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

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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 $\sim$1700 kg m$^{-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
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, serpentine 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 14C 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 14C for NSR with the capacity for disposal of approximately 100 000 m³ of waste was evaluated as 1.43×10^15 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 14C and 36Cl as well. The specific activity of irradiated RBMK-1500 graphite evaluated by modeling is mainly determined by the specific activities of 14C, 3H, 60Co, and 55Fe; however, the presence of 36Cl in graphite is also evident [4]. Activated graphite of INPP, of the long-lived 14C is classified at present as the long-lived radioactive waste due to the high activity, up to 5×10^7 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, 14C and tritium primarily contribute (3.91×10^15 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 14C and 36Cl are significant radionuclides affecting the long-term safety margins of the near surface repository, and because the 14C large and 36Cl have uncertain inventory for INPP NSR, our main focus was to quantitatively evaluate the 14C and 36Cl 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 14C and 36Cl activity in different samples for characterization of the unconditioned operational and decommissioning waste of the INPP. The basic principles of waste sample decomposition, 14C and 36Cl 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 14C and 36Cl in all separation procedures, model samples with the known activity of 14C tracers in inorganic and organic forms and 36Cl 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 14C and 36Cl 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 Hiex 300SL (Hiex, Finland) liquid scintillation counters were used for measurement of 1H, 14C and 36Cl. 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 (Hiex) were used as absorption solution and scintillation cocktails. 14C standard solution (Czech
Metrology Institute) in chemical form of 5 g L\(^{-1}\) Na\(^{14}\)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/).](image-url)

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.
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 a 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 $\text{H}_2\text{SO}_4: \text{HNO}_3: \text{HClO}_4 = 15:4:1$, 20 mL, and stainless steel (1-3 g) by $\text{HCl+HNO}_3 = 3:1$, 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 $\text{HCl+HNO}_3 = 3:1$, 30 mL. The washing bottles were filled with absorption solutions as follows: the first bottle contained 5% $\text{H}_2\text{SO}_4$, 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. The washing bottles were filled with absorption solutions as follows: the first bottle contained 5% $\text{H}_2\text{SO}_4$, 100 mL, the second and third bottles were filled with 2 mol L$^{-1}$ NaOH, 50 mL (Fig. 2, Table 1).

### 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% $\text{H}_2\text{SO}_4$ | 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 |

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% $\text{H}_2\text{SO}_4$, 100 mL, the absorption solutions in the second and third bottles were 30 mL of $\text{CO}_2$ sorbing and scintillation cocktail mixture Oxysolve C-400. 20 mL 3 mol L$^{-1}$ $\text{H}_2\text{SO}_4$ solution was added to the three-neck flask 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 $^{14}$C 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$^{14}$CO$_3$, [U-$^{14}$C]-sucrose forms or a mixture of both were analyzed for a recovery test, and approximately 40 determinations mixed solution is required and it is due to the presence of other interfering radionuclides, especially $^{60}$Co and $^{137}$Cs, in mixed solution.
A number of procedures have been tested to select a method to measure $^{36}$Cl in the spent ion-exchange resins and irradiated-graphite [16-19]. Among them, are methods for decomposition of ion-exchange resins: a few Fenton reaction methods using $\text{H}_2\text{SO}_4 : \text{HClO}_4 : \text{HNO}_3$ (15:1:4), reaction methods using $\text{H}_2\text{SO}_4 : \text{HClO}_4 : \text{HNO}_3$ (15:1:4) and $\text{H}_2\text{SO}_4 : \text{HNO}_3 : \text{HCl}$ (15:4:1). Of these, the catalytic combustion with added $\text{H}_2\text{O}$ and $\text{CO}_2$ vapor were selected as the 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).

To further confirm the quality of determining the $^{14}$C activity concentration in radioactive waste, some samples were decomposed using the Carbolute MTT oxidizer. Carbon and hydrogen of the sample are converted to gaseous $\text{CO}_2$ and $\text{H}_2\text{O}$ vapor by catalytic combustion using the sample oxidizer, and when combusted at high temperature in a stream of $\text{O}_2$ 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% $\text{H}_2\text{SO}_4$, bottles #3 and #4 – 30 mL of $\text{CO}_2$ 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 $80 \pm 5\%$ (2 $\sigma$) and $87 \pm 7\%$ (2 $\sigma$), 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 $^1$H and $^{14}$C analysis after sample decomposition using oxidizer.

| Bottle No | Absorption solution | Amount of solution taken for $^1$H analysis | Amount of solution taken for $^{14}$C analysis |
|-----------|---------------------|--------------------------------------------|---------------------------------------------|
| 1         | 30 mL of Oxysolve T | 20 mL                                      | -                                           |
| 2         | 40 mL of 5% $\text{H}_2\text{SO}_4$ | 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 $^{14}$O(n, $\alpha$)$^{14}$C reaction with a high thermal neutron capture cross-section (0.24 barn); (c) the $^{14}$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 $^{16}$O(n, $\alpha$)$^{14}$C reactions in oxide fuels, moderators and coolants, and by $^{14}$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.

$^{36}$Cl 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. $^{36}$Cl 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 $^{36}$Cl activity concentrations in different waste types, determination of organic and inorganic $^{36}$Cl fractions is important due to higher mobility of organic $^{36}$Cl compared to inorganic $^{36}$Cl in the environment. First systematic determinations of $^{36}$Cl associated with organic and inorganic $^{36}$Cl fractions in samples of the INPP operational waste from main two storage tanks containing spent ion-exchange resins and perlite mixture...
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 $9.43 \times 10^5$ Bq g$^{-1}$. Sub-sample M1 representing only the oxidation layer scraped from the surface layer, had the maximum $^{60}$Co activity concentration of $2.80 \times 10^6$ 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 $1.32 \times 10^6$ and $1.63 \times 10^6$ Bq g$^{-1}$, respectively. After recalulation, it was found that the $^{60}$Co fraction in the oxidation layer was 70% and in bulk metal – 30%.

### 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$_{int}$ Bq g$^{-1}$ | $^{36}$Cl Bq g$^{-1}$ | $^{40}$Co Bq g$^{-1}$ | $^{137}$Cs Bq g$^{-1}$ |
|------------------|------------------------|----------------------------|------------------------|------------------------|------------------------|
|                  |                        | ±2σ, %                     | ±2σ, %                 | ±2σ, %                 | ±2σ, %                 |
| 1                | 4285                   | 202                        | 5.1                    | 0.41                   | 8.1                    | $2.43 \times 10^3$     | 13.4                    | $2.86 \times 10^4$     | 13.4                   |
| 8                | 4286                   | 212                        | 2.1                    | 0.42                   | 5.7                    | $2.54 \times 10^4$     | 13.4                    | $3.01 \times 10^4$     | 13.4                   |
| 10               | 4287                   | 218                        | 2.5                    | 0.31                   | 7.3                    | $2.58 \times 10^4$     | 13.4                    | $3.11 \times 10^4$     | 13.4                   |
| 11               | 4288                   | 210                        | 2.1                    | 0.42                   | 6.2                    | $2.47 \times 10^4$     | 13.4                    | $2.92 \times 10^4$     | 13.4                   |
| 13               | 4289                   | 199                        | 3.0                    | 0.41                   | 7.1                    | $2.40 \times 10^4$     | 13.4                    | $2.81 \times 10^4$     | 13.4                   |
| 15               | 4290                   | 198                        | 3.5                    | 0.42                   | 7.6                    | $2.45 \times 10^4$     | 13.4                    | $2.90 \times 10^4$     | 13.4                   |

The gamma assay was 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 $3.59 \times 10^{10}$ Bq (±32%) and $4.15 \times 10^{11}$ 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 $^{14}$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 $2.48 \times 10^6$ Bq g$^{-1}$ with RSD of 2.7% and $2.94 \times 10^6$ Bq g$^{-1}$ with RSD of 3.6%, respectively.
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 $2.45 \times 10^3$ 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 $1.06 \times 10^3$ to $3.59 \times 10^3$ 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 $^3$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 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 | Gamma assay report No | $^{14}$C | $^{60}$Co | $^{137}$Cs |
|------------|-----------------------|---------|---------|---------|
| ID No      | Bq g$^{-1}$ ±2σ, %    | Bq g$^{-1}$ ±2σ, % | Bq g$^{-1}$ ±2σ, % |
| Construction concrete sample, code 5439 |  |  |  |
| B2 | 8452 | 0.28 | 31.0 | 0.78 | 16.9 |
| B3 | 8453 | 0.59 | 9.4 | <MDA | <MDA |
| B5 | 8455 | 0.13 | 21.8 | <MDA | <MDA |
| B6 | 8455 | 0.13 | 21.8 | <MDA | <MDA |
| B7 | 8457 | n/m | 28.0 | n/m | n/m |
| 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 | $2.80 \times 10^5$ | 7.0 | <MDA |
| M2 (bulk) | 8892 | 0.14 | 24.9 | $1.32 \times 10^5$ | 7.0 | <MDA |
| M3 (bulk) | 8893 | 0.11 | 15.0 | $1.63 \times 10^5$ | 7.0 | <MDA |
| Serpentinite sample, code 5642 |  |  |  |  |
| S1 | 8267 | 6.5 | 6.2 | $2.34 \times 10^3$ | 7.1 | <MDA |
| S2 | 8268 | 7.3 | 16.0 | $2.45 \times 10^3$ | 7.2 | <MDA |
| S3 | 8269 | n/m | 3.31 | 7.1 | <MDA |
| S4 | 8270 | n/m | $2.29 \times 10^3$ | 7.1 | <MDA |
| S5 | 8271 | 5.9 | 6.1 | $2.43 \times 10^3$ | 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
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 $2.85 \times 10^4$ Bq g$^{-1}$ and RSD of 17.7%. After combustion of graphite sub-samples in the oxidizer, the activity concentration of $^1$H was measured to be $1.85 \times 10^4$ 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: $1.67 \times 10^5$ 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-2425 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.

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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., Pluikis A., Gudelis A., Duskesas G., Juodis L., et al., Lith. J. Phys., 2006, 46, 497
[3] Pluikis A., Remeikis V., Juodis L., Plukiene R., Lukauskas D., Gudelis A., Lith. J. Phys., 2008, 48, 375
[4] Ancius D., Ridikas D., Remeikis V., Pluikis 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., Uchner 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., $^{14}$C 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] Rodríguez 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 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 energia, 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., Motiejūnas S., Vaidotas A., Oryšaka A., Ovčinikov S., Radiocarbon, 2013, 55, 783