i.e.*, nitrogen, oxygen and carbon) widely occur in fuel and in cladding, moderator, coolant or structural material, either as major constituents or as impurities.

^{14}C can enter the main circulation circuit (MCC) coolant (reactor water) of the INPP due to fuel cladding defects, corrosion of metal structures of reactor core components and direct generation in the coolant. ^{14}C from the contaminated coolant of MCC can be further transferred to the final waste or to the environment by three main routes: (i) the retention of ^{14}C in structural materials of NPP, (ii) the loss of a coolant through leakages to the drainage system, and (iii) the chemical purification of a coolant by ion exchange resins and perlite. The latter route leads to operational waste of spent ion-exchange resins / perlite stream.

Similarly to ^{14}C, ^{36}Cl is produced in a nuclear reactor by the neutron activation reaction $^{35}Cl(n, \gamma)^{36}Cl$ with a very high thermal neutron capture cross-section (43.6 barn) [26], due to the presence of chlorine in all structural materials of the reactor, *i.e.*, in fuel elements, graphite, coolant (reactor water), construction materials such as concrete, metal, etc.

Besides the total ^{14}C activity concentrations in different waste types, determination of organic and inorganic ^{14}C fractions is important due to higher mobility of organic ^{14}C compared to inorganic ^{14}C in the environment. First systematic determinations of ^{14}C associated with organic and inorganic ^{14}C fractions in samples of the INPP operational waste from main two storage tanks containing spent ion-exchange resins and perlite mixture

Table 3: ^{14}C and ^{36}Cl activity concentrations in integrated sample of spent ion exchange resin and perlite mixture from the operational waste storage tank TW11B03 of INPP with key (reference) nuclides data (analysis was performed in December 2012).

Sub-sample ID No	Gamma assay report No	$^{14}C_{tot}$		^{36}Cl		^{60}Co		^{137}Cs	
		Bq g^{-1}	±2σ, %	Bq g^{-1}	±2σ, %	Bq g^{-1}	±2σ, %	Bq g^{-1}	±2σ, %
1	4285	202	5.1	0.41	8.1	2.43×10^4	13.4	2.86×10^4	13.4
8	4286	212	2.1	0.42	5.7	2.54×10^4	13.4	3.01×10^4	13.4
10	4287	218	2.5	0.31	7.3	2.58×10^4	13.4	3.11×10^4	13.4
11	4288	210	2.1	0.42	6.2	2.47×10^4	13.4	2.92×10^4	13.4
13	4289	199	3.0	0.41	7.1	2.40×10^4	13.4	2.82×10^4	13.4
15	4290	198	3.5	0.42	7.6	2.45×10^4	13.4	2.90×10^4	13.4

were performed in 2011 [27]. For the majority of spent ion-exchange resins and perlite mixture samples, the combination of acid stripping and wet oxidation using the setup similar to that presented in [13, 15] allowed separate extractions of the organic and inorganic ^{14}C from a single sample. The fraction of ^{14}C associated with organic compounds ranged from 42% to 63% for the storage tank TW18B01 and from 30% to 63% for the storage tank TW11B03. These storage tanks represent waste related to different filling time and consequently different operational periods of the INPP with the total ^{14}C activity concentration in waste from the storage tank TW11B03 by more than one order of magnitude higher compared to waste from the storage tank TW18B01. Besides, based on the waste volume and density data, the total ^{14}C activity was estimated as 3.59×10^{10} Bq (±32%) and 4.15×10^{11} Bq (±28%) for radioactive waste stored in tanks TW18B01 and TW11B03, respectively.

Based on the findings from previous studies [27], we carried out a more detailed study of total of ^{14}C and ^{36}Cl activity concentrations in one integrated sample of spent ion-exchange resin and perlite mixture from the storage tank TW11B03 in 2012 (Table 3).

In order to confirm the data of previous studies [27], six sub-samples of well homogenized spent ion-exchange resin and perlite mixture sample taken from the storage tank TW11B03 were investigated using described methods. Approximately 20 ^{14}C and 10 ^{36}Cl specific activity determinations were done. Based on statistical analysis, the average values of $^{14}C_{total}$ and ^{36}Cl specific activities in spent ion-exchange resin and perlite mixture from the radioactive waste storage tank TW11B03 of INPP were 206 Bq g^{-1} of dry weight with a relative standard deviation (RSD) of 4% and 0.40 Bq g^{-1} with RSD of 11%, respectively. The average activity concentrations of reference radionuclides ^{60}Co and ^{137}Cs derived from the same sub-samples was 2.48×10^4 Bq g^{-1} with RSD of 2.7% and 2.94×10^4 Bq g^{-1} with RSD of 3.6%, respectively.

Based on the findings from radiological characterization of Unit 1, the low level of the surface contamination of concrete walls is expected in the reactor building since the concrete vault of the reactor never experienced neutron activation. Activity concentration of artificial gamma emitting radionuclides in most concrete samples was below MDA. Only for sufficiently long counting time in one concrete sub-sample ^{60}Co and ^{137}Cs were observed with activity concentrations of 19.2 and 17.4 Bq kg^{-1}, respectively.

The sand cylinder in some places is more contaminated by gamma emitting radionuclides compared with the concrete vault. These places are the top layer of 0.5 m of sand backfill and the 2 m sand layer under the tanks for getting drainage water. All sand sub-samples contain ^{60}Co and ^{137}Cs with average activity concentrations of 0.25 and 0.58 Bq g^{-1}.

The stainless steel sample attributed to the separator-drum was highly contaminated by gamma emitting radionuclides as it was related to the main circulation circuit. From this stainless steel sample three sub-samples numbered from M1 to M3 were prepared for determination of gamma emitting radionuclides. Sub-sample M1 represented the oxidation layer scraped from the surface layer of a rectangular stainless steel plate of 8 cm^2. Sub-samples M2 and M3 were not pretreated rectangular stainless steel plates with areas of 2.72 and 3.6 cm^2, respectively. Of gamma emitters, two radionuclides – ^{60}Co and ^{54}Mn – were found in the stainless steel sample. ^{60}Co activity concentration of sub- samples was variable with the average value of 9.43×10^5 Bq g^{-1}. Sub-sample M1 representing only the oxidation layer scraped from the surface layer, had the maximum ^{60}Co activity concentration of 2.80×10^6 Bq g^{-1}, while not pretreated samples M2 and M3, *i.e.*, bulk metal with the oxidation layer showed lower ^{60}Co activity concentrations of 1.32×10^4 and 1.63×10^4 Bq g^{-1}, respectively. After recalculation, it was found that the ^{60}Co fraction in the oxidation layer was 70% and in bulk metal – 30%.

Table 4: ^{14}C activity concentrations in samples of solid decommissioning waste of INPP with key (reference) nuclides data (analysis was performed in September – December 2013).

Sub-sample ID No	Gamma assay report No	^{14}C		^{60}Co		^{137}Cs	
		Bq g^{-1}	±2σ, %	Bq g^{-1}	±2σ, %	Bq g^{-1}	±2σ, %
Construction concrete sample, code 5439							
B2	8452	0.28	31.0	<MDA		<MDA	
B3	8453	0.59	9.4	<MDA		<MDA	
B5	8455	n/m		0.0192	32.7	0.0174	32.9
B6	8456	0.13	21.8	<MDA		<MDA	
B7	8457	<MDA		<MDA		<MDA	
Sand sample, code 1174							
P1	8277	n/m		0.23	32.1	0.78	16.9
P2	8278	<MDA		0.28	34.5	0.39	30.4
P3	8279	n/m		0.32	36.9	0.46	21.0
P4	8280	n/m		0.22	35.7	0.34	28.5
P5	8281	0.16	45.0	0.28	27.9	0.84	15.5
P6	8282	0.15	31.0	0.20	25.5	0.56	15.4
P	GWL-364	0.10	15.0	0.23	6.0	0.69	3.0
P: 16-10		0.09	28.0	n/m		n/m	
P: 13-10-12		0.10	15.0	n/m		n/m	
Stainless steel sample, code 448-2							
M1 (ox)	8891	<MDA		2.80×10^{6}	7.0	<MDA	
M2 (bulk)	8892	0.14	24.9	1.32×10^{4}	7.0	<MDA	
M3 (bulk)	8893	0.11	15.0	1.63×10^{4}	7.0	<MDA	
Serpentinite sample, code 5642							
S1	8267	6.5	6.2	2.34×10^{3}	7.1	<MDA	
S2	8268	7.3	16.0	2.45×10^{3}	7.2	<MDA	
S3	8269	n/m		3.31×10^{3}	7.1	<MDA	
S4	8270	n/m		2.29×10^{3}	7.1	<MDA	
S5	8271	5.9	6.1	2.43×10^{3}	7.1	<MDA	
S: 14-9		12.4	9.8	n/m		n/m	
S : 14-10		12.8	6.0	n/m		n/m	
S: 14-12		12.3	6.0	n/m		n/m	
S: 14-13		9.6	5.7	n/m		n/m	

MDA – minimum detectable activity
n/m – not measured
ox – oxidation layer only
bulk – bulk metal plate with oxidation layer

The serpentinite backfill from the top metal structure compared with concrete and sand in some places contains even higher activity concentrations of gamma emitters (^{60}Co and ^{152}Eu were detected). The bottom layer of serpentinite backfill with the thickness of 0.5 m located close to the reactor underwent neutron activation and contained ^{60}Co with activity concentrations up to 2.45×10^{3} Bq g^{-1}. Serpentinite is a rock composed of one or more serpentine group minerals with crystallization water. In serpentinite the substrate atoms (H, mainly) for the activation reactions producing ^{3}H are present [21]. After heating serpentinite sample in the oxidizer, the activity concentration of ^{3}H was additionally measured in released water. Compared to other solid waste samples, the ^{3}H activity concentrations in serpentinite sub-samples were higher and ranged from 1.06×10^{3} to 3.59×10^{3} Bq g^{-1}.

Several sub-samples (from two for metal to seven for serpentinite) of each matrix (concrete sample 5439, sand sample 1174, stainless steel sample 448-2 and serpentinite sample 5642) were investigated for ^{14}C and ^{36}Cl in 2013 (Table 4).

Based on the statistical analysis, the average value of the total ^{14}C activity concentration in solid waste was found to be as follows: in construction concrete – 0.27 Bq g^{-1} with RSD of 88.8%, in sand – 0.13 Bq g^{-1} with RSD of 28.0%, in stainless steel – 0.12 Bq g^{-1} (only two sub-samples or

Table 5: ^{14}C activity concentration in sample of irradiated graphite of INPP with key (reference) nuclide ^{60}Co data (analysis was performed in September – December 2013).

Sub-sample ID No	Gamma assay report No	^{14}C		^{60}Co	
		Bq g^{-1}	±2σ, %	Bq g^{-1}	±2σ, %
G1	8034	2.07×10^5	5.0	3.69×10^4	7.4
G2	8035	1.98×10^5	5.0	2.38×10^4	7.8
G3	8036	2.65×10^5	5.5	2.44×10^4	7.6
G4	8037	2.14×10^5	5.1	3.21×10^4	8.0
G5*	8038	1.19×10^5 1.02×10^5	5.0 3.1	2.62×10^4	7.2
G6*	8039	1.28×10^5 1.03×10^5	5.0 3.1	2.78×10^4	7.1

*Last two sub-samples were measured with two different LS counters

replicates), and in serpentinite – 9.5 Bq g^{-1} with RSD of 31.4%. ^{14}C activity concentrations for sub-samples of construction concrete, sand, and stainless steel were close to the detection limit and rather variable. Serpentinite sub-samples that were contaminated more by ^{14}C. ^{36}Cl activities in all tested samples of solid waste, were evaluated to be <MDA (therefore data are not included into Table 4).

Irradiated-graphite, an important kind of long-lived radioactive waste at the INPP, began to be characterized by modeling and by experiments a few years ago [4]. The following nuclear reactions most contribute to the production of radionuclides in irradiated-graphite: $^6Li(n, \alpha)^3H$, $^{13}C(n, \gamma)^{14}C$, $^{15}N(n, p)^{14}C$, $^{35}Cl(n, \gamma)^{36}Cl$, $^{59}Co(n, \gamma)^{60}Co$.

According to modeling results [4], the corner reflector of RBMK-1500 contains up to to 2.6×10^4 Bq g^{-1} of ^{14}C and up to 250 Bq g^{-1} of ^{36}Cl. Activities ^{14}C and ^{36}Cl, evaluated for the moderator, were more than one order of magnitude higher: ^{14}C – 5×10^5 Bq g^{-1}, ^{36}Cl – 4×10^3 Bq g^{-1}. In order to analyze the inventory of the graphite stack, the following activities were recently performed at the INPP: a program of the graphite sampling from the graphite stack has been developed; an equipment for the long-distance graphite sampling has been designed and manufactured by the INPP personnel; four CPS channels and sixty fuel channels have been retrieved for sampling purposes. The studies of GRP-2-125 grade graphite rings on the content of radionuclides in 2012 revealed the following results: for the inner part of rings the following activity concentrations were found: ^{14}C – 2.6×10^5 Bq g^{-1}, ^{60}Co – 1.4×10^4 Bq g^{-1}, ^{137}Cs – ^{137}Cs – 2.7×10^2 Bq g^{-1}; the activity concentrations for the outer part of rings were those of ^{14}C – 3.9×10^6 Bq g^{-1}, ^{60}Co – 3.6×10^5 Bq g^{-1}, ^{137}Cs – 2.3×10^3 Bq g^{-1}. The activity outer / inner ratios were as follows: for ^{14}C – 15, for ^{60}Co – 25, for ^{137}Cs – 8.

Graphite sub-samples numbered from G1 to G6 and attributed to one sample of the reference bushing segment of the temperature channel made of GR-280, code 6-111, were investigated for the content of ^{14}C (Table 5) and ^{36}Cl (only two sub-samples or replicates) in 2013.

All graphite sub-samples contained ^{60}Co with the average activity concentration of 2.85×10^4 Bq g^{-1} and RSD of 17.7%. After combustion of graphite sub-samples in the oxidizer, the activity concentration of ^3H was measured to be 1.85×10^4 Bq g^{-1} (±1.2%). Based on the statistical analysis, the average value of the total ^{14}C specific activity in graphite was as follows: 1.67×10^5 Bq g^{-1} with RSD of 36.7%. ^{36}Cl activity concentration in graphite samples ranged from 400 to 500 Bq g^{-1}. However, this rough ^{36}Cl data is based on a limited number of incomplete measurements.

Specific activity of ^{14}C in graphite is distributed unevenly, depending on the sample location in the core, the type of item and material (thin ring or block, GR-280 or GRP-2-125 graphite), operation mode (temperature, composition of cooling gases mixture). A comparison has demonstrated a higher ^{14}C activity in the surface layer (up to 2 mm) of graphite rings. It can be explained by the presence of 10% nitrogen in the cooling gas. Concentrations of ^{36}Cl in the irradiated graphite turned out to be almost 10 times lower that the expected ones, a result that has to be carefully explained in future studies.

4 Conclusions

The performed study demonstrates applicability of used analytical methods to a variety of radioactive waste from the INPP. The methods are based on based on sample decomposition by the acid mixtures with

further purification for ^{36}Cl measurements. They are also based on sample decomposition by the acid mixtures or the sample oxidizer, which are applicable to estimate activity concentration of ^{14}C. This is the first systematic attempt to measure the content of ^{14}C and ^{36}Cl in basic operational waste, *i.e.*, spent ion-exchange resins and perlite mixture, in decommissioning waste including construction concrete, sand, stainless steel, serpentinite, and irradiated graphite.

The applied approach will be further developed and data obtained will be used in future assessments as a basis for realistic estimates of the ^{14}C and ^{36}C inventories for the Lithuanian near-surface repository or other disposal options (graphite case). The approach will be also applied to reduce the level of conservatism in safety assessments.

Acknowledgment: This research was partly funded by the Lithuanian Radioactive Waste Management Agency.

References

[1] Almenas K., Kaliatka A., Uspuras E., Ignalina RBMK-1500, Lithuanian Energy Institute, Kaunas, 1998, http://www.lei.lt/insc/sourcebook/
[2] Lukauskas D., Plukiene R., Plukis A., Gudelis A., Duskesas G., Juodis L., et al., Lith. J. Phys., 2006, 46, 497
[3] Plukis A., Remeikis V., Juodis L., Plukiene R., Lukauskas D., Gudelis A., Lith. J. Phys., 2008, 48, 375
[4] Ancius D., Ridikas D., Remeikis V., Plukis A., Plukiene R., Cometto M., Nukleonika, 2004, 50, 113
[5] Huskisson N.S., Ward P.F.V., Int. J. Appl. Radiat. Isot., 1978, 29, 729
[6] Wenzel U., Herz D., Schmidt P., J. Radioanal. Chem., 1979, 53, 7
[7] Salonen L., Snellman M., Carbon-14 releases from Finnish nuclear power plants. Final Report of Research Agreement No 3065/R2/CF. Part of IAEA coordinated program on carbon-14 from nuclear power plants, IAEA, Vienna, 1985
[8] Martin J.E., Health Phys., 1986, 50(1), 57
[9] Veres M., Hertelendi E., Uchrin G., Csaba E., Barnabás I., Ormai P., et al., Radiocarbon, 1995, 37, 473
[10] Yang H.Y., Wang Z.H., Liu W., Wen X.L., Zheng H., Chin. J. Atomic Energy Sci. Technol., 1996, 30(6), 509
[11] Wickenden D.A., Environmental Radiochemical Analysis, Royal Society of Chemistry (Special Publication), 1999, 234, 170
[12] Hou X., Appl. Rad. Isot., 2005, 62, 871
[13] Magnusson Å., 14C produced by nuclear power reactors – generation and characterization of gaseous, liquid and solid waste, PhD thesis, Lund, Lund University, 2007
[14] Hou X., J. Radioanal. Nucl. Chem. 2007, 273, 43
[15] Magnusson Å., Aronsson P.O., Lundgren K., Stenström K., Health Phys., 2008, 95(2), 110
[16] Itoh M., Watanabe K., Hatakeyama M., Tachibana M., Analyst, 2002, 127(7), 964
[17] Rodriguez M., Pina G., Lara E., Czechoslov. J. Phys., 2006, 56, D211
[18] Hou X., Østergaard L.F., Nielsen S.P., Anal. Chem., 2007, 79, 3126
[19] Zulauf A., Happel S., Mokili M.B., Bombard A., Jungclas H., J. Radioanal. Nucl. Chem., 2010, 286(2), 539
[20] Fifield L.K., Tims S.G., Stone J.O., Argento D.C., De Cesare M., Nucl. Instr. Meth. Phys. Res. B, 2013, 294, 126
[21] IAEA. Management of waste containing tritium and carbon-14, Technical Report Series No. 421, IAEA, Vienna, Austria, 2004
[22] IAEA. Characterization, treatment and conditioning of radioactive graphite from decommissioning of nuclear reactors, IAEA-TECDOC-1521, IAEA, Vienna, Austria, 2006
[23] Bushuev A.V., Zubarev V.N., Proshin I.M., Atomnaya energija, 2002, 92, 298 (in Russian)
[24] Yim M.-S., F. Progress in Nuclear Energy, 2006, 48, 2
[25] Metcalfe M.P., Banford A.W., Eccles H., Norris S., J. Nucl. Materials, 2013, 436, 158
[26] Mughabghab S.F., Divadeenam M., Holden N.E., Neutron Cross Sections from Neutron Resonance Parameters and Thermal Cross Sections, Academic Press, New York, 1981
[27] Vaitkevičienė V., Mažeika J., Skuratovič Ž., Motiejūnas S., Vaidotas A., Oryšaka A., Ovčinikov S., Radiocarbon, 2013, 55, 783