^{14}C Produced by Nuclear Power Reactors – Generation and Characterization of Gaseous, Liquid and Solid Waste

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Abstract

This thesis presents the results from studies on carbon-14 produced by nuclear power reactors. Radioactive C-14 enters the carbon cycle and can be taken up by humans, where it will constitute a potential health hazard. Therefore, the main focus of this thesis was to provide new data and knowledge necessary for the implementation of appropriate nuclear waste management strategies. Such data have previously been very limited or non-existent. The studies presented describe the characterization and mapping of C-14 from the source of production, through various waste and release streams, to its final destination; here being the sea, the terrestrial environment and a national disposal facility. The reactor units investigated comprise Swedish BWRs and PWRs (boiling- and pressurized-water reactors, respectively), as well as two power plants located in Lithuania and Romania.

In this thesis, a new method of separately quantifying organic and inorganic C-14 in radioactive liquid, gaseous and solid samples was developed and applied to samples from waste and releases streams in Swedish BWRs and PWRs. Based on the results, mass balance assessments of the C-14 produced in the reactor coolant were made. The assessments showed that the amount of C-14 released to the sea in liquid discharges constituted only a minor fraction (<1%) of the amount originally produced in the coolant. The fraction of C-14 ending up in the solid waste stream, which is dominated by C-14 adsorbed on ion-exchange resins, was found to be 0.5–10%, depending on the reactor type. The remaining fraction is released as gaseous compounds to the air. Since the dominating fraction of the C-14 activity in the Swedish waste repository is expected to be that contained in the spent ion-exchange resins, the total C-14 inventory at the time of repository closure was also estimated and found to be 5.0 TBq; the present disposal limit being 7.2 TBq. However, these studies showed that the approach used by the operator of the repository to estimate the inventory suffers from significant uncertainties. Therefore, an alternative approach is suggested in this thesis.

The studies related to the non-Swedish power plants showed enhanced C-14 levels in plants and trees growing close to the power plants. The most interesting finding was that a few samples contained a C-14 excess of up to 2000% above the contemporary background, which is thought to be the result of releases of particulate material.

Key words: Carbon-14, nuclear power plant, waste disposal, SFR, spent ion-exchange resins, process water, mass balance assessment, PWR, BWR, Ignalina NPP, Cernavoda NPP, environmental impact

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Papers

This thesis is based on the following papers, which will be referred to in the text by their Roman numerals. The papers are appended at the end of the thesis.

I Stenström K and Magnusson Å. 2004. Methods for measuring ^{14}C on spent ion-exchange resins – A review. In: Johnson LH and Schwyn B (eds); Proceedings of a workshop on the release and transport of C-14 in repository environments. Nationale Genossenschaft für die Lagerung radioaktiver Abfälle, NAGRA Interner Bericht 04-03.

II Magnusson Å, Stenström K, Skog G, Adliene D, Adlys G, Hellborg R, Olariu A, Zakaria M, Rääf C, Mattsson S. 2004. Levels of ^{14}C in the terrestrial environment in the vicinity of two European nuclear power plants. Radiocarbon 46(2)863–868.

III Magnusson Å, Stenström K, Adliene D, Adlys G, Dias C, Rääf C, Skog G, Zakaria M, Mattsson S. 2007. Carbon-14 levels in the vicinity of the Lithuanian nuclear power plant Ignalina. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 259(1)530–535.

IV Magnusson Å, Stenström K, Aronsson P-O. 2007. ^{14}C in Swedish PWRs and BWRs – Measurements on spent ion-exchange resins and process water and estimation of the ^{14}C inventory in the Swedish waste repository. In: Proceedings: 2006 EPRI international low-level waste conference and exhibit show. Electric Power Research Institute, EPRI TR-1014823, Palo Alto.

V Magnusson Å, Stenström K, Aronsson P-O. ^{14}C in spent ion-exchange resins and process water from nuclear reactors – A method for quantitative determination of organic and inorganic fractions. Accepted for publication in Journal of Radioanalytical and Nuclaer Chemistry.

VI Magnusson Å, Aronsson P-O, Lundgren K, Stenström K. Characterization of ^{14}C in Swedish light water reactors. Submitted to Health Physics: Operational Radiation Safety.

My contributions to the papers

I I collected most of the reference material and wrote a minor part of the paper.

II I participated in sample preparation, analysis and evaluation of the data. I wrote the paper.

III I participated in sample preparation, analysis and evaluation of the data. I wrote the paper.

IV I conducted the major part of the analyses and evaluated the results together with Per-Olof Aronsson, Ringhals AB. I wrote the paper.

V I conducted the major part of the experimental work. I evaluated the results and wrote the paper.

VI I was responsible for the execution of the study on process water and also took an active part in planning the project. I wrote the paper and performed the evaluation of the results together with Per-Olof Aronsson, but conducted a minor part of the analyses. Klas Lundgren, ALARA Engineering AB, performed the calculations of the production rates.

Other related publications not included in this thesis

Stenström K and Magnusson Å. 2003. Methods for measuring ^{14}C on spent ion-exchange resins from nuclear power plants- A literature survey. Lund University, Internal report LUNFD6/NFFR-3090.

Magnusson Å, Stenström K, Faarinen M, Persson P, Skog G. 2004. ^{14}C in a graphite reflector – Method development and measurement of organic and inorganic ^{14}C. In: Johnson LH and Schwyn B (eds); Proceedings of a workshop on the release and transport of C-14 in repository environments. Nationale Genossenschaft für die Lagerung radioaktiver Abfälle, NAGRA Interner Bericht 04-03.

Magnusson Å, Stenström K, Faarinen M, Hellborg R, Persson P, Skog G. 2005. Measurement of the distribution of organic and inorganic ^{14}C in a graphite reflector from a Swedish nuclear power plant. In: Olariu A, Stenström K, Hellborg R (eds.); Proceedings of the International Conference on Applications of High Precision Atomic & Nuclear Methods.

Magnusson Å and Stenström K. 2005. Determination of organic and inorganic ^{14}C on ion-exchange resins – Method description. Lund University, Internal report LUNFD6/NFFR-3097.

Magnusson Å and Stenström K. 2005. ^{14}C produced in Swedish nuclear power reactors - Measurements on spent ion-exchange resins, various process water systems and ejector off-gas. Swedish Nuclear Fuel and Waste Management Company, SKB Report R-05-78.

Magnusson Å. 2005. Carbon-14 generated by nuclear power reactors – investigations including ion-exchange resins and environmental samples. Lund University, Licenciate Dissertation.

Adlienė D, Rääf C, Magnusson Å, Behring J, Zakaria M, Adlys G, Skog G, Stenström K, Mattsson S. 2006. Assessment of the environmental contamination with long-lived radionuclides around an operating RBMK reactor station. Journal of Environmental Radioactivity, Vol. 90, pp. 68–77.

Stenström K, Leide Svegborn S, Magnusson Å, Skog G, Zakaria M, Mattsson S. 2006. Analysis of ^{14}C at nuclear facilities, industries and laboratories. Final Report to the Swedish Radiation Protection Authority on project SSI P 1378. Lund University, Internal Report LUNFD6/NFFR-3101.

Magnusson Å, Stenström K, Aronsson P-O. 2007. Characterization of ^{14}C in process water systems, spent resins and off-gas of Swedish LWRs. Lund University, Internal Report LUNFD6/NFFR-3102.

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Abbreviations

BDCU	Blow-Down Clean-Up system
BTRS	Boron Thermal Regeneration System
BWR-HWC	Boiling Water Reactor-Hydrogen Water Chemistry
BWR-NWC	Boiling Water Reactor-Neutral Water Chemistry
CANDU	CANada Deuterium Uranium
CCU	Condensate Clean-Up system
LILW	Low- and Intermediate-Level Waste
LSC	Liquid Scintillation Counting
LWR	Light Water Reactor
NPP	Nuclear Power Plant
NVOs	Non-volatile Organic Compounds
PWR	Pressurized-Water Reactor
RBMK	Channelized Large Power Reactor (Russian acronym)
RWCU	Reactor Water Clean-Up system
SFPCU	Spent Fuel Pool Clean-Up system
SFR	The Swedish final repository for radioactive operational waste
SKB	Swedish Nuclear Fuel and Waste Management Company
SKI	Swedish Nuclear Power Inspectorate
SSI	Swedish Radiation Protection Authority
WPCU	Waste Processing Clean-Up system

Contents

1. Introduction and Aims of the Study

Carbon-14 is usually thought of as a naturally occurring radioactive nuclide. Indeed, its natural and continuous production in combination with a long half-life is what enables age determination of biological materials by ^{14}C dating. However, with the advent of the Atomic Era, additional ^{14}C has been, and still is, being supplied to the atmosphere and hydrosphere from man-made sources. The ^{14}C produced by anthropogenic activities, such as nuclear weapons explosions and nuclear power plants (NPPs), eventually becomes part of the carbon found in the biosphere, just as the natural ^{14}C. As ^{14}C is an isotope of carbon, its behaviour in nature is the same as the stable (i.e. non-radioactive) isotopes ^{12}C and ^{13}C. Consequently, ^{14}C is found in all contemporary materials containing carbon, such as the air we breathe (containing CO_2) and the food we ingest; the latter being the main pathway for ^{14}C intake by humans (UNSCEAR 2000). Since ^{14}C decays by emitting a beta particle of low energy, the radiation may only cause cell damage if emitted inside the body. The radiation dose we receive from naturally occurring ^{14}C is low compared to that received from other natural sources of radiation (<1%). Nevertheless, it constitutes a potential health hazard, whose additional production by anthropogenic sources of today will result in an increased radiation exposure to many future generations.

The characteristics of ^{14}C that distinguish it from many other radionuclides produced by nuclear power operation, are the long half-life of 5730 years and ease of assimilation into living matter. Furthermore, releases of gaseous ^{14}C compounds also result in a global dispersion of the nuclide. The consequence is that the total dose resulting from the release of all radionuclides from nuclear power reactors generally is dominated by the contribution from ^{14}C (see e.g. UNSCEAR 2000; Ringhals AB 2003, 2004, 2005, 2006; Forsmarks Kraftgrupp AB 2003, 2004, 2005, 2006, 2007). Therefore, there are several reasons for investigating and characterizing reactor-produced ^{14}C. The reasons behind the research presented in this thesis are related to: health issues, legal issues and economical issues.

The research connected to *health issues* concerns studies of environmental levels of ^{14}C in the surroundings of different nuclear power plants. An excess of ^{14}C in environmental samples (i.e. activities above the contemporary ^{14}C background), such as plants, may be found in the close vicinities of power plants due to the release of, above all, gaseous waste containing ^{14}C. Since the excess will result in an additional dose to the local population, these studies are of importance for radiological protection.

The studies connected to *legal issues* concern quantifying ^{14}C in solid waste generated from nuclear power plants. To minimize the potential impact on health related to nuclear waste disposal, and releases at the power plant site, ^{14}C is controlled by the authorities through regulations. Quantification of ^{14}C in the waste generated allows estimation of the total amount of ^{14}C stored in disposal facilities. Such studies are therefore of importance to verify that the amount is within the stipulated limits.

The *economical issues* of reactor-produced ^{14}C are consequences of the legal issues. The stipulated waste and disposal criteria are often more stringent regarding ^{14}C than for other radionuclides (e.g. IAEA 2002b, 2004). Therefore, the amount of ^{14}C in the waste may dictate the choice of disposal method (shallow or deep repository, i.e. cheap or expensive), as well as limit further disposal of waste in a facility (Yim and Caron 2006; see also SSI 2007a). Minimizing the amount of ^{14}C in solid waste is therefore of importance to nuclear power operators, as well as being able to control and direct ^{14}C to different waste streams.

The Papers on which this thesis is based present the results of specific studies, and the perspective is naturally limited. In the following text my intention is to put the results and my research in a wider perspective, in terms of interpretation and reflections in relation to the underlying issues discussed above. This thesis starts with fundamental background on ^{14}C and research-related issues. The following chapter gives the background to the problems related to reactor-produced ^{14}C. The thesis is concluded with a summary of the results, which are then discussed in the light of the above mentioned aspects.

2. Background

2.1 Carbon-14

2.1.1 Natural production

The radioactive nuclide ^{14}C, the half-life of which is 5730 y, has always been present on earth due to the natural and continuous production taking place in the upper atmosphere. Production mainly occurs through the irradiation of ^{14}N by neutrons of cosmic origin, at an estimated rate of 1.5×10^{15} Bq/y (UNSCEAR 2000). Once produced, ^{14}C is integrated into atmospheric carbon dioxide (CO_2) and mixed throughout the atmosphere and hydrosphere, where the oceans represent the major reservoir. Since CO_2 is absorbed by plants through photosynthesis, ^{14}C eventually becomes incorporated into all living organisms, including humans (through ingestion or inhalation of ^{14}C). This means that the ratio of ^{14}C to stable carbon (^{12}C and ^{13}C) in living organisms will be approximately the same as that in the CO_2 in the surrounding air. About 10^{-10}% of the total carbon supply in the atmosphere, and consequently also in humans, is ^{14}C; the rest being ^{12}C (98.9%) and ^{13}C (1.1%). This small amount corresponds to a ^{14}C *specific activity* of about 230 Bq/kg C (Bq per kg carbon). Assuming that an average person contains 16 kg of carbon (ICRP 1974), this gives a total ^{14}C activity of about 4000 Bq/person. Since ^{14}C emits weak beta radiation (maximum energy 156 keV), it does not constitute an external radiation hazard to humans, but may only induce damage once inside the body. Assuming that the beta radiation is absorbed uniformly in the body and taking the varying sensitivity of different organs and tissues into account, this 4000 Bq correspond to an *effective dose* of about 12 µSv/y. The total background radiation in Sweden (including cosmic radiation and naturally occurring radionuclides such as ^{222}Rn and ^{40}K) is about 2 mSv/y [1] (SSI 2003d), i.e. more than two orders of magnitude higher.

2.1.2 Anthropogenic influence

The absolute as well as the relative amount of ^{14}C (^{14}C relative to stable carbon) in the biosphere depends not only on the natural production but also on anthropogenic activities. These activities may influence the specific activity of ^{14}C on a global scale, as well as on a local scale. Over the past two centuries, the specific activity of ^{14}C in the atmosphere has been influenced by anthropogenic activities related to the burning of fossil fuels. Combustion of fossil fuels introduces stable CO_2 into the atmosphere (i.e.^{14}C-depleted CO_2 since the age of the fossil material is much larger than the half-life of ^{14}C), and therefore has a diluting effect. This effect is called the Suess effect and accounted for a reduction of the ^{14}C specific activity of a few percent between 1850 and 1950 (Oeschger et al. 1975).

After 1950, the Suess effect has been overshadowed by other anthropogenic activities, such as nuclear explosions and nuclear power reactors which result in an additional production of ^{14}C owing to their high neutron fluxes. The most significant

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[1] Assuming you are a non-smoker; smokers receive an effective dose of 7 mSv/y (SSI 2003d).

source was by far the atmospheric nuclear tests which took place from 1945 until 1980 (UNSCEAR 2000). Nearly all the neutrons from a nuclear explosion in the atmosphere are captured by nitrogen atoms, resulting in the formation of ^{14}C (Latter and Plesset 1960). The maximum atmospheric ^{14}C specific activity in the northern hemisphere (where most of the nuclear testing took place) was reached in 1963 (~450 Bq/kg C) and was twice the natural specific activity (Levin and Kromer 2005). Since the peak in 1963, atmospheric ^{14}C levels have steadily decreased due to mixing with the biosphere and oceans. The ^{14}C specific activity of atmospheric CO_2 today is only about 7% above the level of that prior to the weapon tests, i.e. ~240 Bq/kg C, constituting the contemporary ^{14}C background (Levin and Kromer 2004).

Today, the major anthropogenic ^{14}C producer is the nuclear power industry, comprising about 440 nuclear power reactors worldwide and a few fuel reprocessing plants. Carbon-14 is produced in all types of reactors, mainly through neutron-induced reactions with isotopes of carbon, nitrogen and oxygen. The nuclides of most significance, ^{13}C, ^{14}N and ^{17}O, are present in the fuel, fuel cladding, coolant, moderator and structural materials of the reactor (IAEA 2004). The mechanisms and cross sections for the reactions of interest are listed for different neutron energy regimes in Table 1. The ^{14}C produced in the solid materials is generally not available for release at the power plant site. However, upon fuel reprocessing, a significant part of the ^{14}C retained in the fuel and cladding is discharged (IAEA 2004), as both gaseous and liquid releases (UNSCEAR 2000). In most types of reactors, the dominating source of ^{14}C release from the power plant site is the moderator and/or the coolant. The major part of these releases is in the form of $^{14}CO_2$ (IAEA 2004). Increased levels of $^{14}CO_2$ in the air may give rise to an additional dose on a local scale, due to the absorption of $^{14}CO_2$ by plants in the vicinity of the power plants, but also globally due to dispersion of gaseous compounds in the atmosphere (UNSCEAR 2000). Hydrocarbons such as methane, are not able to enter the food chain (i.e. not assimilated by plants) in their original form and, therefore, will only contribute to the global dose after being oxidized to $^{14}CO_2$ (UNSCEAR 2000; Ehhalt 1973).

The total gaseous ^{14}C releases from all operating nuclear power plants (1.1×10^{14} Bq/y), as well as the total ^{14}C releases (gaseous and liquid) from fuel reprocessing plants (3.7×10^{13} Bq/y), are illustrated in Figure 1. The annual release rates (average value over the years 1995–1997; calculated from UNSCEAR 2000) are in the figure shown in relation to the natural production rate of ^{14}C (1.5×10^{15} Bq/y) and to a roughly estimated value of the total annual amount of ^{14}C produced in nuclear reactors (1.1×10^{15} Bq/y; calculated from data in IAEA 2004 for the year 1998). The latter includes all sources of ^{14}C production in the reactors.

Table 1. Neutron activation reactions and cross sections for the production of ^{14}C for different neutron energy regimes, including abundance of target element (data from OECD Nuclear Energy Agency 1997; Forrest et al. 2002; Firestone et al. 1996).

Neutron-induced reaction	Natural isotope abundance of target element	Cross section (barn)		
		Thermal	Resonance integral	Fission
^{17}O (n, α) ^{14}C	0.038%	0.235	0.106	0.095
^{14}N (n, p) ^{14}C	99.6%	1.82	0.818	0.0355
^{13}C (n, γ) ^{14}C	1.1%	1.37×10^{-3}	5.93×10^{-4}	5.16×10^{-5}

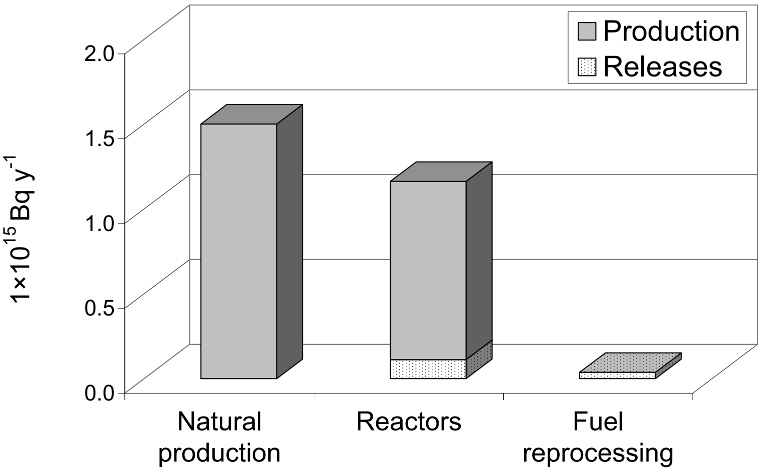

Figure 1. Natural production of ^{14}C versus the production and releases from nuclear power reactors and fuel reprocessing plants. The release rates represent those of 1995–1997 (UNSCEAR 2000). The total production in nuclear reactors represents an estimate of 1998 (IAEA 2004).

The amount of ^{14}C produced by a specific reactor, as well as the chemical forms of ^{14}C and the pathways by which it can be released to the environment, depends on the design of the reactor system and the operating conditions. Therefore, a brief introduction to the major reactor types in commercial operation, including basic design parameters and ^{14}C production sources, will be given in the following section.

2.2 Nuclear power reactors

Generally, the reactors used to produce electricity commercially are classified by their coolant systems and moderators, resulting in four major types (UNSCEAR 2000; IAEA 2002c).

- Light-water-cooled and -moderated reactors (LWRs), comprising pressurized water reactors (PWRs) and boiling water reactors (BWRs).
  - Heavy-water-cooled (under pressure) and -moderated reactors (PHWRs). The Canadian-designed CANDU (CANada Deuterium Uranium) reactor is presently the only commercially available PHWR.
  - Gas-cooled and graphite-moderated reactors (GCRs).
  - Light-water-cooled and graphite-moderated reactors (LWGRs). The Russian-designed RBMK (Russian acronym for Channelized Large Power Reactor) is presently the only commercially available LWGR.

The LWR is by far the most common reactor type used to generate electrical energy in the world (UNSCEAR 2000) and the only type presently existing in Sweden. Sweden has today (2007) three operating PWRs and seven operating BWRs. The PWR units are all located at the Ringhals NPP. The Oskarshamn NPP and Forsmark NPP have three BWR units each, and the seventh unit is located at Ringhals NPP. Two additional BWR units at Barsebäck have been permanently shut down.

This thesis presents the results of measurements carried out on 3 PWRs (Sweden), 6 BWRs (Sweden), 2 RBMKs (Lithuania) and a CANDU reactor (Romania). The studies related to Swedish PWRs and BWRs concern the behaviour of ^{14}C *inside* the reactor units (in terms of production, waste generation and release paths), whereas the study related to RBMK and CANDU reactors concerns the behaviour of ^{14}C *outside* the reactor units, i.e. the ^{14}C released to the surrounding environment (in terms of distribution and concentration of ^{14}C in biota). The basic design and construction features of the reactor types investigated are given in the following sections.

2.2.1 PWRs

The main process in PWRs (see e.g. Neeb 1997; Choppin et al. 2002; KSU 2004) relies on two major systems referred to as the primary and the secondary system. The main components of the primary system are the reactor pressure vessel, the reactor coolant pumps, a pressurizer and the steam generators. The primary system transfers the heat from the fuel to the steam generator, where the secondary system begins. The secondary system comprises the turbines, the generator and the condensate and feedwater systems. An overview of the systems of interest is shown in Figure 2.

The heat transport medium in the reactor vessel, referred to as the reactor coolant, consists of ordinary water, which also acts as moderator (i.e. slowing down the neutrons to increase the probability of fission). The reactor coolant is circulated in a closed loop through the reactor core and the steam generators (i.e. the primary circuit) and is kept under high pressure to prevent boiling. The steam generators act as heat exchangers in which the heat is removed by passing the reactor coolant through narrow tubes surrounded by water at a lower temperature and pressure. The absorbed heat causes the water in the secondary circuit to boil; the steam being generated being directed to the turbines. After passage through the turbines, the steam is directed to another heat exchanger, the condenser, where the steam is condensed by passing it over tubes containing cold sea water. The condensate is then pumped back as feedwater to the steam generators for reuse. Since the primary and secondary circuits are separated from each other by the steam generator tube walls, the secondary circuit should be free from ^{14}C and any other radioactivity. This is an important aspect compared to BWRs, which have only one main circuit, resulting in high activity levels on the turbine side and in the condenser.

A coolant purification and chemistry control system is connected to the primary circuit. The purification system consists of ion-exchange resins with the main task of removing fission products and activated corrosion products present in the water. The primary circuit purification system is here referred to as the Reactor Water Clean-Up system, RWCU (referred to as “mixed bed demineralizers” in Figure 2). There are a number of other clean-up systems apart from the RWCU.

The fraction of ^{14}C produced in PWRs available for release, is that formed in the reactor coolant. Gaseous releases constitute the main release path from this source; the rest being accumulated in the ion-exchange resins or released as liquid discharges. PWRs

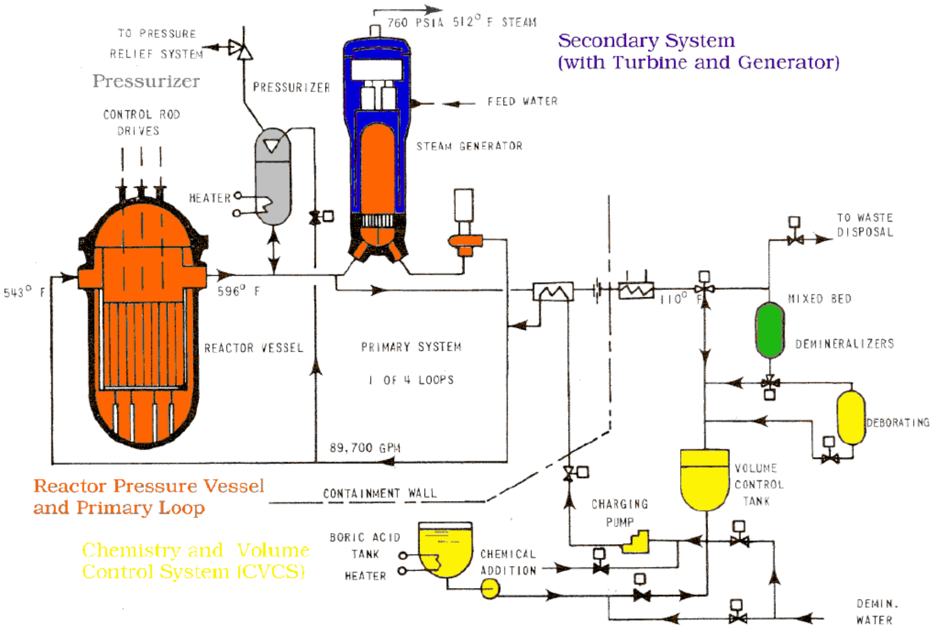

Figure 2. Overview of the process systems of interest in a PWR (the numerical values are not identical to those describing Swedish units). The figure has been taken from Compendium E-114, KSU (2004).

operate under reducing chemical conditions because of the presence of excess hydrogen. Therefore, the major part of the ^{14}C present in the reactor coolant will be in the form of reduced compounds, i.e. organic compounds. Consequently, the gaseous releases comprise mainly hydrocarbons such as methane (see e.g. IAEA 2004). Gaseous compounds are released from the reactor coolant system by venting of the volume control tank (see Figure 2). Depending on the frequency of venting, the gaseous releases will be more or less discontinuously discharged.

2.2.2 BWRs

In boiling water reactors (see e.g. Neeb 1997; Choppin et al. 2002; KSU 2004), the heat generated in the reactor core is removed by boiling water, i.e. a mixture of water and steam. The steam produced is then directly conducted to the turbines. After passing the turbines, the steam is condensed in the condenser and the condensate purified by ion-exchange resins in the condensate clean-up system (CCU), and then finally recycled back to the reactor pressure vessel. An overview of the systems of interest is presented in Figure 3. The lack of steam generators and a secondary circuit, as in PWRs, makes the design of BWRs less complex, but at the expense of radionuclides being able to reach the turbines. Therefore, these must be shielded during normal operation, complicating maintenance during operation. The fact that the fuel elements are surrounded by boiling water makes

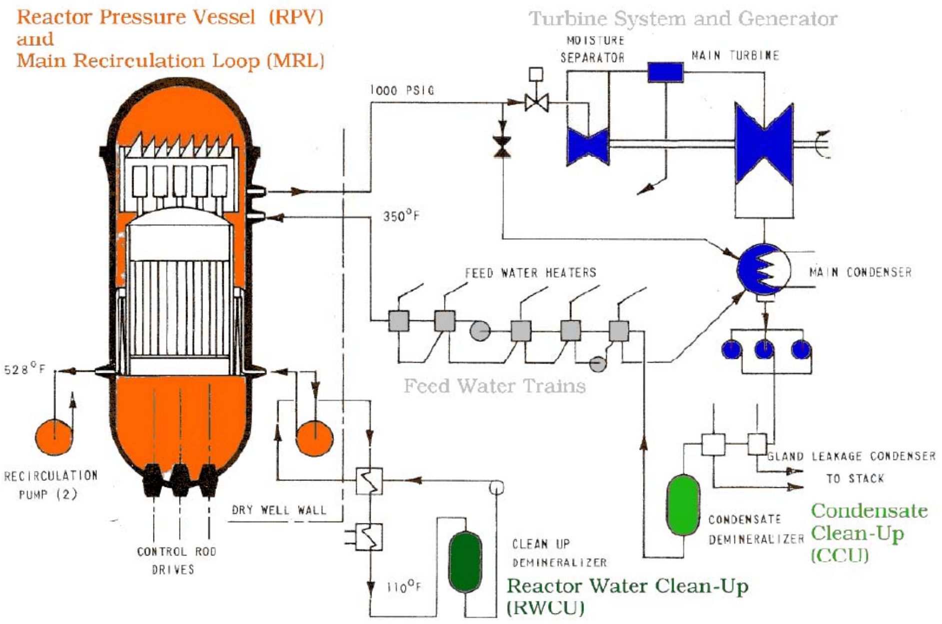

Figure 3. Overview of the process systems of interest in a BWR. The figure has been taken from Compendium E-114, KSU (2004).

BWRs very susceptible to impurities, such as corrosion products, in the reactor water. This is because the non-soluble compounds will be concentrated in the water phase and deposited onto e.g. fuel cladding surfaces (crud formation), which is highly undesirable. To restrict the concentration of impurities to a minimum, BWRs have a special RWCU (see Figure 3), usually consisting of mixed-bed ion-exchangers. Apart from the RWCU and CCU, several other important clean-up systems, exist.

As in PWRs, the production of ^{14}C in the coolant is also the source of the release of ^{14}C from BWRs. The design of BWRs, having only one circuit, leads to a continuous discharge of ^{14}C through the stack. The remaining fraction of the ^{14}C formed in the coolant is absorbed in the ion-exchange resins or released as liquid discharges. BWRs operate under oxidizing chemical conditions; consequently, the gaseous releases mainly comprise CO_2 (see e.g. IAEA 2004). Two different modes of operation, related to the water chemistry in the reactor coolant, are employed in BWRs: hydrogen water chemistry (HWC) or neutral water chemistry (NWC). The latter mode is employed at the majority of the Swedish BWR units, referred to as BWR-NWC units.

2.2.3 CANDU reactors

The CANDU reactor (see e.g. IAEA 2002a; CANTEACH 2004) is a pressurized heavy-water reactor fuelled with natural uranium and moderated and cooled by heavy water (D_2O). Different designs of CANDU reactors have been developed over the years. The most modern class of CANDU reactors in commercial operation today is the CANDU 6 reactor, which is a 700 MW_e (gross capacity) reactor, with 10 units in operation worldwide.

The reactor core is contained in a cylindrical tank, called a calandria, which holds the heavy-water moderator at low temperature (<80°C) and low pressure. The moderator tank is penetrated by a large number of horizontal fuel channels, through which pressure tubes containing fuel bundles are inserted. The fuel is cooled by heavy water pumped through the pressure tubes and the heat is transported to steam generators (system referred to as the heat transport system), where steam is produced in a secondary circuit containing light water. The steam is transported to the turbines and the heavy-water coolant redirected through the pressure tubes. The annulus between each pressure tube and its outer tube (called the calandria tube) is filled with an annulus gas, CO_2, which insulates the cool moderator from the hot heat transport system.

In general, ^{14}C production in CANDU reactors is higher than in both LWRs and RBMKs. The reason for this is the large mass of D_2O moderator which has a higher isotopic abundance of ^{17}O than H_2O. However, because of the chemical conditions prevailing in the moderator, most of the ^{14}C formed will be absorbed on the ion-exchange resins. Therefore, the amount of ^{14}C released with gaseous emissions is greatly reduced, but is still above the release rates from other types of commercial reactors (IAEA 2004; UNSCEAR 2000). In early CANDU designs, nitrogen was used as annulus gas instead of CO_2, causing significantly higher production and release rate of ^{14}C (owing to the high cross section of the $^{14}N(n,p)^{14}C$ reaction, see Table 1). According to UNSCEAR (1993, 2000), the gaseous ^{14}C releases from the early types were one order of magnitude higher than those of the present CANDU 6 reactors. Most of the ^{14}C is released in the form of $^{14}CO_2$ (e.g. Sohn et al. 2003).

2.2.4 RBMKs

RBMKs are light-water-cooled, graphite-moderated reactors with pressure tubes (see e.g. Neeb 1997; Almenas et al. 1998). The reactors are divided into two different classes; RBMK-1000 and RBMK-1500, where the numbers refer to the designed gross electrical power capacity. The only two existing reactor units of class RBMK-1500 are located at Ignalina in Lithuania. However, unit I at the Ignalina NPP has recently (2004) been shut down.

The cylindrical reactor core is made of graphite bricks, which are penetrated by some 1700 vertical, pressurized cooling channels, into which the fuel assemblies are inserted. The heat is removed by the light-water coolant, fed from the bottom of the channels, and the steam generated in the reactor is directed to the turbines. The principle of electricity generation is therefore the same as for BWRs. To prevent graphite oxidation and to improve heat transfer from the graphite to the fuel channels, the reactor space is filled with a helium-nitrogen mixture.

Production rates calculated by Gaiko et al. (1986) indicate that ~90% of the total ^{14}C formed is produced in the graphite moderator; however, not expected to be available for release. Instead, the source responsible for most of the gaseous ^{14}C emission is the extensive use of nitrogen gas (Gaiko et al. 1986; Konstantinov et al. 1989). The ^{14}C releases from RBMKs are expected to be mainly in the form of CO_2 (Konstantinov et al. 1989; Gaiko et al. 1986).

2.3 *Nuclear waste and releases*

2.3.1 Generation and release paths

The releases at the power plant site comprise gaseous and liquid releases containing a broad spectrum of radionuclides, being fission products (e.g. ^{133}Xe), activated corrosion products (e.g. ^{60}Co) and products from the activation of water (e.g. ^{3}H and ^{14}C). Gaseous compounds, such as ^{133}Xe and $^{14}CO_2$, are released to the air from the main stack at the power plant after passage through a gas delay system. Gaseous releases from the main stack are monitored, but the extent of the monitoring programme differs depending on the regulations of each country (see e.g. IAEA 2004). Monitoring of ^{14}C in gaseous releases from Swedish NPPs has been required by the Swedish Radiation Protection Authority (SSI) since 2002 (SSI 2000). Also the liquid releases are subjected to monitoring of the activity concentration of certain nuclides. However, since ^{14}C is not believed to be present at significant amounts, this nuclide is not included in the monitoring programmes (although France appears to be an exception according to the data given in CEPN 2005).

Non-volatile radioactive compounds, such as corrosion products and water-soluble compounds, are captured in various purification systems connected to several systems of the reactor. These purification systems consist of ion-exchange resins (see e.g. IAEA 2002b) intended to keep the concentration of impurities in the different process water systems to a minimum. The ion-exchange resins consist of a polymer matrix with positively or negatively charged sites that attract ions of the opposite charge present in the process water. Depending on the charge of these sites, the resin will function either as a cation exchanger or an anion exchanger. Normally, anionic and cationic resins are mixed together as beads or powder in order to remove all ions from the water. This is called a mixed-bed ion-exchanger and is widely used in Swedish LWRs.

Since the concentration of impurities is highest in the moderator/reactor coolant, the RWCU is the most important purification system. As the reactor water is continuously purified, ionic species such as $^{60}Co^{2+}$ and $H^{14}CO_3^-$ will be adsorbed onto the ion-exchange resins, where they will be concentrated. After use, spent ion-exchange resins are generally immobilized (using cement or bitumen) and disposed of as low- or intermediate-level waste (LILW). The activity contained in the spent resins constitutes a major fraction of the total activity contained in the various waste forms disposed of in LILW disposal facilities worldwide.

2.3.2 Waste disposal

The nuclear waste generated from power plants is characterized by its activity level. *Very-low-level waste* consists of contaminated clothing, tools, paper, etc. This type of waste is generally disposed of at a shallow burial site located in the close vicinity of the power plant. Sweden has four such sites, requiring ~50 years of radiological control, after which the waste is considered to be non-hazardous.

Low- and intermediate-level waste consists of operational waste such as spent ion-exchange resins, scrap metal and filter cartridges. In most IAEA countries, LILW is disposed of in so-called near-surface facilities at a depth of about 10 metres or less (Han et al. 1997). Most of these facilities are engineered concrete structures, as used in the UK, France and Spain, while some countries have more simplified facilities, such as those used in the USA and South Africa (Han et al. 1997). The Swedish LILW facility for operation waste, the SFR, is a mined cavity located about 50 metres below the sea floor off the coast from the Forsmark NPP, see Figure 4. The facility is operated by the Swedish Nuclear Fuel and Waste Management company, SKB, owned by the utilities operating Swedish NPPs. The SFR comprises four rock caverns and a concrete silo; the latter of which is expected to contain 92% of the total activity at the time of repository closure (SKB 2001b). The concrete silo is mainly intended for the disposal of spent ion-exchange resins (SKB 2001b). Regulations for the operation of the SFR are issued by the SSI and comprise regulations such as nuclide-specific disposal limits and dose limits for releases today and in the future. To verify that the operation of the SFR complies with the regulations issued, SKB must conduct a safety analysis – assessing the long-term performance and environmental consequences of the repository – every 10 years. The final safety report will be reviewed by the SSI and the Swedish Nuclear Power Inspectorate (SKI) (SKI 2004; SSI 2004).

High-level waste (HLW) consists of spent nuclear fuel, for which there are no existing disposal facilities anywhere in the world. A Swedish repository for high-level waste is intended to be in operation by 2018 (SKB; www.skb.se).

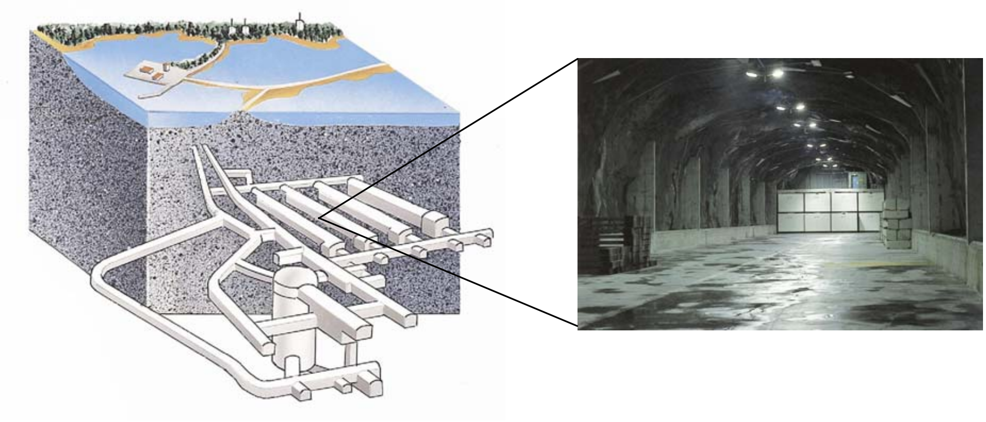

Figure 4. Schematic illustration of the underground part of the Swedish LILW facility, SFR, located below the sea floor off the coast from the Forsmark NPP. The close-up to the right shows waste packages in one of the rock caverns. The figures have been taken from the homepage of SKB (www.skb.se; photo: Bengt O Nordin).

3. ^{14}C Analysis Techniques

The samples studied in this thesis comprise environmental samples, collected *outside* reactor units (Papers II and III) and samples of various process media, collected *inside* the reactor units (Papers I and IV–VI). The activity levels of the samples differ significantly depending on the origin. Therefore, different analysis techniques have been utilized or developed for the environmental samples (low activity) and the samples of process media (high activity). Since the latter samples contain a relatively high amount of ^{14}C, the counting technique selected – liquid scintillation counting (LSC) – is based on decay counting, where the number of disintegrations is registered. However, applying the same technique to the environmental samples would be extremely time-consuming or even impossible due to its relatively high detection limit. Instead, the technique of accelerator mass spectrometry (AMS) was used, which counts the single atoms of ^{14}C instead of waiting for them to decay. Both counting techniques utilized require the carbon to be extracted from the original sample prior to the measurement. The extraction step is generally the most time-consuming part of ^{14}C analysis.

3.1 Low-activity samples

Accelerator mass spectrometry (see e.g. Fifield, 1999) allows the actual number of atoms of a certain radionuclide in the sample to be measured, instead of waiting for the nuclides to decay. This highly sensitive atom counting technique is an extension of conventional mass spectrometry, but instead of accelerating the ions to keV energies, the ions are accelerated to MeV energies using an electrostatic accelerator. Because of the high energy, interference from abundant neighbouring isotopes and atomic and molecular isobars is suppressed. The result is a thousand-fold increase in sensitivity in isotope concentration measurements compared with the LSC technique used for the high-activity samples. The results reported in Paper II were obtained using the 3 MV AMS facility at the Department of Physics in Lund (see e.g. Skog et al. 2001), while the majority of the samples referred to in Paper III were measured at the 250 kV Single Stage AMS facility in Lund (see Skog 2007). By using AMS, the ^{14}C specific activity of a sample can be determined, which means that the ratio of ^{14}C to a stable carbon isotope (^{12}C or ^{13}C) can be determined. The ratio obtained is compared to that in a standard sample, the ^{14}C specific activity of which is known.

The low-activity samples were prepared using the extraction method developed by Stenström et al. (1995). This method is based on combustion of the sample followed by CO_2 reduction over a catalyst, which converts the sample into elemental carbon (graphite), which is a sample target compatible with the AMS system.

3.2 High-activity samples

Liquid scintillation counting (see e.g. Mäkinen 1995; Passo and Cook 1996) is a common technique for measuring the activity of low-energy beta emitters such as ^{14}C and ^{3}H. In LSC, the sample is suspended in a cocktail containing a solvent and the scintillator, which is an organic liquid that fluoresces when energized. A beta-particle emitted from the sample will therefore generate numerous photons by scintillation. These photons are detected by photomultiplier tubes, where an electrical pulse is generated. The number of pulses generated is proportional to the number of disintegrations, i.e. the activity of the measured sample. Different counters have been used throughout the project, including a Wallac Rackbeta 1217, Wallac Guardian 1414, Packard TriCarb 2100TR and a Beckman LS6500.

No reliable extraction method was available for the high-activity samples studied in this thesis. Therefore, such a method was developed within the project; see Sections 4.3 and 5.2.

4. Problems Associated with ^{14}C in Waste and Releases

4.1 Disposal issues

Disposal of waste containing ^{14}C is associated with stringent waste acceptance requirements. The inventory of ^{14}C in a disposal facility may therefore pose a significant problem to the operator when it comes to complying with regulations on e.g. disposal limits and dose limits stipulated for the facility. Therefore, a reliable estimate of the amount of ^{14}C contained in a certain facility is of considerable interest to the operators as well as to the authorities.

Carbon-14 has been recognized as one of the most important radionuclides in the assessment of doses arising from LILW disposal facilities. According to UNSCEAR (2000), the collective effective dose from LILW disposal is expected to be almost entirely due to ^{14}C. Therefore, disposal limits for ^{14}C at disposal facilities for LILW have generally been set by the regulatory body of each country. However, actual measurements of the ^{14}C content in the waste are rarely conducted due to the difficulty in measuring ^{14}C (see Section 4.3). Therefore, the estimated total ^{14}C activity in a disposal facility is highly uncertain, despite the concern accompanying the radionuclide. The general approach to estimating the content of single waste packages, as well as total ^{14}C inventories, is the use of scaling factors (see e.g. James 2006). A scaling factor is based on the ratio between a nuclide that is difficult to measure and a key radionuclide, the latter being an easily measured, gamma-emitting nuclide. The scaling factor applied to estimate ^{14}C assumes that the concentration of ^{14}C in solid waste is correlated to the concentration of ^{60}Co. The ^{14}C/^{60}Co ratio (i.e. the scaling factor) may be based on experimental data, theoretical assumptions and modelling, or on both. Different scaling factors may be applied depending on the waste stream, or a generic value may be applied to all waste streams and total inventories.

In Sweden, SKB uses a generic scaling factor to estimate the total ^{14}C inventory in the SFR (SKB 2001b). This has been criticized by the SSI and SKI in the review of the latest safety report (SKI 2004; SSI 2004) due to the high uncertainties in the factor chosen (Lindgren et al. 1998; see also e.g. Lundgren et al. 2002; James 2006). During the review process, the committee came to the following conclusion regarding the scaling approach used by SKB: "*…the possibility can not be excluded that the inventory of ^{14}C, in particular the organic fraction, may exceed allowable limits*" (SSI 2003b). This was the main reason why SSI restricted the operation of the SFR in 2003 (SSI 2003b), by suspending disposal of spent ion-exchange resins from the Ringhals plant. Since spent resins are the dominating type of operational waste in the SFR (Ingemansson 2001), the ^{14}C inventory is expected to be almost entirely governed by the amount contained in the resins. At the same time (2003), SSI demanded an updated estimation of the inventories to be made by SKB of the most important radionuclides, especially ^{14}C (SSI 2003c).

In the review of the latest safety analysis report, SSI and SKI further state that, "*From the perspective of disposal, the chemical form of the carbon-14 produced is of considerable importance for the waste properties*" (SSI 2004; SKI 2004). The chemical form here refers to organic versus inorganic carbon compounds. Organic and inorganic compounds are governed by different retention mechanisms during migration within the waste package as well as during transport outside the disposal facility. In the case of ^{14}C released from a deep repository, such as the SFR, only the organic ^{14}C compounds usually contribute to the total dose due to their high solubility and lack of retardation during transport (Johnson and Schwyn 2004; Niemayer et al. 2004; Lindgren et al. 2001). In most of the future release scenarios modelled by Lindgren et al. (2001) for the SFR, organic ^{14}C is the main contributor to the total dose received by individuals in the vicinity of the facility, i.e. the critical group, as well as having the highest release rate. The base scenario yielded a maximum total dose (received by an individual of the critical group) of 4 μSv/y, received 3000 years after repository closure. The risk criterion determined by SSI (SSI 1998)[2] corresponds to approximately 15 μSv/y. The modelling performed by Lindgren and colleagues therefore indicates that future releases from the SFR will fulfil the stipulated criterion. However, the model is based on the ^{14}C inventory given by Riggare and Johansson (2001) and the assumption that 10% of this inventory, at the time of closure, is in the form of organic ^{14}C (SKB 2001b). SSI and SKI criticized the assumption made by SKB (SKI 2004; SSI 2004) in the safety analysis report of the SFR (SKB 2001b), probably due to the lack of experimental data supporting the assumed fraction of 10%, and the fact that organic ^{14}C seems to be the most important constituent arising from the SFR from a dose perspective.

On behalf of SKB, we conducted the first Swedish study related to the quantification of ^{14}C in spent resins. Due to the significance of the chemical form, separate analyses of organic and inorganic ^{14}C compounds in the samples were conducted. The aim was to obtain experimental data which were to serve as a basis for more reliable estimates of the ^{14}C inventory of the SFR. The results obtained from the analysis of spent resins are given in Papers IV and VI; additional details can be found in Magnusson et al. (2005b, 2007). A summary of the experimental results is presented in Section 5.3.1. Although not initially part of the project plan (SKB order number 9808), we derived a preliminary estimate of the total, as well as the organic, ^{14}C inventory of the SFR at the time of closure, which is presented in Paper IV. A final estimate, based on updated calculations, including estimation of uncertainties, is given in Magnusson et al. (2007). The implications of the results from the study are discussed at the end of Section 5.3, including suggestions on future work.

4.2 Source control

Depending on the regulations associated with the operation of nuclear power plants and disposal facilities, implementation of source control measures for minimizing ^{14}C in waste and releases may be necessary. Providing experimental data and knowledge required for selecting optimum reduction measures are therefore of importance.

IAEA (2004) states that due to the potential impact of ^{14}C on human health "*...it is necessary to control [the] production at nuclear facilities*" and "*...important to control [its] release from nuclear facilities and waste management sites to the environment*". IAEA also stresses the importance of minimizing waste containing ^{14}C, being of relevance not only from a dose perspective but also economically. For countries with a regulated disposal limit for the nuclide, ^{14}C has proven to be a critical nuclide that may dictate the

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[2] The regulated SSI risk criterion, 10^{-6}, corresponds to an annual risk of 0.001‰ for induced harmful effects to an individual of the critical group as a result of the releases from the repository (ICRP 1990).

choice of disposal method (IAEA 2004), as well as being the inventory-limiting nuclide at the disposal facility (Yim and Caron 2006). This is because the waste acceptance requirements are more stringent for ^{14}C than for other radionuclides (IAEA 2004). Disposal of a waste package in a less qualified facility, for example a shallow land burial site, is more economically beneficial to the nuclear waste operators. However, because of the more stringent requirements for waste packages containing ^{14}C, the package may have to be disposed of in a more qualified facility, such as a deep repository, although the package has a low gamma surface dose rate. In the USA, ^{14}C is expected to be the nuclide that limits further disposal of waste in at least one of their two major LILW disposal facilities (Yim and Caron 2006). This means that the facility may have to be closed and sealed before it is completely filled. This economical drawback may be solved by implementing ^{14}C source control measures at the power plant, such as appropriate waste management strategies and practices, or by ^{14}C production control.

In order to control production and release rates, as stressed by the IAEA, as well as selecting appropriate waste management strategies, experimental and/or theoretical data are required. However, existing data are limited and often outdated or unreliable. In a review of the present knowledge on ^{14}C issues in the nuclear power industry, Yim and Caron (2006) concluded, amongst other things, that previous estimates of ^{14}C production in LWRs, most of them going back to the 1970s, were "*...an issue that needs attention to better manage ^{14}C*". Experimental data published on ^{14}C in process media of LWRs are scarce except for gaseous media, i.e. gaseous ^{14}C releases. Most of the existing data on the quantification and characterization of ^{14}C in liquid and solid samples, such as process water (generally reactor water) and spent ion-exchange resins are from investigations performed in the 1980s and the beginning of the 1990s. Besides being old, the data generally lack information on the chemical form of ^{14}C in the media (see Section 4.3); but above all, the investigations were focused on obtaining the absolute concentration of a specific waste form. Optimal waste management requires that the total amounts of ^{14}C in different waste and release streams are compared to each other in order to focus efforts on the crucial release path or process system. Such a study is referred to as a mass balance assessment, and was suggested by Smith et al. (2002) to obtain a realistic estimate of the ^{14}C inventory in the SFR, as well as to investigate the options for managing discharges to air and water instead of uptake in solid waste (i.e. spent resins).

At the request of SKB, ^{14}C from the production source in the coolant, its route through different process water systems, and eventually its fate in solid waste streams and gaseous and liquid releases have been characterised and mapped. This thorough investigation resulted in a mass balance assessment of the ^{14}C produced in Swedish PWRs and BWRs, which was made possible by combining the experimental results with newly calculated production rates. The assessment, as well as the results from the novel calculations of the production rates, is presented in Paper VI. Individual results from the analyses of gaseous, liquid and solid samples of process media are presented in Papers IV, Paper VI and Magnusson et al. (2005b, 2007). A summary of the results from the study of ^{14}C in process water systems is given in Section 5.4. Section 5.5 presents an overview of the results from the mass balance study of ^{14}C in BWRs and PWRs, and is concluded with a discussion on the significance of the investigation.

4.3 Experimental issues

In the nuclear industry, ^{14}C is referred to as one of the difficult-to-measure nuclides. The reason for this is that ^{14}C decays by beta emission; making its detection difficult at the presence of other radionuclides in a sample. To be able to determine its concentration in process media from nuclear reactors, ^{14}C has to be separated from dozens of other radionuclides present (generally gamma-emitters). The difficulty of the separation, as well as the approach used for the extraction, is dependent on the sample type, i.e. gaseous, liquid or solid. The samples studied within the work of this thesis comprised all three types, consisting of spent ion-exchange resins (solid), process water (liquid and gaseous), and a few samples of ejector off-gas (gaseous).

Separation of ^{14}C is most easily accomplished in gaseous samples. Equipment for monitoring ^{14}C in gaseous releases from power plants is today commercially available. However, published data on ^{14}C in liquid and solid samples are scarce; the major reason probably being the extraction and separation difficulties. The basic principle of extracting ^{14}C from a medium is to convert the carbon compounds to CO_2 by either combustion or acidification; see Figure 5 for a comparison of typical system set-ups. The purpose of combustion is to extract all the carbon compounds present, while acid treatment only extracts the inorganic fraction (i.e. carbonates). The carbon dioxide evolved in the process is led to an absorber (usually NaOH solution) by means of a carrier gas. If combustion is employed, a catalytic furnace is used to ensure complete oxidation prior to CO_2 absorption. The ^{14}C activity is determined by mixing a few millilitres of the absorber with a scintillation cocktail and measuring the activity with LSC. To avoid other radionuclides (e.g. ^{3}H) from reaching the absorber, a water trap may be utilized.

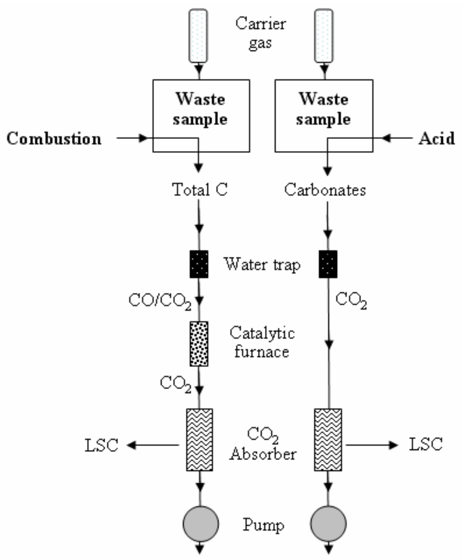

Figure 5. Schematic comparison of system set-ups of the two basic analytical techniques used for ^{14}C determination in process media from nuclear reactors.

Previously developed ^{14}C extraction methods, used for analyses of process water and spent resins, were reviewed (Paper I) to find a suitable method for the present analysis. The majority of the ten methods reviewed were designed to quantify the total ^{14}C concentration or only the inorganic ^{14}C fraction. Since separate determination of organic and inorganic ^{14}C was crucial to our investigation, those methods could not be directly applied. The few methods capable of providing information on the chemical form were considered unreliable due to a lack of satisfactory information on validity and reliability.

By combining existing techniques, a new method was developed for quantifying organic and inorganic ^{14}C compounds separately in samples of various process media. The method was optimized for the analysis of spent ion-exchange resins and process water, resulting in different procedures. The method, together with the validation and reliability of the procedures developed, is presented in Paper V. This paper also includes a further review of previous methods reported in the literature, to which the new method is compared. A description of the development of the method is given in Section 5.2; also including a presentation of the final method and a comparison to the few similar methods existing.

4.4 Environmental considerations

The potential health impact of the gaseous and liquid ^{14}C releases from the power plant site is expected to be of most significance on the local and regional scale due to dilution effects. As mentioned above, the source of these direct releases is the production of ^{14}C in the coolant. Releases from other production sources that might affect the population today (as opposed to releases from LILW disposal facilities affecting future generations), are those from fuel reprocessing plants[3]. The amount of ^{14}C discharged from reprocessing plants is significant. However, it has been extensively studied throughout the years (see e.g. Gray et al. 1995; Cook et al. 2004; Douville et al. 2004; UNSCEAR 2000) and is not further discussed in this thesis.

For all types of reactors except PWRs, most of the ^{14}C released as gas will be in the form of $^{14}CO_2$ (IAEA 2004). Therefore, the environmental effect of the gaseous $^{14}CO_2$ releases may be quantified by investigating the ^{14}C levels in photosynthesizing biota collected from the vicinity of the power plant. In order to determine whether these samples contain any additional ^{14}C, the specific activities obtained (Bq/kg C, i.e. correlated to the ratio: ^{14}C/stable carbon) are compared with those of background samples. The background samples constitute similar types of biota, but are taken from an unaffected site, i.e. only containing the unperturbed contemporary levels of ^{14}C. A large excess of ^{14}C in biota from the power plant site means that the fraction of $^{14}CO_2$ in the air is higher than the natural level, indicating that the site is influenced by gaseous ^{14}C releases. The ^{14}C excess in plants and vegetables will eventually reach humans through food ingestion, which is the main pathway for ^{14}C intake by humans (UNSCEAR 2000). Therefore, the $^{14}CO_2$ releases constitute a potential health hazard due to the additional dose received by the critical group. Studies of the ^{14}C specific activities in the surroundings of nuclear reactors are therefore important for estimates of radiation exposure to the public. Furthermore, studies including

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[3] Currently operational fuel reprocessing plants are located in France, India, Japan, Russia and the U.K. (IAEA 2005).

different types of reactors allow a reactor-type-specific comparison of potential health impact from gaseous ^{14}C releases.

Generally, the release rates of gaseous ^{14}C from different types of nuclear power reactors are in the following order: CANDU>RBMK>BWR>PWR (UNSCEAR, 2000). Therefore, the environmental ^{14}C levels are expected to be higher in the surroundings of CANDU and RBMK reactors than those of BWRs and PWRs. Having already studied the levels in the vicinities of Swedish BWRs, as well as an early type of CANDU reactor (Stenström et al. 2000, 1998), the investigation was supplemented by studying RBMK reactors, as well as a modern type of CANDU reactor. The sites chosen for the study were the Ignalina NPP in Lithuania with two RBMK-1500 units in operation at the time of sample collection, and the Cernavoda NPP with one operational CANDU-6 unit. The RBMK reactors at Ignalina are similar to those previously operated at the Chernobyl NPP; however, differ by several improved safety features.

The ^{14}C levels in samples of grass collected at the Cernavoda site are presented in Paper II together with the first results from the Ignalina study. The ^{14}C specific activities obtained in terrestrial samples (tree leaves and moss) collected in the immediate vicinity of the Ignalina NPP (see Paper II) led to a significantly extended analysis, including new sampling points and objects. The results and a thorough discussion and interpretation are given in Paper III. A comparison of the ^{14}C excess found around the different reactor types studied is also included in Paper III. A summary of the results and their implications are presented in Section 5.1 below.

The amount of ^{14}C discharged with liquid releases from nuclear power plants is believed to be very small, constituting <1% of the gaseous releases (IAEA 2004). Therefore, the resulting dose from this release path should be insignificant. However, the bioaccumulation factor for carbon in fish is one of the highest among the nuclides that could be released from a nuclear power plant (SKB 2001a; UNSCEAR 2000). Therefore, the resulting dose may be significant despite the fact that the release rate is relatively small. The dose perspective together with the fact that the most recent data reported for liquid discharges from LWRs appear to be those of Kunz published in 1985 (Kunz 1985), justified the inclusion of this particular release path in the present studies.

The liquid releases from Swedish reactor units were analysed as part of the SKB projects referred to above and the conclusions are briefly discussed in Section 5.4.2 below. The environmental effects of the releases have also been studied; including samples collected along the Swedish west coast and outside Barsebäck (Stenström et al. 2006), as well as samples of aquatic plants collected outside the Ignalina NPP (Paper III). In Stenström et al. (2006), the ^{14}C levels in marine plants, such as seaweed, were investigated and the ^{14}C excess determined by comparing the ^{14}C specific activities with those of similar plants collected at background sites. Comments on the results presented in Paper III, and on those presented by Stenström et al. (2006), are included in Section 5.4.2.

5. Results and Discussion

5.1 Environmental ^{14}C levels (Papers II and III)

5.1.1 CANDU – Cernavoda

The ^{14}C levels in the grass samples collected 200–4300 m from the power plant were clearly found to be related to the $^{14}CO_2$ releases from the venting stack, see Figure 6. The maximum excess, being 28% above the contemporary background level, was found at the closest sampling point. The excess rapidly decreased with distance from the release source, and was close to zero at about 1000 m. Applying the worst case scenario[4], although unrealistic, the maximum excess would give rise to an additional effective dose being received by the maximally exposed individual, of about 3 μSv/y. The additional dose is insignificant compared with the effective dose resulting from natural radiation sources (worldwide average 2.4 mSv/y; UNSCEAR 2000) and corresponds to ~30% of the dose from the natural production of ^{14}C (12 μSv/y; UNSCEAR 2000).

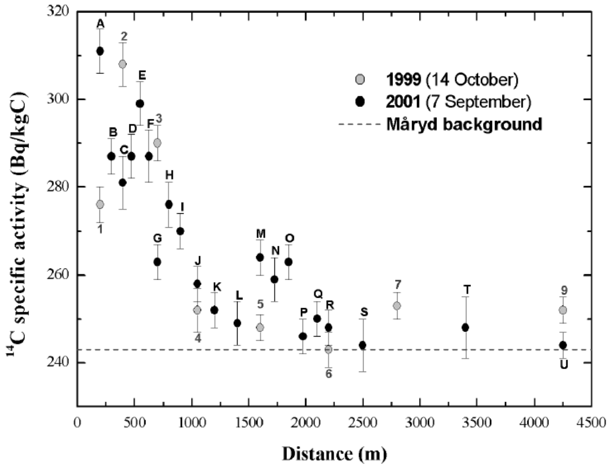

Figure 6. The ^{14}C specific activity (Bq/kg C) found in grass samples collected at increasing distances from the Cernavoda NPP. The background ^{14}C activity was determined from samples of rush collected at Måryd, Sweden.

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[4] Assuming an individual (m_{total} = 70 kg, m_{Carbon} = 16 kg; ICRP 1974) having the same ^{14}C specific activity in the body as the maximum activity observed in the grass sample (i.e. being in equilibrium with the environmental ^{14}C level) and that the energy from the ^{14}C decay is uniformly absorbed in the body.

5.1.2 RBMK – Ignalina

The samples collected at Ignalina comprised various types of materials such as tree leaves, grass, moss, soil, and aquatic plants. About half of the samples were collected within 500 m of the power plant, and the rest at a distance of 1–32 km from the plant. Since leaves and grass are seasonal vegetation samples, their ^{14}C specific activity should reflect the contemporary ^{14}C levels of the year in which they were sampled. These samples showed an average excess of 31% in 2003 and 18% in 2004, the decrease possibly being the result of a lower release rate of $^{14}CO_2$ in 2004. The maximum excess, 42% above the contemporary background level, corresponds to an additional effective dose of 6 μSv/y, received by the maximally exposed individual (calculated as the worst case scenario, as described in footnote 4).

However, the most interesting finding was the high specific activity found in samples of moss and soil. The maximum excess corresponded to 2000% above the background level.

5.1.3 Conclusions

The studies at Cernavoda and Ignalina showed that the potential health impact of the CANDU and RBMK power units appears to be small. Nevertheless, the calculated doses were higher than those resulting from the gaseous releases from the BWRs studied (Stenström et al. 2000, 1998). A rough comparison of the calculated additional effective doses resulting from the reactor types investigated is shown in Table 2. The calculations are based on the maximum ^{14}C excess observed in seasonal vegetation samples and assume that the same excess is reflected in the body of the maximally exposed individual. To enable a comparison of the different types of reactors, the resulting dose has been normalized to the total generated electricity (GW_e·y) of the power plant of interest.

Table 2. A rough comparison of the additional effective dose (μSv/GW_e·y) resulting from the gaseous ^{14}C releases from different reactor types; normalized to the total generated electricity. Included are also estimates of the collective effective dose (man Sv/GW_e·y), calculated by UNSCEAR (2000), presented as generic values for the reactor type of interest, i.e. not site-specific.

Reactor type	Investigated NPP	Maximum ^{14}C excess in seasonal vegetation	Normalized effective dose[a] (μSv/GW_e·y)	Normalized collective effective dose (UNSCEAR)[b] (man Sv/GW_e·y)
CANDU	Pickering[c,d]	1800%	170	0.43
	Cernavoda	28%	7	
RBMK	Ignalina	42%	4	0.35
BWR	Forsmark[d]	11%	0.5	0.14
	Barsebäck[d]	2%	0.4	

[a] Total generated electricity is related to the year of sampling.
[b] Based on local and regional dose components only, i.e. not considering global dispersion.
[c] Early type of CANDU reactor.
[d] Stenström et al. (2000).

According to the calculations, a CANDU 6 reactor would give rise to twice the effective dose of a RBMK unit and more than ten times that of a BWR unit. Based on available ^{14}C release rates, UNSCEAR (2000) calculated normalized collective effective doses[5] (man Sv/GW$_e$·y) from different reactor types using environmental and dosimetric models. The results are included in Table 2 although they are not directly comparable to the doses calculated in the present work. However, the results presented by UNSCEAR are comparable, indicating that the effective dose from a CANDU reactor is a factor of 1.2 higher than that from a RBMK reactor, and a factor of 3 higher than that from a BWR unit. Thus, the rough approach used to calculate the normalized effective dose above may overestimate the differences between the doses from the different reactor types. Nevertheless, the hierarchy of the normalized effective doses calculated from the results in Papers II and III is the same as expected from the hierarchy of gaseous release rates given in Section 4.4 (CANDU>RBMK>BWR>PWR).

The high excess of ^{14}C found in the moss and soil samples at Ignalina seemed to be associated with releases of particulate material, rather than $^{14}CO_2$ (Paper III). Particulate material containing ^{14}C was found in the environment following the Chernobyl accident (Buzinny 2006; Kovaliukh et al. 1998); but, this has not been previously reported in any environmental studies conducted around normally operating reactors. The most likely source of the presumed particulate material is graphite originating from the graphite brickwork constituting the moderator of the RBMK reactor. The total release rate of ^{14}C from RBMK reactors may therefore be higher than that presented by UNSCEAR (2000), since only gaseous components were accounted for. To account for the total environmental and health impact of RBMK reactors, it may be necessary to include releases of ^{14}C particulates in the assessment. Particulate releases of ^{14}C could be confirmed by analysing particle filters from the main venting stack or from other potential release paths.

5.2 The new method for ^{14}C extraction from process media (Papers I and V)

5.2.1 Method development

The literature survey presented in Paper I (with additional details in Stenström and Magnusson 2003) only included methods intended for ^{14}C extraction from spent resins, since these were the main focus of the first project conducted on behalf of SKB (Magnusson et al. 2005b). After reviewing the existing methods, it was decided to test two different types of techniques; acid stripping and combustion. However, the latter technique was later rejected due to the risks associated with combusting a highly radioactive solid sample. The concern regarding the acid stripping methods reviewed was associated with their extraction efficiency and the separation capability of the organic ^{14}C fraction in the sample which were not reported to have been validated[6]. Therefore, the acid stripping method was initially developed and tested using both inorganic and organic ^{14}C-labelled compounds: sodium carbonate, sodium acetate and sodium formate as carbonate, acetate

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[5] The collective effective dose is obtained by multiplying the average effective dose received by an individual by the number of exposed individuals. The product has the units man Sv.

[6] The exception was Park and colleagues (Park et al. 2006), who tested their method using ^{14}C-labelled alcohol and toluene. However, these compounds were not considered to be adsorbed on the resins.

and formate are expected in the reactor coolant of PWRs and BWRs. The ^{14}C-labelled compounds used in the development of the method therefore represent some of the ^{14}C species expected in authentic samples of spent resins.

The acid stripping method was initially developed using ^{14}C-labelled carbonate, which was found to be almost completely extracted from a simulated sample of spent resin. Subsequent tests involving the organic ^{14}C-labelled compounds showed extraction efficiencies close to 0% for both substances, which was expected due to the relatively low volatility of acetic and formic acid. However, by introducing an additional treatment involving wet oxidation, the organic compounds could also be successfully extracted. By collecting the CO_2 generated during the acid stripping (originating exclusively from carbonates, i.e. inorganic compounds) separately from CO_2 generated during the subsequent wet oxidation, the organic and inorganic ^{14}C activity of a sample may be separately determined. The optimization procedure using ^{14}C-labelled compounds is described in detail by Magnusson et al. (2005a).

Following the initial development of the method, further optimization was carried out using authentic samples of spent resins. These tests revealed that the organic ^{14}C in the authentic samples was more difficult to extract than that of simulated samples. By combusting some of the treated resin samples, it was found that some of the organic ^{14}C activity remained in the sample following wet oxidation. Therefore, the procedure was slightly modified resulting in three repeated wet oxidation steps, yielding an extraction efficiency of >95%.

The final system set-up used for the extraction of organic and inorganic ^{14}C from spent resins analysed within the work of this thesis, is schematically outlined in Figure 7. The final procedure (Paper V) consists of two steps, as described above; acid stripping and wet oxidation. The inorganic carbon fraction of a sample is extracted by the addition of sulfuric acid (H_2SO_4) and the carbon dioxide generated is absorbed in a pair of alkaline gas washing bottles (nos. 2–3 in Figure 7, where no. 3 serves as safety flask). Following acid

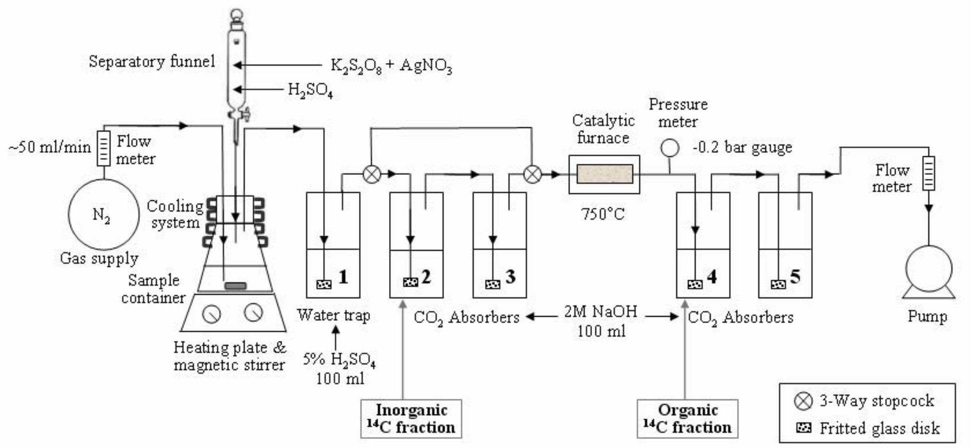

Figure 7. Basic system set-up used for the extraction of organic and inorganic ^{14}C from spent ion-exchange resins and process water. The gas washing bottles are referred to as 1–5 in the text.

stripping, the remaining carbon compounds (i.e. the organic fraction), are extracted by the addition of potassium peroxodisulphate ($K_2S_2O_8$) and silver nitrate ($AgNO_3$) with simultaneous heating. The carbon dioxide evolved is absorbed in a second pair of gas washing bottles (nos. 4–5, where no. 5 serves as safety flask). The latter extraction step, referred to as wet oxidation, is repeated three times in order to achieve efficient extraction of the organic compounds. A catalytic furnace, located between the two sets of washing bottles, ensures oxidation of reduced compounds. A water trap (no. 1) is utilized to avoid interfering radionuclides (e.g. ^3H) from reaching the absorbers.

As the SKB project was extended and other types of process media were included in the study, procedures were also developed and optimized for process water and off-gas analyses. The ^{14}C extraction from process water generally followed a three-step procedure: gas phase extraction, acid stripping and wet oxidation. The procedure developed (Paper V) allows quantification of organic and inorganic ^{14}C compounds in the gaseous phase, as well as in the liquid phase, resulting in four different fractions. The basic system set-up used for the extraction of ^{14}C from process water is the same as that presented in Figure 7.

5.2.2 Conclusions

The method developed enables the separate determination of organic and inorganic ^{14}C in different types of process media from nuclear reactors. Complete extraction of ^{14}C from both gaseous and liquid samples was verified. The extraction efficiency of ^{14}C from spent resins was determined to be >95%. The capability of the method to separate the organic and inorganic ^{14}C compounds extracted from the sample (being crucial to the investigation), was also found to be satisfactory.

One of the main advantages of the method is that the organic and inorganic ^{14}C activity of a spent resin is determined by sequential extraction from a single subsample. Another approach, employed by Vance et al. (1995) and Park et al. (2006), is to determine the activities using two different subsamples, where one of the samples is used to determine the total concentration (by e.g. combustion), and the other is used to determine the inorganic ^{14}C concentration (by acid stripping). The organic ^{14}C concentration is then estimated by subtracting one result from the other. Consequently, their approach is associated with higher uncertainties. The only method found in the literature designed for separate determination of organic and inorganic ^{14}C in the same spent resin sample, is that of Salonen and Snellman (1981). However, they experienced considerable difficulties in extracting the organic ^{14}C compounds from the sample, probably because their method was based solely on acid stripping.

Comparison with existing methods reviewed (see Paper V) indicates that the method developed within the current work has the highest reliability and accuracy, obtained by thorough optimization and validation. A reliable method of separately quantifying organic and inorganic ^{14}C present in process media is highly relevant as the release paths and release rates of ^{14}C, and the resulting effective doses, from NPPs as well as from disposal facilities, depend on the chemical form of ^{14}C. The method presented in Paper V has recently been implemented in Korea for the analysis of ^{14}C in process water systems in PWRs (Kang 2007)[7].

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[7] Kang, Duk Won, Group leader of the Radiation & Chemistry group at the Nuclear Power Laboratory, Korea Electric Power Research Institute; Personal communication, 2007.

5.3 Organic and inorganic ^{14}C in solid waste and estimation of the ^{14}C inventory in the SFR (Papers IV and VI)

5.3.1 ^{14}C in spent ion-exchange resins

The analyses of spent ion-exchange resins were mainly carried out in 2004–2005, with supplementary analyses conducted in 2006 and 2007. In total, 17 batch samples were collected and more than 50 separate ^{14}C analyses performed on the samples. The samples originated from nine different reactor units and represented all clean-up systems. However, only six of the units (Barsebäck 2, Forsmark 2 and 3, Ringhals 2, 3 and 4) can be considered to have been thoroughly investigated.

The results showed that the activity concentration of spent RWCU resins was more than two orders of magnitude higher in resins from PWRs than from BWRs. The reason for this is that most of the ^{14}C in the reactor coolant of BWRs boils off and follows the steam to the turbine, whereas the ^{14}C in PWRs is circulated in a, more or less, closed system. Consequently, the residence time for the ^{14}C formed in the coolant of PWRs is much longer than that of BWRs. Instead, CCU resins contained the highest concentration of ^{14}C in the BWR units. The amount of ^{14}C accumulated in the CCU resins was found to constitute 85–97% of the total amount accumulated in all clean-up systems on the BWRs. Therefore, spent resins from the other clean-up systems are of minor significance in the total reduction of waste containing ^{14}C. For two of the BWR units investigated at Forsmark (F1 and F2), the ^{14}C accumulation in the CCU system was found to be exceptionally high (see Paper IV). The cause was found to be related to a specific type of resin (the carboxylate resin), exclusively employed in the CCU systems of these two reactor units. If these carboxylate resins were to be replaced by the more common type, sulphonate resins, the ^{14}C accumulation would probably decrease by a factor of six (see Paper VI)[8]. Therefore, the difference in accumulation rate between the two types of resin is of importance in waste reduction.

Another important finding of the study on spent resins was the relatively high concentrations determined in resins from the boron thermal regeneration system (BTRS) at the Ringhals units R3 and R4 (Paper VI). The BTRS resins were intended to be disposed of at the shallow land burial site at Ringhals; however, they were found to exceed the maximum allowable ^{14}C concentration proposed by SSI (SSI 2007b). Therefore, the resins must be disposed of in the SFR, as is the case for nearly all resins generated from the PWRs.

The ^{14}C in solid LILW (i.e. in spent resins) generated annually from various waste streams (i.e. clean-up systems) was calculated and the results compiled for all reactor units in operation in 2004. The method of calculation is described in detail in Magnusson et al. (2005b), and the results for the reactor-specific accumulation rates (Bq/y) are given in Paper IV (Figure 4). However, since the annual accumulation of ^{14}C in the clean-up systems depends on the amount of ^{14}C produced in the coolant – being directly correlated to the thermal energy production (i.e. the neutron fluence, see Paper VI) – expressing the accumulation rate in terms of becquerels per year is not optimal for comparison purposes.

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[8] Replacing the existing carboxylate resins with sulfonate resins could, however, result in an increased concentration of sulphate in the water, having a severe effect on corrosion mechanisms.

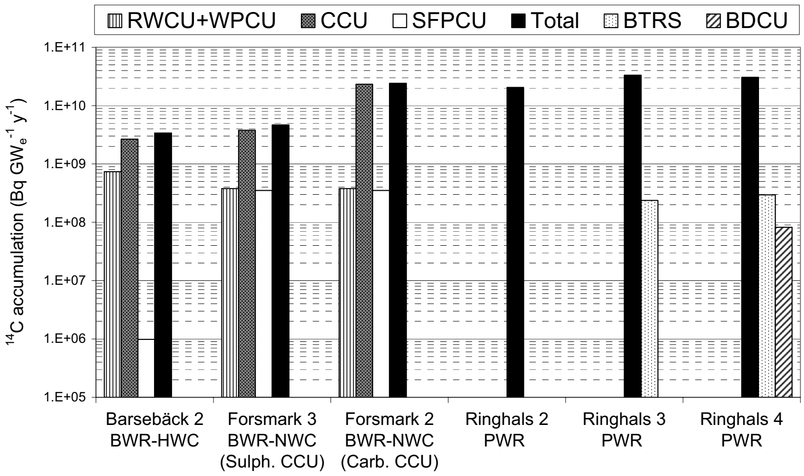

Figure 8. Normalized annual ^{14}C accumulation (Bq/GW$_e$·y) in spent ion-exchange resins from different clean-up systems in BWR-HWC, BWR-NWC and PWR units. WPCU = Waste Processing Clean-Up system; SFPCU = Spent Fuel Pool Clean-Up system; BDCU = Blow-Down Clean-Up system; BTRE = Boron Thermal Regeneration System.

To account for the variation in energy production between the reactors, the annual accumulation was normalized to the electricity generated (Bq/GW$_e$·y). The results of the calculations are presented graphically in Figure 8, being a slight modification of Figure 9 in Paper VI. The results shown represent the reactor units with the most complete set of batch samples collected. The normalized accumulation rates presented (Bq/GW$_e$·y)[9] may be of use to reactor operators in other countries, since they enable the estimation of the amount of ^{14}C generated in solid LILW waste (data on the electricity generated is easily available to the operators; as opposed to those on the thermal energy production). Such reactor-type-specific data are almost non-existent in the literature (see Paper VI). No previously reported system-specific data, such as those presented for the BWRs in Figure 8, have been found at all. It should be noted that the accumulation rates presented in Paper VI are slightly different from those in Paper IV. The main reason is that the various input data (such as thermal efficiencies) used in the calculations and derived from the power plant operators for each reactor unit, have been updated.

5.3.2 The ^{14}C inventory in the SFR

A preliminary estimate of the total ^{14}C inventory in the SFR at the time of closure is presented in Paper IV and was based on the results presented in the same paper. An estimate based on updated data is given in Magnusson et al. (2007); however, this was the

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[9] It should be noted that, due to normalization to the electricity production (as opposed to the thermal energy production), the accumulation rates presented in Figure 8 may be slightly altered upon efficiency-increasing measures implemented on the units, such as replacement of turbines.

same as the preliminary estimate. The estimates were based on a life-time of 40 years for the Swedish reactor units. Therefore, the repository was assumed to contain spent resins from 40 years of reactor operation at the time of closure. The resulting total ^{14}C inventory, at the time of repository closure, was found to be 5.0 ± 1.8 TBq. The prevailing regulation (SSI 2003a) implies a maximum total ^{14}C inventory of 7.2 TBq (SKB 1987). The limit has been set based on the value estimated by SKB in documents accompanying the application to SSI requesting an operating permit for the SFR (SSI 2003a). The theoretical estimate calculated previously by SKB was 2.7 TBq (Riggare and Johansson 2001).

Based on the results presented in the final report to SKB (Magnusson et al. 2005), SKB made a comparison (SKB 2006) between the two different approaches used to estimate the ^{14}C inventory: the approach used and described in this work (Paper IV; method of calculation described in Magnusson et al. 2005b), and the generic scaling factor approach. The resulting values differed by a factor of 2.6; the scaling approach giving the lower values.

SKB has recently presented an updated estimate of the ^{14}C inventory, as requested by SSI in 2003 (SSI 2003c) (see Section 4.1). According to SSI (SSI 2007a), the separate values derived for the different parts of the repository are all above the specific disposal limits set for each of the four rock caverns and the silo. SSI deems the discrepancy in one specific rock cavern, intended for the disposal of intermediate level activity, to be exceptionally grave; the updated estimate of total ^{14}C in this cavern being a factor of 16 above the disposal limit, and the amount of organic ^{14}C being a factor of 35 above the limit (SSI 2007a). SSI has recently issued a new decision regarding the operation of the SFR (SSI 2007a), stating that all further waste disposal is to be suspended. The discrepancies concerning the permissible disposal limits for ^{14}C are one of the main reasons behind their decision (SSI 2007a).

5.3.3 Conclusions

The use of a generic scaling factor (based on ^{60}Co) to estimate inventories and concentrations of ^{14}C involves significant uncertainties and problems (Lindgren et al. 1998; see also e.g. Lundgren et al. 2002; James 2006). The most striking is the different source terms and behaviour of ^{14}C and ^{60}Co. Cobalt-60 is a corrosion product produced by activation of structural materials such as Stellite and stainless steel (e.g. Wikmark 2004). Due to measures to reduce the amount of ^{60}Co in reactor systems, the amount of ^{60}Co in the ion-exchange resins in Ringhals 1, 2, 3 and 4 has decreased by a factor of 8–60 during the past 20 years, depending on the reactor unit (Aronsson 2007). These cobalt reduction efforts are not expected to have had any effect on the concentration of ^{14}C. This implies that the ratio of ^{14}C to ^{60}Co in spent ion-exchange resins from the PWRs has increased by the same factor. Therefore, any generic scaling factor used must take this into account. Furthermore, the experimental ratios of $^{14}C/^{60}Co$, obtained from the study on spent resins showed a considerable scatter, confirming their different behaviour. The ratios derived from the measurements are given in Paper IV, and are presented graphically here in Figure 9. The ratios varied significantly depending on the waste stream and reactor type from which the resin sample originated. Figure 9 shows that that spread in the data is 5×10^3 for PWRs, and 7×10^5 for BWRs. Therefore, a scaling factor approach should make use of reactor-specific as well as waste-stream-specific scaling factors, rather than a generic

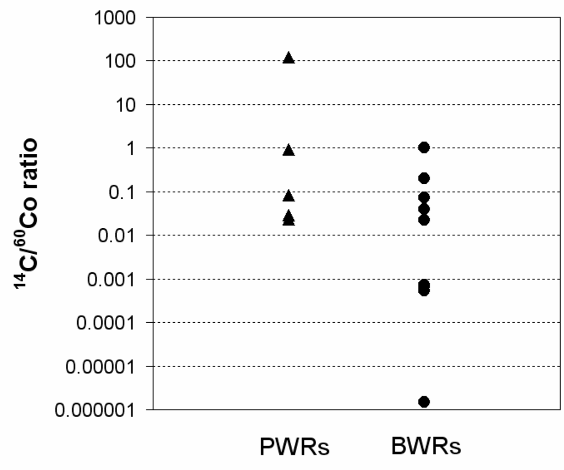

Figure 9. $^{14}C/^{60}Co$ ratios derived from the measurements of spent ion-exchange resins from Swedish PWR and BWR units.

factor, in order to decrease the uncertainty in ^{14}C estimates. The recently updated estimate of the ^{14}C inventory, derived by SKB was, according to SSI, significantly above the maximum disposal limit (SSI 2007a). One possible reason for this may be the use of updated scaling factors (based on current ratios of $^{14}C/^{60}Co$ in waste) with a ^{60}Co inventory constituting waste generated from the 1970s up until today. The result would be a significantly overestimated ^{14}C inventory.

An alternative approach associated with fewer uncertainties than the generic scaling factor approach is suggested here. Since the amount of ^{14}C produced in the coolant of a specific reactor unit is directly correlated to the energy production, the total accumulation of ^{14}C in the ion-exchange resins (constituting the dominant part of the ^{14}C inventory in the SFR) can be estimated if the following factors are known.

1. The generated electricity of the reactor unit (e.g. MWh_e).
2. The thermal efficiency of the unit (e.g. MWh_e/MWh_{th}).
3. The normalized production rate of ^{14}C in the coolant (e.g. Bq/MWh_{th}).
4. The total accumulated fraction of ^{14}C in the clean-up systems (as a percentage of coolant production).

Item no. 1 is known and easily available (therefore selected as input data instead of the thermal production, MWh_{th}); so is item no. 2. Item no. 3 has hitherto been calculated for eight of the Swedish reactor units (i.e. reactor-specific calculations; Paper VI; Lundgren 2007a, 2007b[10]) and also on a generic basis (Lundgren et al. 2002). The normalized production rates from the reactor-specific calculations and the results presented by Lundgren et al. (2002) suggest that a generic normalized production rate can probably be

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[10] Klas Lundgren, ALARA Engineering AB, Personal communication, 2007.

applied to all PWRs, and another to all BWRs. Item no. 4 is presented in Paper VI, which suggests a fraction of 0.6–0.8% for BWRs (3.8% for Forsmark 1 and 2, see Paper VI) and 9–10% for PWRs[11]. Uncertainties related to this suggested approach include e.g. those associated with the calculation of production rates (see Paper VI), and those associated with the experimentally derived ^{14}C accumulations (see Paper VI). Furthermore, it should be noted that major changes in operational practices related to the clean-up systems (such as switching from carboxylate resins to sulphonate resins), might have to be considered in the approach. Nevertheless, the approach is considered to be more reliable than the generic scaling factor approach for deriving estimates of ^{14}C inventories associated with spent ion-exchange resins[12]. Estimates based on reactor-specific contributions (integrated over the time period of interest) are preferable to generic approaches for inventory calculations. Further recommendations, prior to an implementation of the approach, are given in Section 5.5.3.

Prior to this study SKB had assumed that 10% of the total ^{14}C inventory is in organic form. According to the final estimate of the inventory derived within this work (Magnusson et al. 2007)), 24–28% is in organic form. The preliminary estimate was 19% (Magnusson et al. 2005b). These calculations indicate that the fraction of organic ^{14}C in the SFR at the time of closure will be higher than previously assumed. Nevertheless, the absolute amount of ^{14}C calculated is less than that used for the modeling of future releases from the SFR (Lindgren et al. 2001). Higher organic fractions may pose a serious problem considering the maximum disposal limits for certain parts of the repository, as recently concluded by SSI (2007a). However, it should be noted that the recently updated value of the ^{14}C inventory, derived by SKB, is believed to be significantly overestimated (see above).

5.4 Organic and inorganic ^{14}C in process water and liquid waste (Papers IV and VI)

5.4.1 ^{14}C in process water

A 10-month survey of all process water systems of importance, including waste water tanks (i.e. the liquid releases), was conducted on the PWR unit R4 at Ringhals in 2006. In total, more than 300 subsamples were collected and 70 composite samples analysed with respect to ^{14}C concentration and chemical (organic or inorganic) and physical (volatile or non-volatile) composition. The survey, which is presented in Paper VI (additional details are given in Magnusson et al. 2007), was proceeded by a preliminary study including both BWRs and PWRs, presented in Paper IV (additional details in Magnusson et al. 2005b). The results from the survey showed that the concentration as well as the distribution of different ^{14}C species in the reactor coolant of the PWR exhibited large variations during the

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[11] For the PWR unit Ringhals 2 an accumulated fraction of 6% was derived; however, the batch sample collected was believed to be unrepresentative for the unit due to an abnormal operation time of two years. See Paper VI for further details.

[12] An alternative approach of estimating the total accumulation in spent resins would be that of subtracting the reported gaseous releases rates of ^{14}C (e.g. Bq/y; being routinely monitored) from the calculated production rates of ^{14}C (Bq/y). However, due to the high uncertainties related to the gaseous release rates reported, this is not an option; see Section 5.5.

fuel cycle. This is illustrated in Figure 10, which summarizes the results from the analyses of composite samples originating from the reactor coolant prior to passage through the RWCU. As expected from the reducing chemical conditions in the coolant, organic ^{14}C compounds generally constituted ~100% of the total ^{14}C during power operation. Volatile organic compounds (such as methane) accounted for ~60%; the remaining part being non-volatile organic compounds (NVOs). The latter fraction is of considerable interest since part of it will be adsorbed on the ion-exchange resins. It is well known that the inorganic ^{14}C fraction in spent resins consists of carbonates; however, the speciation of the organic fraction is unknown. Matsumoto et al. (1995) assumed that acetaldehyde and acetic acid may be contained in low-level waste from Japanese PWRs (probably referring to spent ion-exchange resins). Lundgren et al. (2002) believe that, under reducing chemical conditions, formate may be found in the ion-exchange resins. Based on the tests carried out during method optimization using ^{14}C-labelled formate and acetate (see Section 5.2), on the prevailing chemistry conditions and the discussion by Lundgren et al. (2002), and on routine analyses of organic compounds at the Ringhals units, the NVOs are believed to be comprised mainly of formate and acetate (Paper VI; additional details can be found in Magnusson et al. 2007).

The results from the survey of ^{14}C in process water systems also enabled calculations of the ^{14}C removal rate from the reactor coolant system of the PWR (Paper VI). By comparing the removal rates with calculated production rates, it was found that ^{14}C was accumulated in the system during the beginning of the fuel cycle (i.e. the production rates exceeded the removal rates). However, at the end of the fuel cycle, the calculations instead indicated a high excess of ^{14}C in the system (as the removal rates significantly exceeded

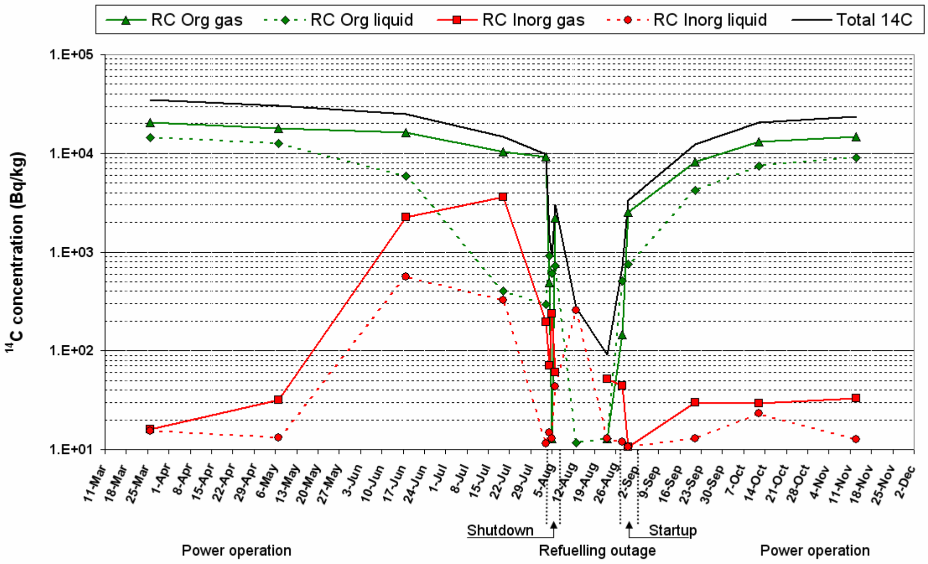

Figure 10. Chemical and physical composition of ^{14}C in samples of process water collected in the reactor coolant prior to the RWCU. Note the logarithmic scale.

the production rates). This was interpreted as an initial accumulation of ^{14}C in the RWCU resins (at the beginning of the fuel cycle), followed by the release of accumulated ^{14}C towards the end of the operation period of the resin (i.e. at the end of the fuel cycle).

5.4.2 ^{14}C in liquid releases

The amount of ^{14}C discharged with liquid releases from the power plants was found to be small for both PWRs and BWRs. Although the value derived for BWRs is considered to be uncertain, it can be concluded that the ^{14}C in the liquid waste constitutes less than 1% of the original amount produced in the coolant (see also Section 5.5), thereby verifying the previous assumptions (see Section 4.4). A supply of reactor-derived ^{14}C was also indicated in marine plants outside the Barsebäck NPP, housing one operational BWR unit at the time of sampling. The maximum ^{14}C concentration, observed in samples of seaweed, was found to be 15% above that of the background samples (Stenström et al. 2006, corresponding to roughly 1 Bq/m^3 of sea water. For comparison, it can be mentioned that we obtained ^{14}C concentrations roughly 30–40% above the background in aquatic plants outside the Ignalina NPP (see Paper III). However, if the excess levels observed in the waters outside Barsebäck and Ignalina are normalized to their respective energy production, the difference becomes less pronounced.

5.4.3 Conclusions

This survey provided an overview of the concentration and potential inventory of ^{14}C in different process water systems, and of its behaviour and variation during the fuel cycle. The detailed characterization and mapping of ^{14}C in PWR process systems, which is summarized in Paper VI, is by far the most complete investigation hitherto reported[13].

The reason for the physical characterization of ^{14}C in the samples (apart from the chemical characterization), is the different behaviour and fate of the volatile and non-volatile compounds in the water. The volatile fraction will end up as gaseous waste released from the venting stack, whereas the non-volatile fraction will be recirculated in the primary system and eventually be captured in the RWCU (or possibly in another clean-up system) or released with liquid discharges. The ^{14}C contained in the latter waste stream was, however, found to be very small. Therefore, the non-volatile fraction – possibly comprising ions such as formate, acetate and carbonates – is expected to govern the content of the spent resins and consequently be of specific interest in waste management issues. However, from the survey it was found that most of the ^{14}C formed in the reactor coolant remained within the primary system, despite operation with leaking steam generator tubes resulting in transport of process water from the primary to the secondary side. This suggests that the ^{14}C content of spent resins from the secondary side and auxiliary systems (such as the spent fuel pool) should be small compared to that of RWCU resins.

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[13] A similar study, including the analysis of organic and inorganic ^{14}C in samples from the reactor coolant and spent fuel pool, is currently (2007) being conducted on PWR units in Korea (Kang, Duk Won, Group leader of the Radiation & Chemistry group at the Nuclear Power Laboratory, Korea Electric Power Research Institute; Personal communication, 2007).

The behaviour of ^{14}C in the reactor coolant during the fuel cycle was found to be more complex than previously believed; generally no obvious explanations were found for the variations observed. An important finding of the survey was that the deposition of ^{14}C on system and fuel surfaces appeared to be small. Such a deposition would have caused transient releases of non-volatile ^{14}C during shut-down; a phenomenon not observed (see Figure 10). A large amount of ^{14}C deposited on system and fuel surfaces would result in a high content of ^{14}C in decommissioned solid waste such as steam generators, and releases of ^{14}C from the storage of spent fuel during storage, respectively (see Section 5.5.2 for a further discussion).

5.5 Mass balance assessment (Paper VI)

A mass balance assessment of the ^{14}C produced in Swedish PWRs and BWRs was performed based on the experimental results obtained within this thesis. The assessment concerns the ^{14}C originating from production in the coolant and shows its fate in different waste and release streams. Such an assessment enables the significance of a certain waste or release stream to be deduced; this by expressing the contents of ^{14}C as a proportion of the amount originally produced in the coolant. These proportions were calculated based on the results presented in Papers IV and VI, and on newly calculated production rates (Paper VI; Lundgren et al. 2002; Lundgren 2007a). The combination of experimental data and the updated and thorough calculations on the production rates, make the mass balance assessment presented here unique.

5.5.1 BWRs

The mass balance assessment for the BWRs is summarized in Table 3. The ranges given correspond to the spread observed in reactor-unit specific data; whereas all other values are considered to be generic values of the reactor type of interest (i.e. BWR-HWC or BWR-NWC). It should also be noted that the proportion of ^{14}C in gaseous waste presented in Table 3 is based on values reported from the routine measurements of ^{14}C in stack releases (see Section 2.3.1). The assessment for the BWRs showed that, in general, all waste and release streams, apart from gaseous releases, were of minor significance. An exception was the two BWR-NWC units F1 and F2, for which the amount of ^{14}C accumulated in the CCU resins is of importance (see Section 5.3.1). Based on the experimental results presented in this thesis, the proportion of ^{14}C released through the stack should account for nearly 100% of the amount originally produced in the coolant. However, based on the gaseous releases of ^{14}C reported from the power plants, this was rarely found to be the case. Instead, large variations were observed between the units; a proportion well above 100% being derived for the Forsmark units and the opposite for the Oskarshamn units. These uncertainties (being further discussed in Magnusson et al. 2007) limit the usefulness of the mass balance assessment and prevent verification of the experimental results.

Table 3. Summary of the results from the mass balance assessment of ^{14}C produced in the reactor coolant in BWR-HWC and BWR-NWC units. The values presented for gaseous waste were calculated based on values reported from the power plants.

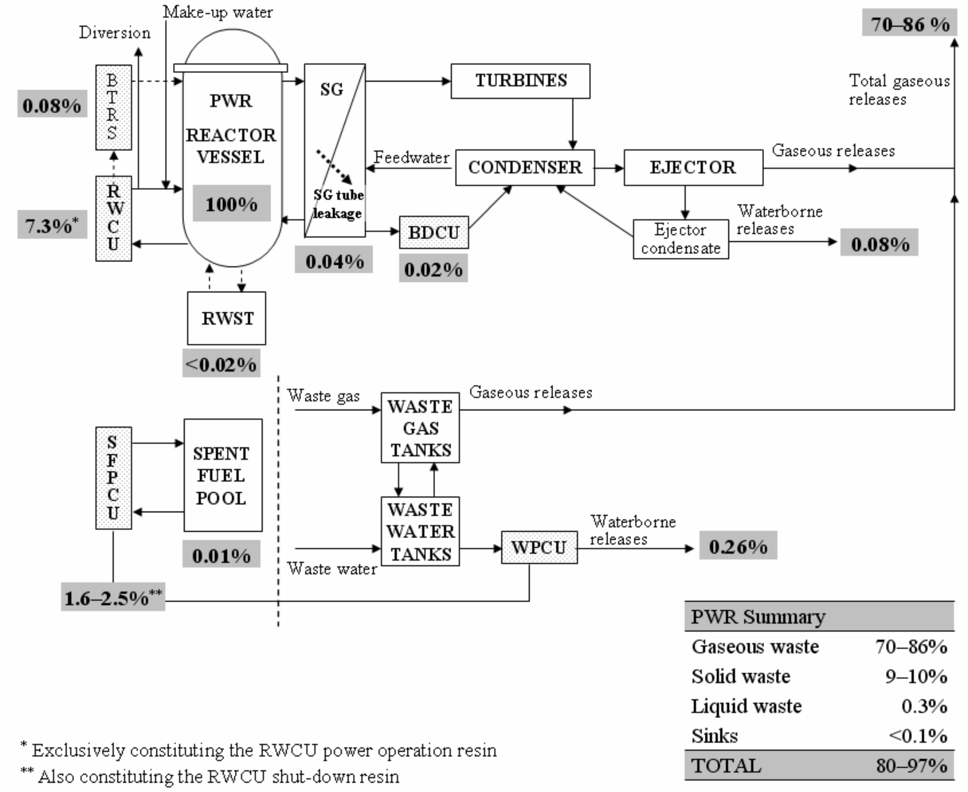
BWR Summary	BWR-HWC	BWR-NWC
Gaseous waste	59–120%	63–150%
Solid waste	0.6%	0.8–3.8%
RWCU	0.1%	0.02%
WPCU		0.04%
CCU	0.4%	0.6–3.7%
SFPCU	<<0.01%	0.06%*
Liquid waste	0.04%*	0.04%*
Sinks		2%*
TOTAL	60–120%	66–160%

* Experimental values associated with high uncertainties; see Paper VI for details.

5.5.2 PWRs

An overview of the mass balance assessment for the PWRs studied is presented graphically in Figure 11. The values are based on experimental data obtained from the PWR units Ringhals 3 and 4 (with the exception of gaseous releases, see Section 5.5.1), meaning that the data presented here are, to some extent, generalized. However, any differences in the behaviour of ^{14}C between the two units are expected to be insignificant due to their close similarity in operational parameters and design (at the time of the measurements).

The amount of ^{14}C contained in solid LILW waste streams (i.e. spent resins) was found to account for 9–10% of the amount originally produced in the coolant. This proportion (as well as the absolute amount) is significantly higher than that found in the solid waste stream from BWRs. This means that the ^{14}C inventory in the SFR will be dominated by the contribution from PWRs (see e.g. Table 9 in Paper IV), although constituting only three of the nine Swedish reactor units. From Figure 11, it is clear that most of the ^{14}C contained in solid waste generated by the PWRs is contained in the RWCU resins. For the PWRs, the proportion of gaseous waste derived was found to be more consistent with the expected proportions than for the BWRs. Since the concentration of ^{14}C in the reactor coolant is much higher in PWRs (due to the primary system being a more or less closed system), it is possible that significant amounts of ^{14}C may be accumulated at places other than the RWCU, such as on surfaces of the steam generator or on the fuel, thereby acting as sinks for ^{14}C. Such deposition is highly undesirable as it may, for example, prevent a potential clearance of the material at the time of decommissioning; being of economical significance. However, although the total amount of ^{14}C recovered in different waste and releases streams (80–97%) did not add up to the amount produced, potential sinks investigated were found to be insignificant. Therefore, the missing proportion is again probably due to uncertainties in the measurement of gaseous stack releases. Part of the discrepancy may also be attributed to uncertainties in the calculation of production rates (see Paper VI for further details).



PWR Summary	
Gaseous waste	70–86%
Solid waste	9–10%
Liquid waste	0.3%
Sinks	<0.1%
TOTAL	80–97%

* Exclusively constituting the RWCU power operation resin

** Also constituting the RWCU shut-down resin

Figure 11. Overview of individual results, as well as a summary, of the mass balance assessment of ^{14}C produced in the reactor coolant in PWR units. SG = Steam Generator. The values presented for gaseous waste were calculated based on values reported from the power plant. It should be noted that the proportions presented on the accumulation and release of ^{14}C from the secondary system (SG, BDCU, ejector condensate) only apply to the PWR unit Ringhals 4; operating with leaking steam generator tubes (leakage rate 7 kg/h).

5.5.3 Conclusions

The mass balance assessment for the Swedish reactor units shows that in order to reduce the amount of ^{14}C in waste being disposed of in the SFR, waste reduction efforts should focus on the PWRs, and above all, on the accumulation in the RWCU resins. This is not surprising; however, its significance has now been quantified. By combining the results of this assessment with those of the final estimate of the ^{14}C inventory in the SFR (Magnusson et al. 2007), spent RWCU resins from the PWRs were found to constitute ~42% of the total ^{14}C inventory. For the ^{14}C fraction of radiological significance in the SFR, i.e. the organic fraction (Lindgren et al. 2001), the RWCU resins are responsible for as much as 75%. Therefore, the validity of the suggested approach for estimating the ^{14}C inventory in the SFR (Section 5.3.3) would be further strengthened, and the reliability of the resulting estimate be improved, by increasing the amount of experimental data on which the accumulated fraction of ^{14}C in the RWCU resins is based.

Theoretically, it should be possible to decrease the amount of ^{14}C accumulated in the RWCU resins in the PWRs by increasing the frequency of venting of the volume control tank (see Section 2.2.1). This would increase the removal of ^{14}C from the coolant and consequently decrease the concentration of volatile as well as non-volatile ^{14}C compounds in the water, resulting in a lower accumulation rate in the RWCU. Therefore, increasing the venting rate of the volume control tank would result in a higher amount of ^{14}C being released as gaseous waste, and in a lower amount of ^{14}C accumulated in the solid waste. Such a management strategy would be beneficial both from a legal, as well as from an economical, point of view. The reason for this is that the limit on the total dose resulting from the release of radionuclides from the operation of nuclear power plants, has been set less rigorously (0.1 mSv/y; SSI 2000) than that applied to the future release from the SFR (0.015 mSv/y; see Section 4.1). Optimum waste management would therefore involve directing all the ^{14}C produced to the gaseous waste stream, which would probably also lower the cost of solid waste disposal. However, even if such an approach were operationally possible, it may not be recommendable due to the potentially increased releases of noble gases (resulting from a shorter retention time in the gas delay system), as well as due to the more stringent environmental regulations that can be expected in the future (see e.g. IAEA 2004).

Waste reduction by affecting the source of ^{14}C production, i.e. the reactor coolant, does not seem to be a reasonable alternative. The calculations presented in Paper VI showed that more than 99% of the production could to be attributed to the activation of ^{17}O, i.e. a constituent of the water, making it unrealistic to influence the source term.

Remaining means of reducing the amount of ^{14}C in solid and gaseous waste streams involve methods such as acid or thermal stripping to remove ^{14}C from spent ion-exchange resins (see e.g. IAEA 2002b), and the installation of gas scrubbers for the removal of ^{14}C in the off-gas system (see e.g. IAEA 2004). The ^{14}C activity released or absorbed, respectively, in the process requires subsequent treatment, producing a concentrated waste form suitable for disposal. However, these methods are in different stages of development and are probably only economically beneficial on reactors with significantly higher amounts of ^{14}C contained in the solid and gaseous waste streams (i.e. CANDU reactors), than those found in Swedish PWRs. Furthermore, the resulting concentrated waste form might require disposal in a more qualified repository than is generally available. Therefore, before considering the implementation of more sophisticated forms of waste reduction, it is suggested to re-estimate the ^{14}C inventory in the SFR (as is suggested in Section 5.3.3 of this thesis) to enable an evaluation of the importance of such implementations, from a legal as well as from an economical perspective.

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M!

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Paper I

Methods for measuring ^{14}C on spent ion exchange resins – a review

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Abstract

A literature survey of methods used for measuring ^{14}C on ion exchange resins is presented. Two types of methods are mainly employed: acid stripping and combustion. Some of the methods aim to measure only the inorganic fraction of ^{14}C in the waste, others the total amount of ^{14}C, and some separates the inorganic CO_2 fraction from CO and organic hydrocarbons. The review will be used as a base for setting up methods to measure organic and inorganic ^{14}C in spent ion exchange resins from Swedish nuclear power plants.

Introduction

Ion exchange resins are used in nuclear facilities for the removal of radioactive contaminants in a number of liquid processes and waste streams. For suitable final treatment and/or disposal of spent ion exchange resins, the content of radionuclides needs to be known. ^{14}C is one of the radionuclides ($T_{1/2}$=5730 years) that is of special interest to quantify, because of its long half-life, potential concentration, and environmental mobility. The environmental behaviour of ^{14}C in disposed radioactive waste is greatly dependant upon its chemical form. Therefore not only the total ^{14}C activity is of interest, but also the chemical speciation.

In light-water reactors (LWRs) ^{14}C is produced *e.g.* in the fuel, structures and in the primary coolant. Part of the ^{14}C produced in the primary coolant escapes through the off-gas system, and part is retained in the resins in the water clean-up system.

The aim of this article is to present a literature survey of the methods used to measure ^{14}C on spent ion exchange resins used for clean-up of various water streams in nuclear power plants. Special attention is paid to methods which concern the chemical speciation of ^{14}C in terms of organically (*e.g.* hydrocarbons) and inorganically bound ^{14}C (*e.g.* carbonates). Several of the reviewed documents contain results from measurements on spent ion exchange resins from nuclear power plants. In this paper, however, only the techniques are presented. First, a brief survey about the chemical forms of ^{14}C in the primary coolant and on ion exchange resins is given.

Chemical speciation

Chemical forms of ^{14}C in the primary coolant

There are considerable differences in the chemical form of ^{14}C present in the primary coolant depending on reactor type and mode of operation. In BWRs (boiling water reactors) the major part of ^{14}C is in the form of CO_2. As the conditions at PWRs (pressurized water reactors) are highly reducing, a major portion of ^{14}C appears as hydrocarbons or CO, and a minor portion as CO_2 or carbonates. Several reports on direct measurements of the airborne ^{14}C releases (mainly originating from ^{14}C production in the coolant) exist, by *e.g.* Bleier (1983), Hertelendi *et al* (1989), Kunz (1985), Salonen and Snellman (1985), Uchrin *et al* (1992) and Stenström *et al* (1995). In several of these, the chemical speciation of ^{14}C in the airborne releases has been determined, mainly by determining the fraction of $^{14}CO_2$ compared to the total ^{14}C releases. Reports of ^{14}C measurements on reactor water can also be found (*e.g.* Bleier, 1983; Kunz, 1985; Knowles, 1979; Soman, 1984).

Some authors describe the chemical speciation of ^{14}C in the coolant more in detail. Rosset *et al* (1994) describe the possible forms of ^{14}C in the reactor water at high temperature and reducing conditions (methane and methanol at 300 °C and pH 7.1). When the reactor cools, Rosset *et al* state that methane escapes in the atmosphere, and ^{14}C can be found in methanol, hydrogencarbonate, carbonate and formiate. Matsumoto *et al* (1995) estimate that the organic ^{14}C in the coolant in Japanese PWRs mainly consists of acetaldehyde, methanol, ethanol, acetone and acetic acid. Lundgren *et al* (2002) discuss the chemical forms of ^{14}C in BWRs, and conclude that "lack of accurate data on carbonic chemistry at higher temperature and lack of reports on accurate radiolytic measurements in high temperature water with high intensity radiation makes a quantitative assessment of the C-14 chemistry impossible". Lundgren *et al* however conclude that under reducing conditions the formation of methane, and possibly also formaldehyde and formic acid is expected. Under oxidising conditions Lundgren *et al* anticipate oxidised carbon forms, possibly mainly carbon dioxide and bicarbonate forms.

Chemical forms of ^{14}C on primary coolant ion exchange resins

Different opinions can be found in the literature about the retention of various carbon species on ion exchange resins. Kunz (1985) measured ^{14}C before and after the passage of the primary coolant through the clean-up demineralizers in two PWRs (containing mainly organic ^{14}C) and no removal of ^{14}C was detected. For a BWR (containing mainly $^{14}CO_2$) Kunz (1985) reports two sets of primary coolant samples taken before and after the clean-up and condensate demineralizers. No detectable removal of ^{14}C was found for the condensate demineralizers. For the clean-up demineralizers the first set of samples showed a decontamination factor of about 7, whereas for the second set of samples no decontamination factor could be determined. To Martin (1986), it appears highly unlikely that hydrocarbons are present in mixed ion exchange resins used for water cleanup in PWRs or BWRs; instead Martin believes that the collection of ^{14}C on the mixed resins most likely is in a carbonate form. According to Hesböl *et al* (1990) organic carbon is not retained in the ion exchange system.

However, according to Vance *et al* (1995) it is known, that most of the ^{14}C in PWR and some BWR spent primary coolant demineralizer resins is predominantly organic. Vance *et al* also claim that the attachment mode of these organic species of ^{14}C on the resin is unknown, but probably occurs by some type of sorption process rather than by a classical ion exchange mechanism. Vance *et al* further state that the organic ^{14}C species also can become attached to particulates in the reactor coolant water as witnessed by the relatively high concentrations of ^{14}C measured on some primary coolant filter cartridges. According to Torstenfelt (1996) it has been shown that very little or no ^{14}C is taken up in BWR demineralizers (as non-condensable gases are removed from the reactor coolant together with the steam and released via the off-gas system), but a substantial amount is taken up in PWR demineralizers. Torstenfelt summarizes that in PWRs, both organic and inorganic carbon is taken up by the demineralizers, with the organic fraction dominating, and with the inorganic fraction dominating only in a few cases. The variation depends mainly on the partial pressure in the hydrogen gas in the reactor coolant. Nott (1982) states that ^{14}C in both organic and inorganic forms may be present on the resins. In Ruokola (1981) it is stated that fresh resins from PWRs have been found to contain mainly ^{14}CO and hydrocarbons, whereas spent resins from PWRs have a completely dominating $^{14}CO_2$ fraction. From this, Ruokola concludes that hydrocarbons and CO are released from resins much more easily than CO_2.

In Gruhlke *et al* (1986) it is suggested that compounds such as formaldehyde, formic acid, and acetic acid may be produced in small amounts in PWR wastes. As mentioned in the previous section, Matsumoto *et al* (1995) estimates that in Japanese PWRs ^{14}C in the coolant composed to 40 % of acetaldehyde, 20 % of methanol, 30 % of ethanol and acetone, and 2 % of acetic acid. Matsumoto *et al* further state that it is generally assumed that most of ^{14}C discharged as alcohol or acetone would be released via off-gas during the waste packaging process because of their high volatility. Therefore Matsumoto *et al* consider that the ^{14}C contained in low-level waste packages are mainly carbonate, acetaldehyde, and acetic acid. Lundgren *et al* (2002) believe that under reducing conditions some formate could end up on the reactor water clean-up ion exchange resin, while the formic acid form is expected to mainly form formate salts with the corroding steel, and probably be retained in the condensate cleanup. Under oxidizing conditions Lundgren *et al* anticipate that bicarbonate may be caught in the reactor water clean-up.

In conclusion, there are still uncertainties regarding the size of the fraction of ^{14}C that is retained in ion exchangers and its chemical composition. As an example, Smith *et al* (2002) states that the technical measurements, which can provide good data, are limited to relatively few examples, and the results cannot be readily extrapolated to other circumstances.

Reviewed methods of measurements of ^{14}C in ion-exchange resins

In the following sections some methods to measure ^{14}C in ion exchange resins from nuclear power plants are presented. Special attention is paid to if the performance of the methods has been evaluated. Methods for measuring the chemical speciation of ^{14}C are reviewed as well as methods for measuring the total ^{14}C activity or only the inorganic fraction. Methods found in the literature for measuring ^{14}C on resins have been applied on light-water reactors as well as for heavy-water reactors (HWRs). Two main types of methods are employed: acid stripping and combustion.

Acid stripping methods

Aittola and Olsson (1980)

Aittola and Olsson (1980) used an acid stripping technique for measuring only the inorganic fraction. The experimental setup is outlined in Figure 1. Apart from the resin sample, that flask contained 4 ml 0.05 M Na_2CO_3 with 1 mg formaldehyde/ml and 20 ml of water. 30 ml of concentrated HCl was added to the resin sample in order to evolve carbon dioxide, which was carried by streaming air to the NaOH flasks, where it was absorbed as soluble Na_2CO_3. The purpose of the flask containing $Ca(OH)_2$ in Figure 1 was to visually control that all CO_2 had been absorbed in the NaOH, as the precipitate $CaCO_3$ would be formed by any unabsorbed CO_2. After terminating the flow of air, $BaCl_2$ was added to the NaOH flasks with the absorbed CO_2 and solid $BaCO_3$ was precipitated. The precipitate was cleaned and solved in a suitable medium for LSC analysis.

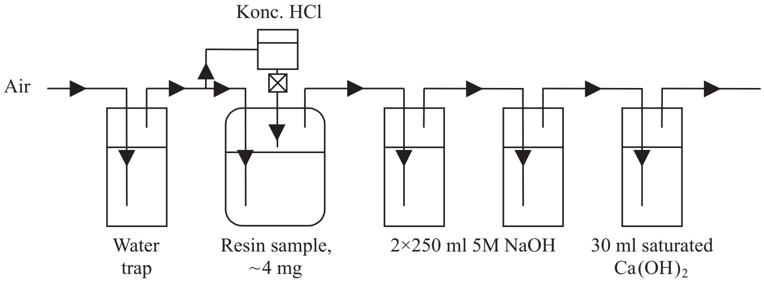

Fig. 1: Schematic layout of the experimental setup in Aittola and Olsson (1980)

To determine the recovery of the process, two tests were done where a ^{14}C standard (not specified) was added to a non-radioactive resin sample. The recovery was 49 % and 33 % respectively. Aittola and Olsson also tried to change the NaOH to Ethanolamine-Methanol, however with an even lower recovery, 34 % and 35 %, in two tests with a ^{14}C standard. To increase the recovery some modifications were done. About 4 g of resin sample was mixed with 1 ml of 10 % NaOH, possible ^{14}C standard and 0.100 g $NaHCO_3$. 250 ml 5 M NaOH was used to absorb the CO_2. The sample was heated to ca 50 ºC when adding the HCl. To precipitate $BaCO_3$ the NaOH was heated to 50 ºC and 100 ml NH_4Cl and 40 ml 1 M $BaCl_2$ were added. The solution was heated to 70 ºC and filtered while still warm. The precipitate was washed with water and acetone, followed by drying at 105 ºC for 2 hours. The resulting recovery of this procedure was 85 % (determined by one test). No information is given about reproducibility and memory effect of the method.

Nott (1982)

In Nott (1982) a method for removing inorganic ^{14}C from spent ion exchange resins (from CANDU reactors) is described. The apparatus (Figure 2) - almost entirely constructed of glass - consisted of a resin stripping column with an ultrasonic probe (to enhance the release of $^{14}CO_2$), an acid circulation pump and container, and NaOH absorption traps for CO_2. The bulk of the apparatus was kept under slight vacuum to prevent escape of $^{14}CO_2$ from the system. For the LSC analysis the NaOH concentration of all samples was adjusted to the same level of 0.1 mmol NaOH/ml of sample (in order to avoid variability of the LSC counting efficiency depending on NaOH concentration). At the end of each run, a sample of the acid was also counted for ^{14}C after neutralization with NaOH.

The method was tested on synthetic spent ion exchange resins (Amberlite IRN-150, 30 ml) prepared in the laboratory by addition of known amounts of bicarbonate ^{14}C to the resins (56 MBq of $NaH^{14}CO_3$ solution). The experimental variables (with their ranges within parentheses) were:

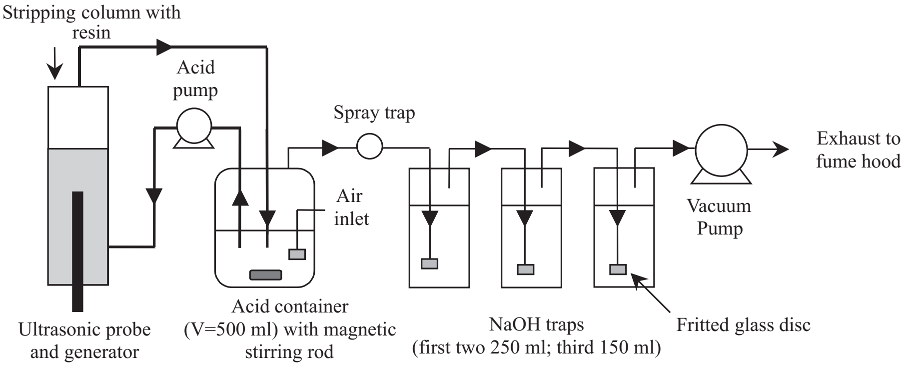

Fig. 2: Acid stripping apparatus for ^{14}C determination (Nott, 1982)

Acid concentration (HCl, 2.0-3.0 mol/l), acid volume (360-480 ml), acid circulation rate (50-90 ml/min), run time (45-90 min), peak ultrasonic power (20-40 W), on/off cycle times of ultrasonic power application (5/55-10/50 s) and NaOH concentration (0.5-2.0 mol/l). The ^{14}C found in the absorption traps and in the acid container after stripping (usually a very small amount) was compared with the ^{14}C in the resin batch prior to stripping.

The resulting recovery varied between 91.8 % and 102.1 %. The mean recovery was 97.4 % with a standard deviation of 3.6 %. In the ranges tested, none of the experimental variables showed an effect on the recovery that was significantly greater than the standard deviation. Hence, the author states that further experiments are required to determine the effect of the individual parameters. Nott also recognises the potential problem of interfering radionuclides to be absorbed in the NaOH traps. Information is lacking about the memory effect of the method.

Salonen/Snellman (1981, 1982, 1985)

Salonen/Snellman (1981, 1982, 1985) have analyzed spent ion exchange resins for ^{14}C by using a technique for simultaneous determination of ^{14}C either in the form of CO_2 or in the form of hydrocarbons and CO. A schematic diagram of the system is shown in Figure 3. The resins samples were first made alkaline in order to avoid the escape of ^{14}C as CO_2. A known amount of the ion exchange resin was then transferred to the sample vial in Figure 3, already containing 200 ml of 2 M NaOH solution, ca 100 mg $NaHCO_3$ carrier, some drops of methyl orange as indicator and a magnetic stirrer. The sample vial was closed and connected to the separation system. Both absorbers were filled with 100 ml 2 M NaOH.

The pressure in the separation system was first lowered by a vacuum pump using a flow rate of 0.8-1 l/min. After a few minutes 6 M HCl was let into the sample vial (to release $^{14}CO_2$) until the colour of the indicator changed from orange-yellow to red. After another few minutes an air flow (purified from CO_2 by a molecular sieve) of 0.2-0.3 l/min was applied, which carried the evolved gases into the absorbing NaOH solution during 1.5 hours. The flow rate of the air was less than that of the vacuum pump to prevent over-pressure in the system.

The separation of the different chemical forms was accomplished by using two absorbers with a catalyst - copper oxide at 800 °C - in between. With this arrangement CO_2 was absorbed in the first absorber, whereas hydrocarbons and CO passed it, were oxidized in the catalyst and absorbed in the second absorber. After completing the collection, the absorbed CO_2 was precipitated as $BaCO_3$, which was filtered, washed, dried, weighed and measured in a rigid gel by LSC.

Three tests with a known amount of $NaH^{14}CO_3$ showed that only 0.2 % of the ^{14}C was found in the second absorber. The mean recovery was 93 % with minor variations. No recovery determinations were done with ^{14}C-labelled hydrocarbons or CO. However, neither hydrocarbons nor CO were trapped in the first absorber, shown by using a sample from a spent ion exchange column, which first was made alkaline to fix CO_2. It was not possible to make the recovery determinations on the basis of the barium carbonate precipitate, as the weight of the precipitate was always higher than the value calculated from the amount of $NaHCO_3$ carrier added. The origin of the excess precipitate was not localised.

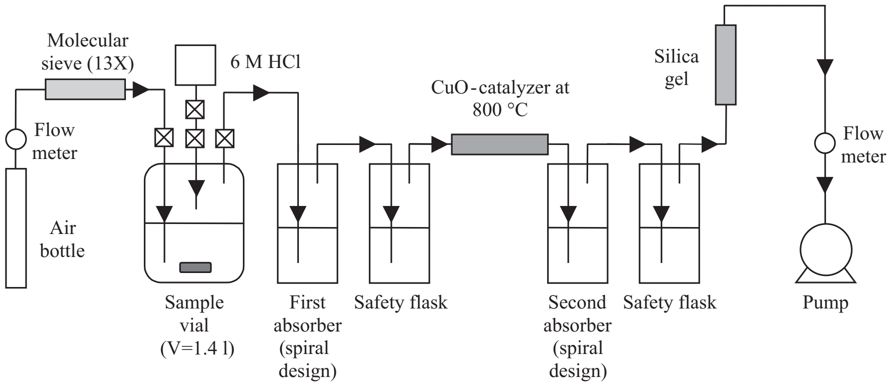

Fig. 3: Schematic diagram of the system used for separation and speciation of ^{14}C from ion exchange resins according to Snellman and Salonen (1981)

The system showed no memory effect. The radiochemical purity of the $BaCO_3$ was controlled by gamma spectrometry for all samples and LSC beta spectrum analysis for some samples. No contamination was observed. There are no reports about the efficiency of the catalyst.

Tests were made to see whether some additional activity would be released during a longer contact of the resin with HCO_3^- or CO_3^{2-} ions. A second separation of ^{14}C was carried out. The resin samples were made alkaline again, $NaHCO_3$ carrier was added and the samples were left for some days. Salonen and Snellman reason that during that time the ^{14}C which originally must have been retained into the resins through ion exchange reactions, would now have a possibility of being exchanged back into the solution. As only minor amounts were released during the second separation (between 0.3 % and 9.0 % of that in the first separation), Snellman and Salonen conclude that combustion of the samples was unnecessary.

In Salonen and Snellman (1985) further tests are reported. After absorption of ^{14}C-labelled carbonate in resin samples, these were left to stand for a month or longer. The average ^{14}C content of the resins was 15 % lower than that adsorbed into the resins. Salonen and Snellman conclude that this amount of ^{14}C may still be adsorbed into the resins or it may have been lost during the adsorption process or when transferring the sample from one vial to another.

For actual samples of spent resins duplicate samples were measured. Duplicate samples showed larger variety in the results for the CO/hydrocarbons than for the CO_2. Salonen and Snellman believe that this originates from that CO/hydrocarbons were more easily lost during the sampling and when handling the sample than CO_2, as this was fixed when the sample was made alkaline. The error introduced due to sample preparation and counting statistics was estimated to be 5-10 %. The differences between ^{14}C bound to CO_2 were however bigger for the duplicate samples, probably due to the difficulty of taking sub-samples with identical ratios of resin to NaOH solution. It was also seen that the second separation gave lower results than the first, which indicates some losses during opening the vial in which the resin was sent to the laboratory. The retention of hydrocarbons or CO in the resin was shown to be poor, and these fractions will be easily lost not only during storage and final management of the resins, but also during sampling and sample preparation.

In Salonen and Snellman (1985) it was shown that drying the resin evaporates ^{14}C from the resin mass. One test using "simulated spent" resins showed that as much as 97 % of the ^{14}C activity of the samples was lost during drying at 150 °C. Other experiments indicated losses of 96-99 % when drying.

Chang et al (1989)

Chang *et al* (1989) have done extensive laboratory tests on simulated spent resins using acid stripping for determining the amount of inorganic ^{14}C. The experimental set-up is outlined in Figure 4. 30 ml of resin containing ^{14}C (1.8 TBq/m^3) was mixed with a stripping solution (HCl, NaCl, Na_2CO_3 or NaOH) in a glass flask containing a magnetic stirrer. Air was bubbled through the solution (135-150 ml/min) to purge the CO_2 evolved, and to carry the off-gas through the system. A vacuum pump was used for drawing the gas though the system and at the same time maintaining a slight negative pressure within the system to avoid leakage of ^{14}C. The water trap was acidified with 5 % HCl and the CO_2 was absorbed in 2 M NaOH.

Experiments were also performed using acid fluidized columns, where acid and air was introduced from the bottom of the column to fluidize the resin. In those experiments magnetic stirring was not applied.

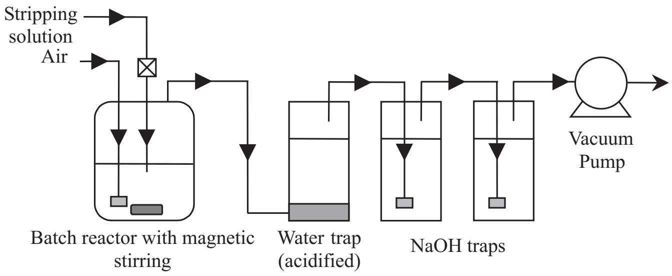

Fig. 4: Apparatus for ^{14}C removal by acid agitation (Chang *et al*, 1989)

Laboratory simulated resins with a known amount of ^{14}C-labelled $NaHCO_3$ or Na_2CO_3 in water solution were used to test the method. The most promising results were obtained with agitating the resins in aerated HCl solution, which gave recoveries of 92-99 %. The high efficiency was attributed to the combined effect of air bubbling and mechanical agitation.

In the acid fluidization without aeration, removal of the CO_2 produced was by diffusion alone, which according to the authors explains a slightly lower recovery by this procedure. When aeration was introduced, the efficiency was further reduced, as the gas bubbles tended to adhere to the resin beads and resulted in their floating together. This isolated the resin beads from reacting with the acid. Ten further tests were performed with aerated agitation in HCl giving recoveries of 98.5-100 (each run used 30 ml of IRN 150 resin with 1.8 TBq/m^3 ^{14}C). Five runs with resins preloaded with 7.4 TBq/m^3 gave similarly results (30 ml resin per run, acid concentrations 0.5-6 M, acid volumes 58-125 ml, aeration rates 100-135 ml/min and reaction times 45-225 min). Almost all the activity was found in the first absorber (<0.1 % in the second absorber, and even lower levels in the spent acid and stripped resin).

The acid stripping technique was also evaluated using 15 samples of spent resins from various sources. In four of the samples $Na_2{}^{14}CO_3$ was added to raise the activity to about 7.4 TBq/m^3 (to approximate the maximum ^{14}C level measured on CANDU moderator spent resins). All the runs demonstrated a ^{14}C removal of over 99 %. It must however be noted that the initial activity of the resins were of course not known. Instead the total activity was calculated by summing up the amounts remaining in the various solutions (spent acid, water trap and absorber traps) and on the treated resin after each experiment. The activity balance was thus assumed to be maintained.

Small amounts of residual ^{14}C (<0.5 % of the total ^{14}C) were detected on the treated spent resins. Chang *et al* believe that the residual ^{14}C was probably present in some organic forms that did not react with HCl. By adding the strong oxidizing agent potassium persulfate ($K_2S_2O_8$), the residual ^{14}C was found to be completely eliminated.

Other radionuclides were also removed from the resins by the acid stripping. Gamma spectrometry of the resins and the various solutions showed that a significant fraction of gamma emitters were found in the acid, and a much smaller amount in the water trap. No detectable quantities were found in the alkaline absorbers.

Acid stripping and combustion methods

Martin (1986)

Martin (1986) presents one combustion method and one acid stripping technique, used for various types of samples. The combustion method used by Martin (1986) is outlined in Figure 5. A tube furnace at 600-700 °C was used to oxidise the samples (liquid or solid) to CO_2. Solid samples were placed in a foil-lined sample boat and combusted for 1 hour at 700 °C. After combustion a few drops of HCl were added to assure release of any residual carbonate. No attempts were made to specify the chemical form of ^{14}C. The volatized carbon from the sample was passed through a ceramic tube packed with copper oxide to convert all carbon species to CO_2. After drying the gas in Drierite, the stream passed through two bubblers filled with Oxyflour-CO_2 (for trapping CO_2).

The acid stripping method shown in Figure 6 is based on resin regeneration procedures. First 3 ml KOH (25 %) was added to a flask containing the resin sample followed by 4 ml of HCl (37 %). The gases produced were drawn through a gas drying tube containing Drierite and through two midget bubblers filled with Oxyflour-CO_2.

The system for liquid or solid samples was checked for memory effects after each run. No significant residual deposition was found in the apparatus. The recovery of the same system was 93 % based on processing of standard solutions (chemical form not given). The efficiency of the stripping of the resin samples was not tested, nor was the absorption in the bubblers or any possible memory effect.

Martin et al (1993)

Here Martin *et al* (1993) have again tested two techniques for the recovery and analysis of ^{14}C in carbonate form: combustion/oxidation and resin regeneration. A mixed anion/cation type resin (Epicor EP-II, Dow Chemical Co.) was used. A solution containing 50 kBq of ^{14}C in carbonate form was added to a 50 g sample of resin for a period of 4 h. The sample was vacuum filtered to remove the spent solution. LSC measurement of the solution before and after resin treatment showed that 99.8 % of the ^{14}C was transferred to the resin beads, and no gaseous release of $^{14}CO_2$ was observed. Weighed aliquots of the treated resin were processed to compare the techniques of combustion/oxidation and resin regeneration.

In the combustion/oxidation technique (outlined in Figure 7) the sample (0.5 g) was placed in a nickel boat, and was combusted in an electric tube furnace for 30 minutes at 740±6 °C. A 25 mm fused quartz tube was packed at one end with mixed catalysts; CuO wire and platinum on alumina beads. Air of 200 ml/min was drawn through the system by a vacuum pump, carrying the off-gases through an ice bath (two traps) and a system of dryers to remove water, followed by two bubblers filled with an LSC cocktail to trap the oxidized carbon.

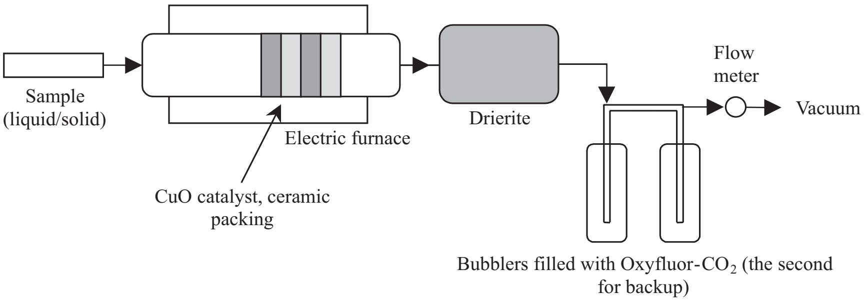

Fig. 5: Layout of the apparatus used for analyzing ^{14}C in liquid and solid samples (Martin, 1986)

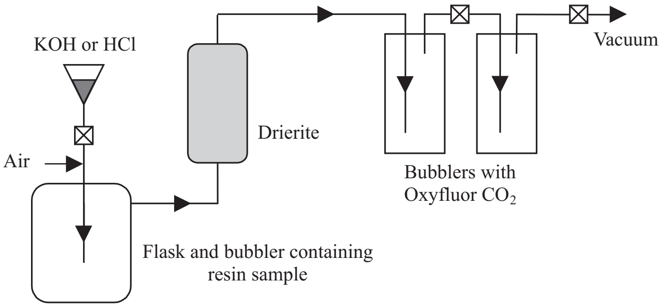

Fig. 6: Layout of the apparatus used for analyzing ^{14}C in resin samples (Martin, 1986)

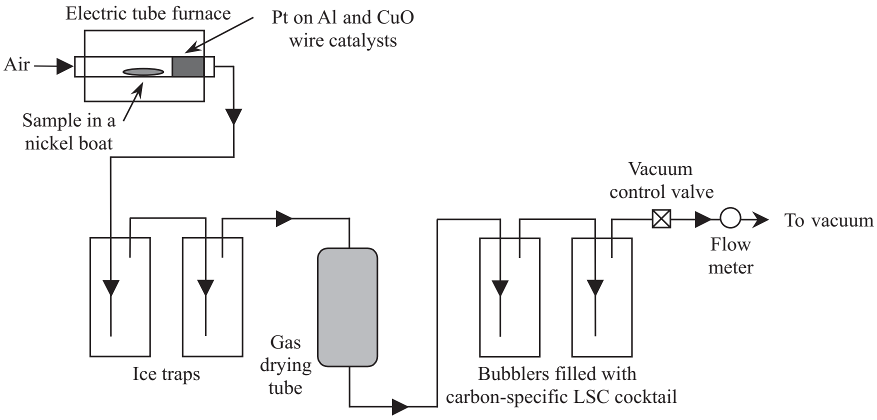

Fig. 7: Apparatus for combustion/oxidation of resin to recover $^{14}CO_2$ (Martin *et al.*, 1993)

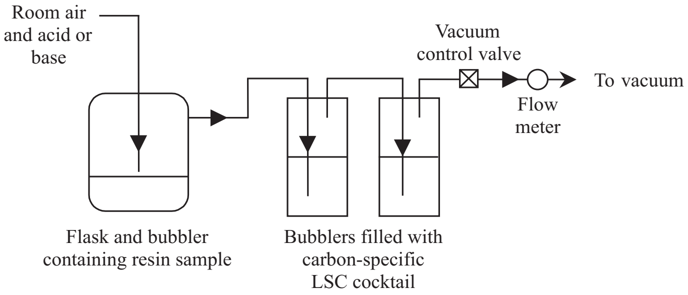

Fig. 8: Apparatus for regeneration of resin to recover $^{14}CO_2$ (Martin *et al.*, 1993)

The resin regeneration technique (schematically drawn in Figure 8) was tested in the following way. About 0.5 mg of the resin samples were regenerated by placing them in a 30 ml reaction vessel (midget bubbler). The off-gas was drawn by vacuum through two bubblers, each containing 15 ml of LSC cocktail. Air was drawn through the system at 200 ml per min. 10 ml of 6 M HCl were pipetted into the reaction vessel and swirled occasionally. The flow rate was applied for 30 minutes.

Dual regeneration by acid/base stripping was also tested by applying KOH prior to HCl. To determine the interference of other possible radionuclides in the LSC measurements one aliquot was dual-loaded with ^{60}Co.

The results showed that the mean recovery of the combustion/oxidation procedure was 63±9 %, while the resin regeneration procedure yielded a mean recovery of 85± 7 %. It is however not stated how well the procedures (*e.g.* combustion temperatures and efficiency of the catalyst) are optimized.

The dual regeneration by acid/base stripping using KOH prior to HCl yielded the same recovery as using HCl only; this is not surprising as the resin tested contained only carbonate. The test using ^{60}Co showed that the regeneration procedure was selective to carbon.

Moir et al (1994)

Moir *et al* (1994) have analyzed two moderator spent-ion exchange resins from the CANDU reactor Bruce Nuclear Generating Station A in Canada. Mixed beds were separated into anion and cation fractions using a sugar solution, and ^{14}C was determined in each fraction. Acid stripping and Parr bomb combustion were used and compared. Also other radionuclides on the resins were studied using γ-spectrometry.

The analysis scheme was designed to provide a detailed characterization of the resin, including not only the distribution of ^{14}C but also other radionuclides on the cation or anion beds. First the liquid in which the resin had been shipped was decanted and filtered, and the filter and filtrate were measured by γ-spectrometry. The filtrates were also analysed with LSC for the study of ^{14}C.

Ten millilitre samples of the two resins were subjected to a two-part ultrasonic washing (water and methanol). The solutions were filtered, and the filter as well as the filtrate was measured by γ-spectrometry. LSC was performed on the filtrates for determination of ^{14}C. The resin was analysed by γ-spectrometry after each washing to ensure that a mass-balance existed.

Ten millilitre samples of the two resins were separated using a sugar solution and the resulting cation and anion fractions were rinsed with 5 to 10 ml of distilled deionised water, and the weight of each fraction was determined. The sugar solution and rinse solutions from the separation procedures were filtered; filters, filtrates and resins were measured by γ-spectrometry, and the filtrates were analysed for ^{14}C by LSC.

As in the case of the separated cation and anion fractions, samples of unseparated samples were subdivided into subsamples of 0.2-0.25 ml. After subdivision, two samples of each of the unseparated resins and subdivided anion and cation fractions of each resin type were selected for combustion in a Parr bomb. The bomb assembly was connected to a gas collection line consisting of an acid trap (100 ml of 2 M HCl), followed by a condensation trap (methanol and dry ice) and two base traps (100 ml of 2 M NaOH in each). Prior to combustion, the samples were dried in the bomb using a heat gun while nitrogen gas flowed through the system. After drying, the Parr bomb was removed from the gas collection line and pressurized to 2.5 MPa using oxygen, then the combustion was carried out (the sample placed in a fused-silica crucible with some special fuel and the bomb fused by platinum wire). After combustion, the Parr bomb was attached to the gas collection line and the gases produced were released into the collection line. The bomb was purged for 10 minutes with nitrogen gas after the release of the gases in the bomb. ^{3}H and ^{14}C was collected as off-gases during the drying and depressurising steps, trapped in the HCl and NaOH solutions, respectively. The inside of the bomb was rinsed with distilled deionised water. 1 ml of the bomb rinse solutions as well as each trap solution was prepared separately with Instagel or Hionic-Flour cocktail prior to ^{14}C determination with LSC.

Two samples (0.2-0.25 ml) of unseparated resin, and cation and anion frations of each resin type, were subjected to acid stripping using HCl. The samples were placed in a reaction vessel connected to a gas collection line consisting of a 50 ml trap of 2 M HCl and two 50 ml traps of 2 M NaOH. 5 ml of 8 M HCl was added to the reaction vessel to release ^{3}H and ^{14}C from the resin sample to be collected in the HCl and NaOH traps, respectively. 1 ml of each trap solution and 100 μl of the acid stripping solution were then prepared separately in either Instagel or Hionic-Flour cocktail prior to ^{14}C determination with LSC. Aliquots of the acid stripping solutions were also measured with γ-spectrometry to determine if any other radionuclides had been removed from the resins in the stripping procedure. Parr bomb combustions were also done on samples of unseparated resins and separated anion and cation fractions following acid stripping.

Control samples (a series of 0.2-0.25 g inactive unseparated resins, spiked with ^{14}C-labelled carbonate solution) were prepared to determine the yields for ^{14}C during the acid stripping and Parr bomb combustions analyses. Recoveries were (93±5) % by the acid stripping and (100±10) % by Parr bomb combustion. The control samples were run after every eight resin samples analysed by either method. All samples (unseparated, anion or cation) were analysed in duplicate using either analysis procedure. Method blanks (inactive unseparated resin) were analysed periodically to ensure that cross-contamination of the samples was not occurring.

No ^{14}C was detected in the shipping solutions received with the resins, in either the distilled deionised water or methanol filtrates from the ultrasonic cleaning procedure, or in the filtrates from the sugar solutions used to separate the resins. Hence, Moir *et al* conclude that ^{14}C is not easily removed from the resins by simple washing procedures.

For the unseparated resin samples the results of the two methods showed differences between the subsamples, suggesting that some inhomogeneity existed within the bulk resin, possibly in the fraction of cation and anion beads. From the results of the separated fractions of anion and cation beads, it was seen that >99 % of the ^{14}C was associated with the anion component of each resin. Moir *et al* claim that the small amount of ^{14}C on the cation resin fraction may indicate the presence of ^{14}C-containing organic compounds or carbonates directly bound to metal ions, or that the separation of the anion and cation resin resins fractions was incomplete.

The ^{14}C concentrations for the anion and cation fractions, and unseparated resins by Parr bomb combustion after they have been acid-stripped, showed that the acid stripping appeared to remove almost all ^{14}C from the resins. The small fraction left behind was suspected to be in the form of organically bound species.

Some samples of sugar-separated anion resins that were stored for a few months before analysis were found to have little or no ^{14}C associated with them when acid-stripped or Parr bomb combusted. No leaks were found in the sample preparation systems. A test was made to determine the fate of ^{14}C: 10 ml of one of the resin samples was freshly separated into anion and cation fractions, and the anion fractions were subsampled further. These 0.2 to 0.25 ml samples were acid-stripped periodically over 5 months to determine whether the ^{14}C concentration was decreasing with time. The results showed that the concentration did decrease with time, with a total factor of 4.5. Several theories were suggested for the loss: sample inhomogeneity, change of pH of the samples while stored, or microbial activity due to the sugar-solution. Tests indicated that the third theory was the most likely. Unseparated resin samples did not show this loss of ^{14}C activity with time.

Vance et al (1995)

Vance *et al* (1995) evaluate ^{14}C production in light-water reactors and characterization of its chemical speciation and environmental behaviour. The occurrence of inorganic and organic forms of ^{14}C in reactor coolant water and in primary coolant demineralization resins was identified.

Two mixed-bed test resin-sampling devices were designed to simulate a scaled-down version of a nuclear power plant's purification demineralization system. The devices were installed at a number of PWR's and BWR's and operated at scaled-down flow rates and operating durations to simulate the cleanup of the reactor coolant.

For some samples the total ^{14}C content was determined by using a combustion technique followed by purification and liquid scintillation counting. A modified version of the method of Knowles (1979) was used for determining the inorganic fraction of ^{14}C on the resin. The resin samples were placed in sparging flasks and 6 M H_2SO_4 was used to release $^{14}CO_2$. A stream of CO_2-free air carried the $^{14}CO_2$ through acid purification traps to a saturated $Ca(OH)_2$/methanol trap for absorption. The $CaCO_3$ precipitate formed was further purified. The fraction of organic ^{14}C was estimated by subtracting the inorganic fraction from the total ^{14}C.

No tests of the method are reported.

Combustion methods

Speranzini and Buckley (1981)

Speranzini and Buckley (1981) have made a report on various methods for treatment of spent resins from CANDU reactors.

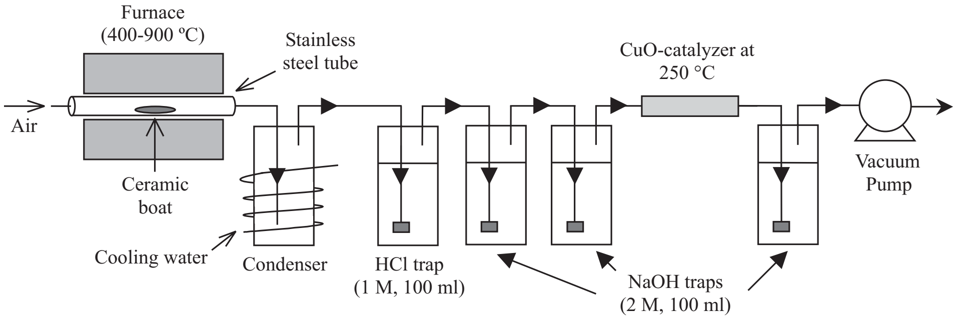

Fig. 9: Schematic drawing of the incinerator with off-gas system presented by Speranzini and Buckley (1981)

For disposal. Among other methods they evaluate the incineration of resins in order to better characterize the gaseous release of ^{14}C when the resins are burnt. In particular, they report a pretreatment procedure which can be used to release ^{14}C at temperatures below 500 °C, which is the combustion temperature of the resin. With the method presented it is also possible to quantify ^{14}C in the resins.

In the experiments reported, IRN-150 resin, traced with ^{14}C, and reactor-contaminated resins were used. For the off-gas studies, the experimental setup outlined in Figure 9 was used. A vacuum pump was used to draw air into the combustion chamber at a rate of 0.4 l/min. The off-gases from the combustion chamber were drawn into a scrubbing system consisting of a condenser, a HCl scrubber (to trap fission products), two NaOH scrubbers, a CuO catalyst (250 ºC) to oxidize organic ^{14}C (CH_4, C_2H_6) and a third NaOH flask to trap the oxidized organics.

Samples of Amberlite IRN-150 mixed bed resin (1-2 grams traced with 1200 MBq/l of ^{14}C as carbonate) were heated in excess air at temperatures ranging from 440 ºC to 850 ºC for 1.5 hours. The results showed that the ion-exchanged carbonate was not thermally stable (the decomposition temperatures of $CaCO_3$ is 900 ºC and 1430 ºC for $BaCO_3$). 15 % of the ion-exchanged carbonate was combusted at 440 ºC; 90 % of the initial ^{14}C was combusted when the temperatures reached higher than 850 ºC. Longer combustion times were also tested: At 440 ºC the combustion time was increased to 4 hours, and then the amount of ^{14}C recovered in the scrubbers increased from 15 % to 45 %. When the residual ashes of the resin combusted at 440 ºC and 580 ºC were reheated to 850 ºC for 1.5 hours, the total recovery ranged from 93 % to 98 %.

Unsuccessful attempts were made to convert the ion-exchanged carbonate to thermally stable calcium or barium carbonates by adding $CaCl_2$ and $BaCl_2$. The treated resins were heated in excess air at temperatures ranging from 440 ºC to 800 ºC for 1.5 hours. For $CaCl_2$ pretreated resin, ^{14}C releases ranged from 80 % to 99 % for temperatures ranging from 440 ºC to 740 ºC; for $BaCl_2$ pretreated resin, the ^{14}C releases ranged from 45 % to 99 % for temperatures ranging from 440 ºC to 850 ºC. Speranzini and Buckley have an explanation for this. The releases of $^{14}CO_2$ from $CaCO_3$ and $BaCO_3$ at temperatures lower than their decomposition temperatures may be related to the thermal decomposition of the sulfonic acid groups in the ion exchange resin at 300 ºC to produce SO_2, which then reacts with $CaCO_3$:

$$CaCO_3 + SO_2 + \tfrac{1}{2} O_2 \rightarrow CaSO_4 + CO_2$$

The rate of this reaction is substantially increased in the presence of $CaCl_2$ (van Houte *et al*, 1981).

Bleier (1983)

Bleier (1983) has analyzed ion exchange resins, with respect to the total amount of ^{14}C, from three German PWRs using a combustion method.

The sample consisting of either cation or anion resin was combusted together with PbO_2 (used as catalyst) at 1200 °C in a flow of oxygen. The off-gases were collected in NaOH and the ^{14}C precipitated as $BaCO_3$. To get rid of interfering radionuclides, the precipitate was acidified and reabsorbed in NaOH. The final precipitate was then analyzed using a proportional counter.

No tests of the system are presented in the article. No error estimations or tests of the method are given in the article.

Other methods

A few other methods that could be used for determining the ^{14}C content - apart from combustion and acid stripping - also exist. Dias and Krasznai (1996) present a method to remove inorganic ^{14}C from ion exchange resins using supercritical carbon dioxide. Another method of removing ^{14}C from dry organic wastes (including resin wastes) has been tested in a pilot-plant at Loviisa nuclear power plant in Finland (Tusa, 1989). A microbial process was capable of decomposing radioactive resin waste completely within about seven days, producing mainly CO_2 and CH_4.

Discussion

Based on the information given in the articles reviewed in this report we plan to design and test a combustion system as as well as an acid stripping system to measure organic and inorganic ^{14}C. The relative merit of the two will be compared. The acid stripping system will be a modified setup of the system of Salonen and Snellman. The combustion system will use the principle of Speranzini and Buckley. Extensive tests using various ^{14}C-labelled species will be made on the systems to ensure the correct function of each and every part.

One (or both) of the optimized systems will then be used to examine spent ion exchange resins from Swedish nuclear power plants.

Acknowledgement

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Paper II

RADIOCARBON, Vol 46, Nr 2, 2004, p 863–868

LEVELS OF ^{14}C IN THE TERRESTRIAL ENVIRONMENT IN THE VICINITY OF TWO EUROPEAN NUCLEAR POWER PLANTS

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ABSTRACT. Radiocarbon is produced in all types of nuclear reactors. Most of the ^{14}C released into the environment is in the form of gaseous emissions. Recent data on the ^{14}C concentration found in terrestrial samples taken in the vicinity of nuclear power plants in Romania and Lithuania are presented. We found increased ^{14}C levels in the surroundings of both power plants. At the Romanian power plant Cernavoda, we found excess levels of ^{14}C in grass within a distance of about 1000 m, the highest ^{14}C specific activity being 311 Bq/kg C (approximately 28% above the contemporary ^{14}C background) found at a distance of 200 m from the point of release (nearest sampling location). At the Lithuanian power plant Ignalina, samples of willow, pine, and spruce showed a ^{14}C excess of similar magnitude, while significantly higher values were found in moss samples. The samples were analyzed at the accelerator mass spectrometry facility in Lund, Sweden.

INTRODUCTION

Radiocarbon is produced in all types of reactors through neutron-induced reactions with isotopes of carbon, nitrogen, and oxygen present in the reactors. Since most of the ^{14}C released into the environment is in the form of gaseous emissions (such as $^{14}CO_2$), terrestrial samples will constitute the primary indicators of increased ^{14}C levels in the surroundings of the nuclear power plant (NPP). Because the food chain starts with plants, measurements of ^{14}C in environmental samples are important for estimates of radiation exposure to the public.

We have investigated the ^{14}C levels in the surroundings of 2 different types of reactors: the Romanian Canadian Deuterium Uranium (CANDU) reactor at Cernavoda and the Lithuanian RBMK (light-water-cooled, graphite-moderated) reactor at Ignalina. These 2 types of reactors are known to release higher amounts of airborne ^{14}C than light-water-moderated reactors. According to UNSCEAR (2000), the mean normalized ^{14}C release to air from 1990–1994 from CANDU reactors was 1.6 TBq/GW$_e$·yr, and for RBMK reactors, 1.3 TBq/GW$_e$·yr (estimated). Corresponding values for light-water-moderated pressurized water reactors (PWRs) and boiling water reactors (BWRs) were 0.22 and 0.51 TBq/GW$_e$·yr, respectively. Published data involving ^{14}C levels in the areas surrounding the Cernavoda and Ignalina NPPs are scarce, which justifies further investigations.

We have collected various vegetation samples in the area surrounding the 2 NPPs. At Cernavoda, we collected grass samples at various distances from the NPP, and from the immediate vicinity of the Ignalina NPP, we collected various vegetation samples.

In this paper, we have included a brief description of the 2 reactor types, as well as a summary of previous measurements involving ^{14}C emission and ^{14}C levels in the area surrounding the 2 NPPs.

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SITE DESCRIPTIONS AND PREVIOUS MEASUREMENTS

Cernavoda, Romania

The Cernavoda NPP is located 180 km east of Bucharest and is designed for 5 CANDU-6 (600 MW_e) reactors. So far, only 1 reactor has been built—with a maximum electrical output of 706 MW_e—and this has been in operation since April 1996; a second reactor is under construction. The CANDU-6 reactor is heavy-water-moderated and -cooled and uses natural uranium as fuel. The height of the venting stack is 50 m. About 220,000 people live within 30 km of the site (AECL 2001).

The largest contributor (>95%) to the production of ^{14}C in CANDU reactors is neutron activation of ^{17}O in the heavy-water moderator. Minor quantities are generated in the heat transport system by the annulus gas (CO_2) system (IAEA 2002) and in the fuel elements (Milton 1995).

According to Boss and Allsop (1995) and ACRP (1995), the total ^{14}C production in a CANDU-6 reactor is about 18 TBq/yr (approximately 33 TBq/GW_e·yr, assuming an electrical output of 0.600 GW_e and operation of 90% of the time) and 28 TBq/GW_e·yr, respectively, and it has been estimated that less than 4% is released to the atmosphere (ACRP 1995). Measurements have shown that about 70% of this ^{14}C is released in the form of CO_2 (Cooper 1998).

According to Dubourg (1998), the approximate release rate of ^{14}C with gaseous effluents from a CANDU-6 reactor (assuming operation of 80% of the time) is 4.1 TBq/yr (approximately 8.5 TBq/GW_e·yr, assuming an electrical output of 0.600 GW_e and 80% operation). Baciu et al. (1996) report that "the normal operation source term of ^{14}C in gaseous effluents" from the CANDU-6 at Cernavoda is 5.7 TBq/yr (approximately 11 TBq/GW_e·yr, assuming an electrical output of 0.600 GW_e and 90% operation). However, since these data were reported before the NPP was operational, the value probably refers to typical values for CANDU-6 reactors.

Bobric and Simionov (1999) presented annual ^{14}C emission data from the Cernavoda NPP, measured at the release point, from April 1996 to December 1998. The values are: 0.035 TBq/yr (0.26 TBq/GW_e·yr), 0.18 TBq/yr (0.32 TBq/GW_e·yr) and 0.29 TBq/yr (0.52 TBq/GW_e·yr) for 1996, 1997, and 1998, respectively. They also measured ^{14}C concentrations in terrestrial biota (e.g. vegetables and fruits) within 30 km of the NPP but did not find any detectable amounts with the liquid scintillation counter used.

Tenu et al. (2002) measured ^{14}C in atmospheric CO_2 samples collected monthly from April 1995 to November 1998 at a site close to the Cernavoda NPP. During this period, ^{14}C activities corresponding to values ranging from 210–440 Bq/kg C were recorded, with large fluctuations. Increased ^{14}C levels, compared with the values from the previous year, were found during the same month as the NPP started (April 1996). During 1998, they recorded an increase in ^{14}C activity at the Cernavoda site, from a level corresponding to 250 Bq/kg C in April 1998 to 440 Bq/kg C a month later. The values remained above 280 Bq/kg C until the end of the year.

Ignalina, Lithuania

The Ignalina NPP is located close to the border between Belarus and Latvia and consists of 2 units which were put into operation in 1983 and 1987, respectively. The reactors are graphite-moderated BWRs of channel type (model RBMK-1500) and have a maximum electrical output of 1300 MW_e each. The height of the venting stack is 150 m. About 210,000 inhabitants live within 30 km of the power plant (Almenas et al. 1998).

The emission of ^{14}C from a RBMK-1500 reactor mainly originates from ^{14}C production in the nitrogen-helium mixture that fills the entire reactor space and from ^{14}C production in the coolant. During the initial period of reactor operation, pure nitrogen is used instead of the nitrogen-helium mixture. During this period (approximately 18 months), the formation of ^{14}C is about 10 times higher than during the subsequent normal operation at rated power (Konstantinov 1989). Measurements performed in 1985–1986 of atmospheric ^{14}C release at the high-altitude pipe gave a value of 1.4 ± 0.3 TBq/GW$_e$·yr (Konstantinov 1989).

Mikhajlov et al. (1999) measured the ^{14}C distribution near the Ignalina NPP, and the highest value found corresponds to a ^{14}C specific activity of 430 Bq/kg C recorded in 2-yr-old pine cones that were collected at a distance of 5 km east of the location. Jakimaviciute-Maseliene et al. (2003) measured the ^{14}C concentration in plants (*Artemisia L.* [stem] and *Alnus L.* [leaves]) in the surroundings of the Ignalina NPP in 1996 and 2001. The highest value they found, within 1 km northwest of the NPP, corresponds to a ^{14}C activity of 400 Bq/kg C (in *Alnus L.* in 2001). From this maximum value, they derived a rough value of the atmospheric ^{14}C release from the Ignalina NPP of 49 TBq/yr (approximately 38 TBq/GW$_e$·yr, derived from the 2 units mean electrical energy generated during 1996 and 2001).

SAMPLING

Grass samples were collected in 1999 (14 October) and in 2001 (7 September) at various distances (200–4300 m) from the Cernavoda NPP. On the first sampling occasion, 9 samples were collected for ^{14}C analysis, and on the second, 21 samples were collected. The sampling locations and the general wind direction at Cernavoda are shown in Figure 1.

Different types of vegetation samples from trees and moss were collected in the immediate vicinity of the Ignalina NPP on 10 April 2003. All 9 samples were taken within a distance of 400 m from the stack. The approximate sampling locations and the general wind direction at Ignalina can be seen in Figure 2. Additional details are given in Table 1.

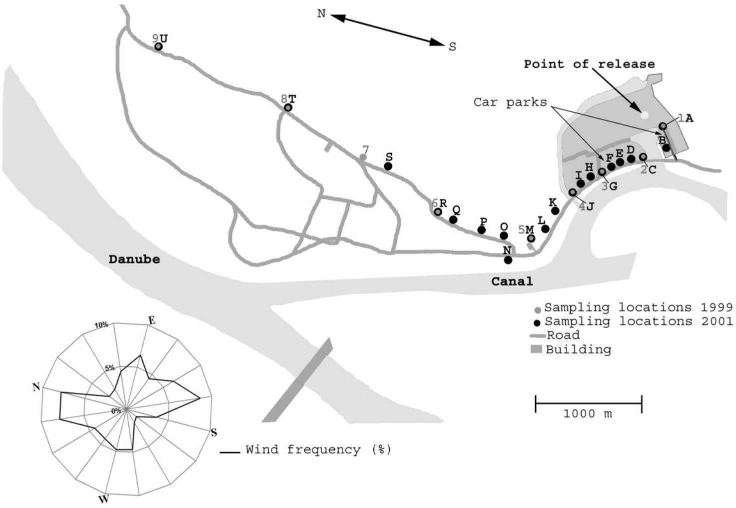

Figure 1 Sampling locations at Cernavoda in 1999 and 2001 and the wind frequency at Cernavoda from March to October 1999.

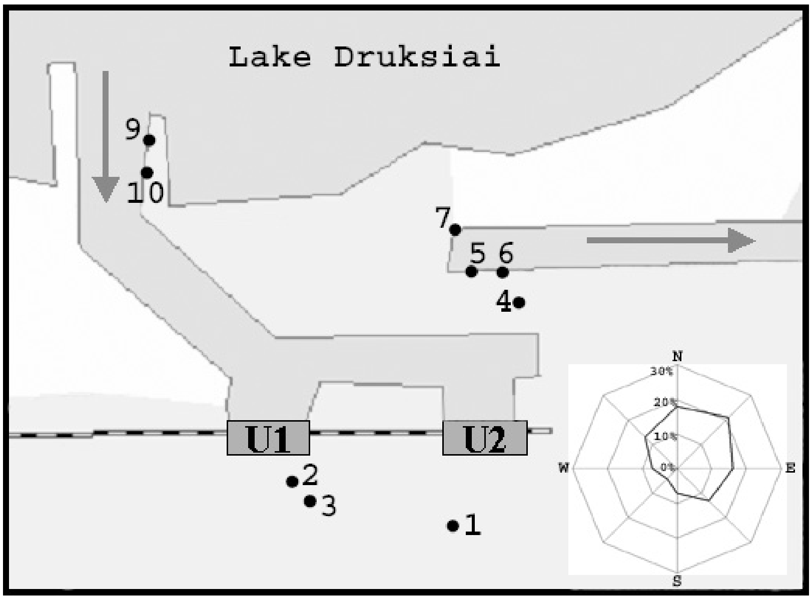

Figure 2 Approximate sampling locations at the Ignalina NPP in April 2003 (additional information is given in Table 1) showing Unit 1 and 2. The wind frequency at Ignalina during 2002 is also shown.

The samples were dried, ground, combusted, and graphitized according to standard procedures at our laboratory (Stenström 1995) and analyzed at the accelerator mass spectrometry facility in Lund, Sweden. The moss samples were fractionated into 1 upper layer (mainly moss) and 1 or 2 lower layers (moss and soil).

RESULTS

Cernavoda, Romania

The results from Cernavoda, which can be seen in Figure 3, show the typical distribution of ^{14}C from a point source. Excess levels of ^{14}C were found within a distance of about 1000 m from the point of release, with a maximum ^{14}C specific activity of 311 Bq/kg C found at the closest sampling location (A, 200 m).

Ignalina, Lithuania

The data given in Table 1 from the Ignalina NPP show similar levels of ^{14}C in willow, pine, and spruce to those found in grass from Cernavoda. The concentration in the moss samples and in the soil is significantly higher.

DISCUSSION

Increased ^{14}C levels were found in the surroundings of both NPPs. At Cernavoda, excess levels of ^{14}C were found in grass up to a distance of about 1000 m. Similar values of ^{14}C excess were found in the samples of leaves, shoots, and twigs from trees and bushes close to the Ignalina NPP. These do not necessarily reflect the maximum levels since they were collected only in the immediate

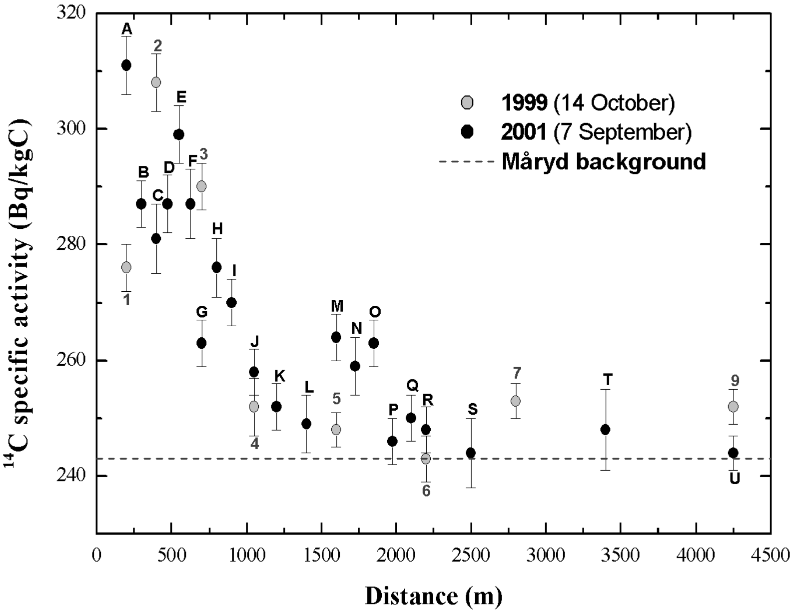

Figure 3 The ^{14}C specific activity (Bq/kg C) found in grass samples collected at various distances from the Cernavoda NPP. The background ^{14}C activity, 243 ± 2 Bq/kg C, measured in rush (*Juncus L*) from Måryd, Sweden, is the mean value for the period 1999–2001. Figures and numbers refer to the sampling times and locations shown in Figure 1.

Table 1 ^{14}C specific activity (Bq/kg C) found in various vegetation samples collected in the immediate vicinity of the Ignalina NPP in April 2003. The sampling locations are indicated in Figure 2. U1 and U2 = Units 1 and 2. The background ^{14}C activity, 241 ± 2 Bq/kg C, measured in rush (*Juncus L.*) from Måryd, Sweden, is the mean value for the period 2002–2003.

Nr	Sample description	Location	Background activity (Bq/kg C)
1	Goat willow (shoot, twig and flower bud)	150 m in front of U2	302 ± 7
2	Pine (shoot and twig)	50–70 m in front of U1	315 ± 7
3	Spruce (shoot and twig)	100 m in front of U1	302 ± 10
4	Goat willow (shoot and twig)	200 m behind U2	309 ± 7
5a	Moss (upper layer of a few cm)	Along outlet canal	362 ± 6
5b	Moss (soil and moss from lower layer)		1960 ± 20
6a	Moss (upper layer of a few cm)	Along outlet canal	370 ± 7
6b	Moss (soil from lower layer)		598 ± 10
7	White willow (shoot and twig)	Beginning of outlet canal	323 ± 7
9	Goat willow (shoot and twig)	Along inlet canal	342 ± 5
10a	Moss (upper layer of a few cm)	Along inlet canal	1020 ± 10
10b	Moss (middle layer of a few cm)		1570 ± 20
10c	Moss (soil and moss from lower layer)		4730 ± 60

vicinity (within 400 m) of the NPP. Because of the considerable height of the venting stack, the maximum ^{14}C concentrations are most likely found at a distance beyond the 400 m. High ^{14}C specific activities were found in the moss samples from Ignalina, with increasing concentrations with increasing depth. As moss grows from the top, the different layers should reflect different time periods, the oldest being the bottom layer. The results obtained may thus indicate that the release of ^{14}C has decreased during the lifetime of the moss. But as the ^{14}C concentrations found in the moss samples are higher than expected, the possibility of airborne ^{14}C particulates must be considered (Marsden et al. 2002; Mikhajlov et al. 1999). According to UNSCEAR (2000), the amount of particulates released with airborne effluents from the Ignalina NPP is considerable. Because of the great number of factors that determine depletion of particulates from a plume, it is extremely difficult to relate the concentration of assumed ^{14}C particulates found on the ground to the emission rate of these particulates.

Further data on moss samples and soil profiles at larger distances (up to ~30 km) from Ignalina NPP will be reported. This study was partly financed by grants from the Swedish Radiation Protection Authority and Carl Tryggers Stiftelse.

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Paper III

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Carbon-14 levels in the vicinity of the Lithuanian nuclear power plant Ignalina

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Abstract

Carbon-14 levels in the vicinity of the Lithuanian nuclear power plant Ignalina have been investigated. During 2001–2004, approximately 70 samples were collected and analysed using accelerator mass spectrometry. The study included samples of leaves, grass, moss, soil and aquatic plants, covering a distance up to 32 km from the power plant. The highest ^{14}C specific activities were found in soil samples from moss-covered sites close to the power plant, probably indicating the release of particulate material. The results are compared with those from studies around other types of reactors also investigated within the project.

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Keywords: Carbon-14; Ignalina nuclear power plant; Moss; Soil; Aquatic plants; AMS

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1. Introduction

Carbon-14 (half-life 5730 years) is produced in all types of nuclear reactors mainly through neutron-induced reactions with isotopes of carbon, nitrogen and oxygen present in the fuel, cladding, coolant, moderator and structural materials of the reactor [1]. As a result, ^{14}C will be present in gaseous, solid and liquid waste generated during the reactor operation. The influence on the ^{14}C levels in the close vicinity of the power plants is normally dominated by gaseous ^{14}C releases, whereas the liquid effluents normally contain only small quantities of ^{14}C. Generally, the annual gaseous release rates of ^{14}C from various types of nuclear power reactors are in the following order (average-normalized release rates from 1990 to 1994 in TBq/GW$_e$ year in brackets): CANDU[1] (1.6) > RBMK[2] (1.3) > BWR[3] (0.51) > PWR[4] (0.22) [2]. For all types of reactors except PWRs, most of the gaseous releases of ^{14}C are in the form of $^{14}CO_2$ [1], which is easily assimilated by plants through photosynthesis. As a consequence, increased ^{14}C levels may be found in surrounding plants and all other types of biota (including man), as reported in several publications, e.g. [3–5]. Studies of the ^{14}C levels in the vicinity of various kinds of reactors are therefore important from a radiation protection, technological and environmental point of view. It may also be of relevance during the decommissioning of reactors.

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[1] CANada Deuterium Uranium.
[2] Channelized Large Power Reactor.
[3] Boiling Water Reactor.
[4] Pressurized Water Reactor.

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The different types of samples collected from the surroundings of Ignalina were chosen to represent both airborne and liquid effluents and to cover both short and long distances (up to 32 km radius) from the power plant. The samples included tree leaves and grass, collected at short distances; aquatic plants from Lake Drūkšiai; and moss and soil collected at both short and long distances from the power plant. Sampling was carried out from 2001 to 2004. The results from the initial analysis of samples (moss, soil and trees within 500 m) have been published elsewhere [6] as well as the preliminary data for the ^{14}C analysis of aquatic plants [7]. The ^{14}C specific activities previously reported [6] were generally moderate (130–150 pMC; 1 pMC = 2.27 Bq/kgC) with a few exceptions for moss and soil, showing ^{14}C levels of up to 2100 pMC. These findings led to a significantly extended analysis including new sampling points and objects. The results and a detailed interpretation of these are presented in this paper.

The study conducted around the Ignalina RBMK reactor is part of a larger investigation that includes ^{14}C measurements of mainly terrestrial samples from the surroundings of CANDU, PWR and BWR reactors. The aim of the present investigation was to study the ^{14}C concentrations in various species and materials in the environment of the Ignalina nuclear power plant and to compare the results with those from studies around other types of reactors. The results obtained will also be important for calculations of the effective dose to various population groups.

2. Site and power plant description

The Ignalina nuclear power plant consists of two RBMK-1500 reactors. "RBMK" is a Russian acronym for "Channelized Large Power Reactor" and "1500" refers to the designed electrical power in units of MW. The RBMK is a graphite-moderated boiling water channel-type reactor. This means that each fuel assembly is located in separately cooled fuel channels, all surrounded by graphite. The two reactor units, Units 1 and 2, were put into operation in 1983 and 1987, respectively. In the end of 2004 Unit 1 was shut down and is now under decommissioning. The cooling water is taken from Lake Drūkšiai; inlet and outlet sites are shown in Figs. 1 and 2. Apart from the outlet of heated cooling water there is also a small outlet channel, into which wastewater, also containing some radioactive effluents, is discharged (indicated in Fig. 1). The only out-flowing river from Lake Drūkšiai is the Prorva, located in the southern part of the lake.

The airborne releases are discharged via the main stacks at an altitude of 150 m. More than 70% of the gaseous ^{14}C releases are in the form of $^{14}CO_2$ [8]. The dominating wind direction is from the west or southwest. About 140,000 inhabitants live within a radius of 30 km of the power plant, but none within a radius of 3 km.

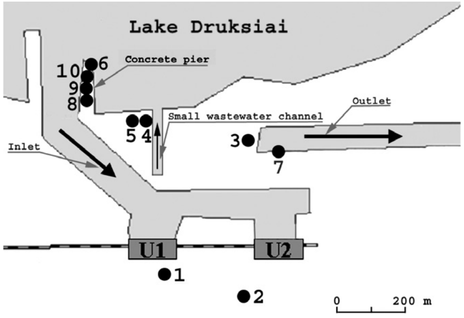

Fig. 1. Sites of collection of terrestrial samples (no. 1–10) at short distance in 2004 (11 May) in the vicinity of the Ignalina nuclear power plant. U1 and U2 = Units 1 and 2.

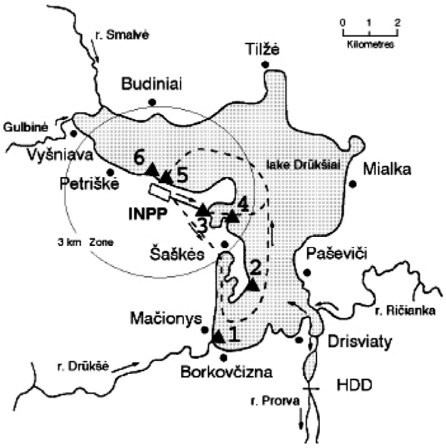

Fig. 2. Locations for the collection of aquatic plants (no. 1–6) in Lake Drūkšiai and the outlet channel in 2002 (3 July).

3. Sampling and analysis

3.1. Terrestrial samples

In 2001 (10 July), moss samples were collected at distances of 4–32 km from the power plant. In 2003 (12 December), the sampling at long distance was completed by the collection of moss, and in most cases also litter and soil from layers beneath the moss vegetation, at distances of 1–32 km southwest from the power plant. Due to the location of Lake Drūkšiai (see Fig. 2), the possible sampling directions for terrestrial material were limited. In 2004 (11 May), samples of tree leaves and grass, as well as a large number of moss and soil samples, were collected within a distance of approximately 500 m of the power plant (referred to here as short distance). The sampling locations are shown in Fig. 1. Generally, several different types of samples were collected at the same sampling location. Some of these samples represent a depth profile (see Table 1). The moss and deeper layers collected at distances of 1–32 km were partitioned into sections of 3 cm in the laboratory. After drying, any foreign material was removed from the moss samples by hand. The soil samples were sieved through a 2 mm mesh and any roots and plant material removed by hand. Litter samples were analysed without any pre-treatment.

3.2. Aquatic plants

Different species of aquatic macrophytes were collected in 2002 (3 July) along the shoreline of Lake Drūkšiai. The sampling locations are shown in Fig. 2. Sample no. 5 was collected close to the small wastewater channel (indicated in Fig. 1); no. 6 was collected close to the inlet channel, and no. 3 was collected from the outlet channel.

The terrestrial and aquatic samples were after drying and grounding, combusted and graphitized according to standard procedures [9]. The ^{14}C analysis was performed at the 3 MV AMS facility or at the 250 kV Single State AMS facility both located in Lund [10,11].

4. Results and discussion

4.1. Short distance

The results of the ^{14}C analysis of samples collected at short distances in 2004 are presented in Table 1. The highest concentration of ^{14}C observed in seasonal vegetation samples (tree leaves and grass) in terms of excess pMC was 33 pMC relative the contemporary background level (106 pMC) measured in rushes, *Juncus* L., from Måryd in southern Sweden. The average ^{14}C excess for all seasonal vegetation samples collected was 19 pMC. Tree leaves collected the year before showed a maximum excess of 45 pMC (average value 33 pMC) [6]. According to rough (a few unknown parameters of minor importance had to be estimated) Gaussian plume dispersion modelling [12], the maximum ground level activity due to gaseous releases from a 150 m high venting stack would occur at a distance of approximately 3 km from the power plant (east to north east direction). Since this distance considerably exceeds the sampling performed at short distance, the maximum ground level activity due to $^{14}CO_2$ releases could not be expected to be found in this set of data. The lower ^{14}C activities recorded in 2004 may be a result of a decrease in the release of $^{14}CO_2$ from 2003 to 2004, but could also be the result of changes in weather conditions, influencing the plume dispersion.

Table 1
^{14}C specific activity (pMC) found in vegetation samples and soil collected within 500 m of the Ignalina nuclear power plant in 2004

Sample	Site and ID	Approximate distance from reactor (m)	Sample type	^{14}C specific activity (pMC)	^{14}C excess (pMC)
1		50	Pine, needles	139 ± 1	33 ± 1
2		150	Goat willow, leaves	127 ± 1	21 ± 1
3		300	White willow, leaves	118 ± 1	12 ± 1
4:1		400	Grass	126 ± 1	20 ± 1
4:2	a		Soil, depth 0–1 cm	125 ± 1	19 ± 1
	b		Soil, depth 1–2 cm	123 ± 1	17 ± 1
	c		Soil, depth >2 cm	174 ± 1	68 ± 1
5		400	Goat willow, leaves	117 ± 1	11 ± 1
6		500	Goat willow, leaves	124 ± 1	18 ± 1
7	a	300	Moss, total layer	131 ± 2	25 ± 2
	b		Soil	280 ± 3	174 ± 3
8:1		450	Moss, top layer	136 ± 1	30 ± 1
8:2			Moss, top layer	137 ± 1	31 ± 1
8:3	a		Moss, total layer	161 ± 1	55 ± 2
	b		Soil	370 ± 3	264 ± 3
9:1	a	460	Moss, total layer	185 ± 1	79 ± 1
	b		Soil, upper layer	931 ± 6	825 ± 6
	c		Soil, lower layer	599 ± 3	493 ± 4
	d		Decomposed concrete + clay	1610 ± 60	1500 ± 60
9:2			Soil, upper layer	1090 ± 10	980 ± 10
10:1		480	Moss, top layer	135 ± 2	29 ± 2
10:2			Moss, total layer	143 ± 1	37 ± 1
10:3	a		Moss, total layer	179 ± 1	73 ± 1
	b		Soil	2310 ± 30	2200 ± 30
10:4	a		Moss, total layer	150 ± 1	44 ± 1
	b		Soil	508 ± 8	402 ± 8
10:5			Solid concrete	459 ± 5	353 ± 5

Sampling sites (no. 1–10) are shown in Fig. 1 and subsamples a–d refer to the same depth profile. The contemporary background from 2004, 106 pMC, was measured in rushes (*Juncus* L.) from Måryd, southern Sweden.

The moss samples all showed higher ^{14}C levels than the seasonal vegetation samples. The top layers (a few mm) showed a ^{14}C excess of 30 pMC relative the contemporary background, whereas the ^{14}C levels in the total moss layers were enhanced by 25–79 pMC. Mikhajlov et al. [13] found similar activities (corresponding to excess values of 2–80 pMC relative the Måryd background) in moss samples collected within 6 km of the power plant in 1997 and 1998.

The ^{14}C levels in the soil samples were generally found to be several orders of magnitude higher than in any of the vegetation samples, with ^{14}C specific activities up to 2310 pMC (sample ID 10:3b). The highest ^{14}C excess was observed in the samples from the pier (made of large concrete blocks) (sample sites no. 8–10), whereas the soil collected at sample site no. 4, below referred to as the "reference site", only showed moderate specific activities (123–174 pMC). It seems unlikely that the high ^{14}C excess in the pier samples would be caused by high release rates of $^{14}CO_2$ in the past. An analysis by Mazeika [14] of a tree-ring sequence from a tree (*Pinus Sylvestris* L.) located at a distance of 500 m covering the period 1988–1994, do not indicate significant releases of $^{14}CO_2$ in the past. However, to cover the whole period of reactor operation, ^{14}C analysis of a complete tree-ring sequence from a tree within 500 m of the power plant will be done. Waterborne ^{14}C-releases have not been considered here as a plausible source of contamination. This because of the distance from the pier samples to the water level (>1.5 m) and the intermediate ^{14}C levels seen in aquatic plants (see Table 4).

In a previous study [6], where we found ^{14}C activities of up to 2100 pMC in soil samples from the concrete pier, it was suggested that airborne ^{14}C particulates released from the power plant, might be the origin to the extreme activities observed. According to Wickham and Marsden [15] and Bush et al. [16] graphite particles contaminated with ^{14}C may be released from the graphite moderator through corrosion. In Magnox and advanced gas-cooled reactors (AGRs), Bush et al. [16] further states that some of the ^{14}C in the graphite moderator will pass into the coolant via this corrosion mechanism and finally be discharged to the atmosphere. If this is the case also for RBMKs, the high ^{14}C activities found at 1 km in the moss and litter samples collected at long distances (see Fig. 3) might be explained. The fact that the maximum ^{14}C excess seems to be concentrated to the close vicinity of the stacks, as seen in Fig. 3, implies a particulate source rather than a gaseous source.

If the ^{14}C excess found in the soil originates from particulate material, at least two factors will influence the results when expressed as ^{14}C specific activity; (1) the amount of material in which the particulates are deposited and distributed and (2) the carbon content of this material. The first factor might explain the considerable difference in the results obtained from the soil samples from the pier and from the reference site. As the moss samples on the pier were growing on a solid concrete surface, the soil layer was very thin. This means that any particulate material distributed over the surface would be concentrated in a small amount of material, resulting in a high ^{14}C specific activity. However, at the reference site, characterized by a deep soil layer, the particulates would be distributed throughout a large amount of material, resulting in a comparatively low ^{14}C specific activity. The result of the second factor is that the specific activities (pMC, where 1pMC = 2.27 Bq/kgC) obtained from the different soil samples may no longer be intercomparable. This is because the carbon content may vary considerably between different soil samples. However, a rough estimate (based on the graphitization protocols) showed that all soil samples had equal or higher carbon content than the reference site, which means that ^{14}C specific activities found in the pier samples show a true excess relative to the reference site.

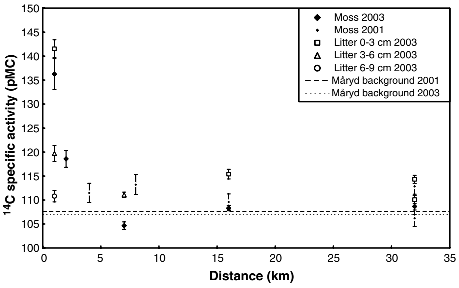

Fig. 3. ^{14}C specific activity (pMC) found in moss and litter underneath the moss vegetation collected at distances of 1–32 km from the Ignalina power plant in 2003 and 2001. The contemporary atmospheric background in 2003 and 2001, measured in rushes (*Juncus* L.) from Måryd in southern Sweden, was 107 pMC and 108 pMC, respectively.

Since most soil samples taken under the vegetation layer were collected from concrete surfaces, a fraction of a concrete block from the pier was also sampled in order to investigate whether the material could be a source of contamination. Since the ^{14}C specific activity, as well as the carbon content, in the concrete was lower (see sample ID 10:5) than the maximum values found in the soil, this could not be the case. However, a sample which appeared to be a piece of partially decomposed concrete surrounded by clay (found within the soil fraction) proved to contain a high excess of ^{14}C (see sample ID 9:1d). The specific activity was also significantly higher (regardless of carbon content) than in the soil from which the sample was collected. The reason for this might be that the clay more effectively absorbs the ^{14}C contaminant.

The ^{14}C levels in terrestrial seasonal vegetation (i.e. tree leaves and grass) in the immediate vicinity of the Ignalina power plant are similar to those found close to the modern CANDU-6 reactor Cernavoda in Romania [6]. However, apart from the reactor-specific differences in basic design and construction, the production rate of ^{14}C in nuclear

Table 2
A rough comparison of the maximum ^{14}C excess found in terrestrial seasonal vegetation samples in the vicinity of different types of reactors

Reactor type	Power plant (height of venting stack)	Total generated electricity (GW_e year)	Maximum ^{14}C excess (pMC) (sampling distance)	^{14}C excess per generated electricity (pMC/GW_e year)
CANDU	Pickering ($h < 20$ m)	1.51	1940 ($d = 0.9$ km)	1300
	Cernavoda ($h = 50$ m)	0.58	31 ($d = 0.2$ km)	54
RBMK	Ignalina ($h = 150$ m)	1.63	45 ($d = 0.3$ km)	28
BWR	Forsmark ($h = 100$ m)	2.77	12 ($d = 1.5$ km)	4
	Barsebäck ($h = 110$ m)	0.90	3 ($d = 0.9$ km)	3

The total generated electricity [18] is related to the year of sampling.

reactors is also directly related to the reactor power. Therefore, to be able to compare the results from different types of reactors, the maximum ^{14}C excess per unit installed electric power capacity has been calculated to enable a rough comparison. The results are presented in Table 2. The normalized data indicate that CANDU reactors affect the ^{14}C levels in their vicinity to a higher degree than the RBMK reactor investigated. As expected from the relationship between reactor power and gaseous releases of ^{14}C given previously, the ^{14}C levels around the RBMK reactor were higher than those detected in the vicinity of Swedish BWRs [17]. The maximum ^{14}C concentration recorded in terrestrial seasonal vegetation during the reactor study was found at Pickering Nuclear Generating Station in Canada [17], which employs an early type of CANDU reactors.

4.2. Long distance

The results of the analysis of moss, litter and soil samples collected at distances of 1–32 km in 2001 and 2003 are presented in Table 3 and Fig. 3. In the moss samples, excess ^{14}C specific activity is observed up to a distance of about 4 km (see Fig. 3). According to Gaussian plume modelling of gaseous releases from a 150 m venting stack, the maximum ground level activity would be found at a distance of approximately 3 km from the stacks as previously mentioned, i.e. not concentrated to the close vicinity of the stacks as in Fig. 3. The distance dependence seen in Fig. 3 can therefore probably not be explained by the distribution of $^{14}CO_2$ releases.

For the litter samples, elevated ^{14}C levels were found at all sampling sites, which mainly is supposed to be associated with the nuclear weapons fallout of ^{14}C (the bomb pulse) and possibly also to earlier ^{14}C-releases from the power plant at the closest sampling site.

The ^{14}C levels in the soil samples indicate a mixture of a young (influenced by bomb ^{14}C) and an older (^{14}C depletion by radioactive decay) component. The levels do not seem to be affected by ^{14}C releases from the power plant.

The results may be compared with those from the study conducted at the Romanian power plant Cernavoda (CANDU; height of venting stack 50 m), where grass samples were collected at distances of 0.2–4.3 km in 1999 and 2001. Excess levels were found up to a distance of about 1 km from this reactor [6].

Table 3
^{14}C specific activity (pMC) found in moss and underlying layers, collected at distances of 1–32 km from the Ignalina power plant in 2003 and 2001

Sampling distance (km)	Depth (cm)	Material	Sampling year	^{14}C specific activity (pMC)
1	–	Moss	2003	136 ± 3
	0–3	Litter	2003	142 ± 2
	3–6	Litter	2003	120 ± 2
	6–9	Litter	2003	111 ± 1
2	–	Moss	2003	119 ± 2
	0–3	Soil	2003	103 ± 2
	3–6	Soil	2003	89 ± 1
	6–9	Soil	2003	84 ± 1
4	–	Moss	2001	111 ± 2
	0–3	Soil	2003	98 ± 1
	3–6	Soil	2003	98 ± 1
	6–9	Soil	2003	74 ± 1
7	–	Moss	2003	105 ± 1
	3–6	Litter	2003	111 ± 1
	3–6	Soil	2003	97 ± 1
	6–9	Soil	2003	86 ± 1
8	–	Moss	2001	113 ± 2
16	–	Moss	2003	108 ± 1
	–	Moss	2001	110 ± 2
	0–3	Litter	2003	115 ± 1
	0–3	Soil	2003	113 ± 1
	3–6	Soil	2003	100 ± 1
	6–9	Soil	2003	103 ± 1
32	–	Moss	2003	109 ± 2
	–	Moss	2001	106 ± 2
	–	Moss	2001	113 ± 2
	0–3	Litter	2003	110 ± 1
	0–3	Litter	2003	114 ± 1
	6–9	Soil	2003	109 ± 1

The results of the analysis of aquatic plants are presented in Table 4. The lowest ^{14}C specific activity (131 pMC) was detected at the greatest distance from the power plant. The highest ^{14}C levels were found close to the inlet channel (155 pMC) and in the outlet channel (153 pMC), clearly influenced by the liquid effluents from Ignalina power plant. Since the contemporary background level in water reservoirs is different from that in the atmosphere, the excess ^{14}C specific activity should be determined using background data from Lake Drūkšiai. However, analyses of ^{14}C in the dissolved inorganic carbon fraction

Table 4
^{14}C specific activity (pMC) measured in aquatic plants collected along the shoreline of Lake Drūkšiai in 2002

Sampling site	Species	^{14}C specific activity (pMC)
1	*Ceratophyllum demersum*	131 ± 1
2	*Cladophora glomerata*	145 ± 2
3	*Chara vulgaris*	153 ± 2
4	*Myriophyllum*	147 ± 2
5	*Chara vulgaris*	141 ± 2
6–1	*Potamogeton*	155 ± 2
6–2	*Ceratophyllum demersum*	150 ± 2

Sampling sites are shown in Fig. 2.

of water from the northern part of the lake [14,19] indicated elevated values that could be related to the liquid effluents from Ignalina power plant. Therefore, reference data from Lake Dysnos [14,19], a similar lake located nearby, would probably serve as a more valid reference site. Depending on the choice of reference lake, the maximum ^{14}C excess found in the aquatic plants was 35–50 pMC. Mazeika [14] reports a ^{14}C concentration of 133 pMC, measured in *Myriophyllum spicatum* collected in 1996 from approximately the same site as no. 4 in this study.

A similar study was conducted at the Swedish nuclear power plant Barsebäck (BWR), where marine plants (mainly *Fucus vesiculosus*) were collected in 2002 and 2003. The maximum ^{14}C excess found was 15 pMC, which is believed to originate from the power plant [20].

5. Conclusions

The ^{14}C levels in the surroundings of the Ignalina nuclear power plant have been studied by analysing various types of terrestrial and aquatic samples using AMS. A ^{14}C excess of 10–80 pMC relative the contemporary background was found in the vegetation samples within a distance of 32 km of the power plant. The excess ^{14}C specific activities measured in moss samples collected at distances of 1–32 km indicate a distance dependence which probably cannot be explained by the distribution of ^{14}CO$_2$ releases from the venting stack of the power plant. Soil samples from moss-covered sites within 500 m of the power plant showed highly elevated ^{14}C levels, probably indicating releases of particulate material.

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Paper IV

^{14}C in Swedish PWRs and BWRs – Measurements on Spent Ion Exchange Resins and Process Water and Estimation of the ^{14}C Inventory in the Swedish Waste Repository

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Abstract

This paper presents the results from a study to determine the concentration of ^{14}C – in terms of both organic and inorganic ^{14}C species – in spent ion exchange resins and process water from Swedish BWRs and PWRs. The purpose was to obtain data for reliable estimates of the ^{14}C inventory in the Swedish waste repository. This is important when calculating the total inventory and the radiological consequences of the repository.

The study included three PWRs, four BWRs (NWC) and two BWRs (HWC). The average-normalized ^{14}C activity in the spent resins was found to be 30, 12 and 3.3 $\mathrm{GBq \cdot GW_e^{-1} \cdot year^{-1}}$ for PWR, BWR-NWC and BWR-HWC units, respectively. The total amount of ^{14}C accumulated in the spent resins annually from a PWR represents 5–9% of the calculated ^{14}C production in the reactor water. For BWRs, the corresponding range was 0.5–4%. The accumulated ^{14}C activity in spent resins, generated by all Swedish reactors during their life-time, was estimated to be 5.0 TBq, of which 24% will be in organic form. Our results confirmed that the estimated ^{14}C inventory in the waste repository was within the limits stated in the safety analysis report.

Measurements of organic and inorganic ^{14}C in various process water systems showed that the average activity concentration in the reactor water was 28 kBq/kg in PWR samples and ~3 Bq/kg in BWR samples. However, the measurements indicated that a substantial fraction of the organic ^{14}C in the liquid phase of the investigated PWR was not taken up by the resins.

Introduction

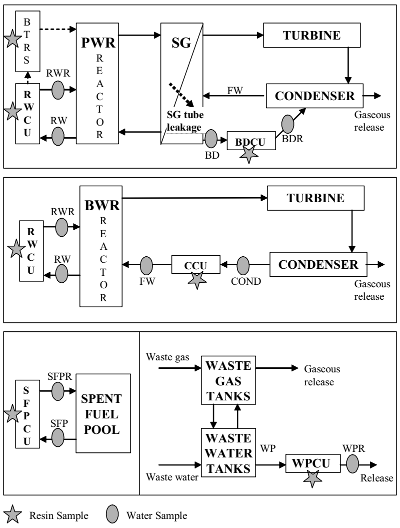
Sweden has three nuclear power plants with ten operational reactor units including both PWRs and BWRs. At the start of the study presented here, a fourth power plant (Barsebäck) was also in operation. Spent ion exchange resins are the dominating type of intermediate level waste in the Swedish final repository for radioactive operational waste, SFR[1]. Studies on the consequences of possible leakages from the repository have identified ^{14}C as one of the most important nuclides in the inventory, since it constitutes one of the main dose contributors in future release scenarios[2]. The reason for this is its high mobility in the environment, biological availability and long half-life (5730 y). For reliable modeling and predictions of future release and migration of ^{14}C from the repository, knowledge of the ^{14}C inventory in the spent resins deposited is required. Moreover, because the chemical form of ^{14}C will affect the mobility of the radionuclide – if released from the repository – chemical speciation in terms of organic and inorganic ^{14}C present in the waste is also important.

In light water reactors, the major part of the ^{14}C entering the reactor water clean-up system, originates from ^{14}C produced in the reactor water[3]. The chemical species of ^{14}C compounds found in the ion exchange resins is therefore directly correlated to the prevailing chemical conditions in the water, i.e. oxidizing or reducing. In BWRs, where oxidizing conditions prevail (i.e. under Neutral Water Chemistry (NWC) conditions), oxidized forms such as carbon dioxide and bicarbonate (i.e. inorganic carbon compounds) are expected in the reactor water[4]. PWRs are operated under reducing conditions, resulting in the formation of mainly organic carbon species, often generalized to hydrocarbons (e.g. methane) and CO. Other possible organic compounds formed are acetaldehyde, formaldehyde, methanol, ethanol, acetone, and acetic and formic acid[4,5,6]. However, according to Lundgren et al.[4], the only compound with a possibility to attach to the ion exchange resins is formate. The chemical conditions prevailing in Swedish BWRs operated with hydrogen injection (i.e. Hydrogen Water Chemistry, HWC) will generally be closer to the NWC operated BWRs rather than the PWRs. Therefore, inorganic carbon species are expected to be the predominant form also in the reactor water of HWC operated BWRs[4,7].

This study has focused on determining the concentration of ^{14}C – in terms of both organic and inorganic ^{14}C content – in spent ion exchange resins from Swedish PWRs and BWRs. The purpose was to provide data that can serve as a basis for reliable estimates of the total ^{14}C inventory in SFR. The ^{14}C inventory has hitherto been estimated based on the correlation factor $^{14}C/^{60}Co = 0.001$[1], which has been believed to best reflect the average relationship in the spent resins from PWRs and BWRs in Sweden. However, the chosen correlation factor is considered very uncertain[1,8].

Measurements of organic and inorganic ^{14}C in various process water systems have also been performed for both types of reactors. The results have been used to obtain a rough partial mass balance with respect to ^{14}C produced in the reactor water.

Figure 1 gives an overview of the process systems in PWR and BWR plants and includes indications of sampling points relevant for the collection of spent resins and process water. The abbreviations in Figure 1 will be used in the subsequent text to identify the sampling points.



ABBREVIATIONS	
BD	steam generator Blow-Down water
BDR	steam generator Blow-Down water Return after clean-up
BDCU	steam generator Blow-Down Clean-Up system
BTRS	Boron Thermal Regeneration System
CCU	Condensate Clean-Up system
COND	Condensate
FW	Feed Water
RW	Reactor Water
RWR	Reactor Water Return after clean-up
RWCU	Reactor Water Clean-Up system
SFP	Spent Fuel Pool water
SFPR	Spent Fuel Pool water Return after clean-up
SFPCU	Spent Fuel Pool Clean-Up
SG	Steam Generator
WP	Waste Processing water
WPR	Waste Processing water after clean-up
WPCU	Waste Processing Clean-Up system

Figure 1. Overview of the process systems in BWR and PWR plants, including spent fuel pool and waste processing systems. Sampling points relevant for the collection of spent resins and process water are indicated in the figure.

Experimental Procedures

Sampling and Sample Description

Spent Ion Exchange Resins. Fifteen batch samples containing 50–2000 ml spent resins were collected from different storage tanks in the Ringhals (PWR; unit R2, R3 and R4), Barsebäck (BWR-HWC; unit B2), Oskarshamn (BWR-HWC; unit O1 and O2) and Forsmark plants (BWR-NWC, unit F1, F2 and F3) in the period 2004–2006. See Table 1 and Figure 1 for an overview. The storage tanks in the Ringhals PWRs generally contained spent resins from a variety of process systems, whereas the BWR tanks were system specific. From each batch sample, 2–8 subsamples were used for ^{14}C analysis and 1 sample for gamma analysis. The origin and number of collected batch samples, as well as the number of processed subsamples for ^{14}C analysis, from each reactor type and process system are given in Table 1. The BDCU sample from R4 at Ringhals was collected to estimate the amount of ^{14}C resulting from a primary-to-secondary leak rate of 5 kg/h. A detailed description of the samples, including resin type and specification, can be found in Table 2.

Table 1

System-Specific Overview of Collected Batch Samples of Spent Ion Exchange Resins
The number of processed subsamples given within brackets.

System	CCU	SFPCU	RWCU	WPCU	BTRS	BDCU
Reactor type						
BWR-NWC	2 (7)	1 (2)	1 (2)	1 (2)		
BWR-HWC	2 (4)	1 (2)	1 (2)			
PWR		4 (22)			1 (2)	1 (2)

Table 2

Detailed Description of Collected Samples of Spent Ion Exchange (IX) Resins

Batch sample ID	Reactor type*	Origin	Resin type** / Specification
IX R:1	PWR (R3)	RWCU operation	Mixed bed, bead resins
IX R:2	PWR (R2)	RWCU operation, RWCU shut-down, SFPCU and WPCU from two years of production	Mixed bed, bead resins
IX R:3	PWR (R4)	RWCU shut-down, SFPCU, WPCU	Mixed bed, bead resins
IX R:4	PWR (R3)	RWCU shut-down, SFPCU, WPCU	Mixed bed, bead resins
IX R:5	PWR (R4)	BDCU	Mixed bed (1:4), bead resins
IX R:6	PWR (R4)	BTRS	Anion, bead resins; intermittent operation
IX B:1	BWR-HWC (B2)	CCU	Mixed bed (1:2), powdered resins, sulfonate
IX B:2	BWR-HWC (B2)	CCU	Mixed bed (1:2), powdered resins, sulfonate
IX B:3	BWR-HWC (B2)	RWCU+WPCU	Mixed bed, bead resins
IX O:1	BWR-NWC (O1)+ BWR-HWC (O2)	SFPCU	Mixed bed (1:3), powdered resins
IX F:1	BWR-NWC (F1+F2+F3)	RWCU	Mixed bed, bead resins
IX F:2	BWR-NWC (F1+F2+F3)	Mostly SFPCU (minor fraction from CCU)	Mixed bed (1:3), powdered resins
IX F:3	BWR-NWC (F1+F2+F3)	WPCU	Mixed bed, bead resins
IX F:4	BWR-NWC (F2)	CCU	Mixed bed (1:2), powdered resins, carboxylate
IX F:5	BWR-NWC (F3)	CCU	Mixed bed (1:2), powdered resins, sulfonate

* Reactor unit/units represented in the sampled storage tank given within brackets
** The anion:cation relationship in mixed bed resins is 1:1 unless stated otherwise

Process Water. Water samples from a wide range of process systems were collected at Ringhals, Oskarshamn and Barsebäck in March–July 2005. The total number of samples processed was 34 including 9 samples where the ^{14}C concentration in both liquid- and gas phase was determined. An overview of the sampling points can be found in Figure 1 with additional details presented in Table 6. Generally, 100 ml process water was collected in pre-evacuated 100 or 250 ml gas pipettes and analyzed within a month.

^{14}C Extraction

Spent Ion Exchange Resins. To separately determine the fractions of inorganic and organic ^{14}C compounds attached to the ion exchange resins, a method developed by Magnusson and Stenström[9] was used, see Figure 2. This method is based on acid stripping followed by wet oxidation in combination with N_2 purging and magnetic stirring. Carbonates are extracted as $^{14}CO_2$ and absorbed in alkaline (2 M NaOH) gas-washing bottles prior to a catalyst. Organic ^{14}C compounds are oxidized by means of a strong oxidant or by the catalyst and absorbed as $^{14}CO_2$ in alkaline bottles after the catalyst. This should allow complete extraction of inorganic and organic ^{14}C species separately. An additional, slightly acidic, wash bottle prior to the alkaline bottles prevents tritium and acidic fumes from reaching the rest of the system. The reliability of the system has been assessed by Magnusson and Stenström[9,10]. In their tests, the recoveries obtained for three ^{14}C-labeled compounds (sodium carbonate, sodium acetate and sodium formate) varied from 94% to 97% (median values). However, wet oxidation proved to be much more complicated when processing spent resins than laboratory prepared ^{14}C-spiked resins. Despite repeated wet oxidation (performed on the same sample) the efficiency seldom reached 100%. This meant that a fraction of the organic ^{14}C still remained attached to the resins after the wet oxidation. In order to fully extract the organic ^{14}C compounds, eight of the treated resin samples were therefore combusted after the chemical treatment. Since the efficiency of the acid stripping was found to be ~100%, any activity remaining after the wet oxidation is assumed to be organic ^{14}C. The remaining ^{14}C found after combustion was compared to the organic ^{14}C activity detected after the chemical treatment in order to obtain correction factors (median value = 1.065) for uncombusted samples.

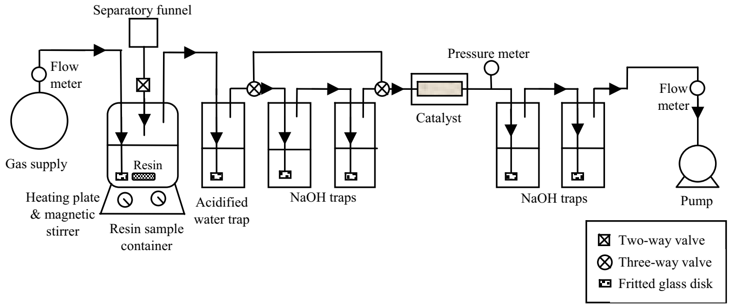


Figure 2. Schematic overview of the system used for extracting ^{14}C from spent ion exchange resins.

Process Water. The method used was based on the same principle as that described above for the ion exchange resins, but with the chemical treatment optimized for 100 ml of process water. The method was optimized using ^{14}C-labeled sodium carbonate and sodium acetate with recoveries of >95% for both compounds. The loss of sodium acetate during acid stripping (resulting in an overestimation of the inorganic ^{14}C content) was determined to be 1.2%. For samples containing both liquid- and gas phase, the sample was purged with N_2 prior to acid stripping and wet oxidation to collect any volatile compounds. During sample processing, the efficiency of the degassing of the water samples prior to processing the liquid phase was found to be 100%. The efficiency of the wet oxidation process was also 100%. Detailed information regarding the method and chemical procedure can be found in Magnusson and Stenström[10].

Analysis

Samples collected from the alkaline gas-washing bottles after the chemical treatment and combustion were measured by Liquid Scintillation Counting (LSC) in duplicate to obtain the activity concentrations of the inorganic and organic ^{14}C fractions. The LSC detection limit obtained from a processed resin sample of 1.0 g ww (wet weight) was about 750 Bq/kg ww or 2200 Bq/kg ww depending on the instrument used. The detection limit associated with process water was ~20 Bq/kg. Samples below the detection limit were precipitated as $BaCO_3$ and the precipitate remeasured using LSC giving an improved detection limit of ~0.4 Bq/kg. The background was determined by regularly processing blank samples.

Gamma analysis was performed on one subsample from each batch sample to obtain the activity concentration of ^{60}Co. The results were used to calculate the correlation factor between ^{14}C and ^{60}Co in the spent resins analyzed.

To determine the fraction of dry solids (D.S.) of each batch sample, generally one additional subsample was taken from the batch, giving dw/ww (dry weight/wet weight) values of 0.36–0.55 for bead resins and 0.35–0.47 for powdered resins.

Results

Spent Ion Exchange Resins

The average ^{14}C concentrations – in terms of both organic and inorganic ^{14}C – obtained from the LSC analysis of processed subsamples of spent resins are presented in Tables 3–5. Based on these results, the total ^{14}C activity in spent resins from the investigated reactors has been calculated. This was done by using the total dry mass of spent resins produced during the fuel cycle/cycles represented by the sampling and the determined D.S. fraction in the batch sample. The accumulated activity was then compared to the calculated ^{14}C production in the reactor water for the same period. The resulting reactor-type-specific correlation factors (system-specific where possible) have been applied on reactor units not investigated when estimating the total ^{14}C inventory (see below). The calculated ^{14}C production in Tables 3–5 is based on production rates of 15.6 kBq/MWh_{th}[11] and 24 kBq/MWh_{th}[4] for PWRs and BWRs, respectively. The net capacities (MW_e) of the investigated reactor units can be found in Table 9.

PWR. The total concentration of ^{14}C found in the spent resins after complete treatment was 3 kBq/kg ww–20 MBq/kg ww (6 kBq/kg dw–50 MBq/kg dw) and the organic fraction 28–98%; see Table 3 for details. The highest activities were found in the RWCU resins. Batch samples IX R:1 + R:4 together typically represent one year's production of spent resins from R3, giving a total amount of 27 GBq of ^{14}C in the resins used during one fuel cycle. The derived value corresponds to 9% of the calculated ^{14}C production in the reactor water. Batch sample IX R:2 represent two years of production and the total amount of ^{14}C in the spent resins from R2 represents 5% of the calculated ^{14}C production in the reactor water during two fuel cycles.

Table 3

Results Based on the Analysis of Spent Ion Exchange Resins (IX) from PWRs

Sample ID	Reactor	Origin	^{14}C concentration in spent IX sample (MBq·kg^{-1} ww)			$\sigma_{relative}$*	Organic fraction	D.S. content	Total ^{14}C activity in spent IX (GBq)	Calculated ^{14}C production (GBq·year^{-1})	IX / Production	Correlation factor ^{14}C/^{60}Co
			Inorganic	Organic	Total							
IX R:1	R3	RWCU operation	13.9	5.65	19.6	16%	29%	43%	20.1	312	6.4%	0.92
IX R:2	R2	2 years of production	6.00	2.28	8.29	23%	28%	42%	32.0	649	4.9%	0.084
IX R:3	R4	RWCU shut-down, SFPCU, WPCU	1.07	0.571	1.64	10%	35%	43%	4.39	297	1.5%	0.023
IX R:4	R3	RWCU shut-down, SFPCU, WPCU	0.997	0.420	1.42	14%	30%	43%	6.80	312	2.2%	0.029
IX R:5	R4	BDCU**	1.8E-03	1.3E-03	3.2E-03	76%	43%	55%	0.20	350	0.06%	—
IX R:6	R4	BTRS	8.47E-03	0.339	0.347	4%	98%	39%	0.894	350	0.26%	120

* Maximum standard deviation; based on the variation among analyzed subsamples OR the average standard deviation from the ^{14}C analysis of the subsamples (typically ~4%)

** Primary-to-secondary leak rate 5 kg/h

Tests carried out during the chemical treatment showed that it is possible that a fraction of the ^{14}C activity in the spent resins could be degassed during storage and handling. This may explain the comparatively low activity accumulated in IX R:2, representing two years of production.

BWR-HWC. The maximum total concentration of ^{14}C was 0.13 MBq/kg ww (0.28 MBq/kg dw); found in the spent CCU resins; see Table 4 for details. The organic fraction was generally 6–16%. Batch samples IX B:1/B:2 + B:3 + O:1 together represent one year's production of spent resins from one BWR-HWC unit. This gives a total amount of 1.8 GBq, corresponding to 0.5% of the calculated ^{14}C production in the reactor water.

BWR-NWC. The total concentration of ^{14}C found in the spent resins was 0.059–1.9 MBq/kg ww (0.14–4.3 MBq/kg dw); see Table 5 for details. The highest activities were found in the carboxylate CCU resins, which contained a factor 5 more ^{14}C than the sulfonate CCU resins. The organic fraction in the BWR-NWC resins was 5–24%, the highest fraction being found in the sulfonate CCU resins. The two reactor units operating with carboxylate CCU resins (F1 + F2) accumulate a total amount of 21 GBq/(unit·year) of ^{14}C in spent resins, of which 97% originates from the CCU resins. The reactor operating with sulfonate CCU resins (F3) accumulate a total amount of 5 GBq/year. The figures correspond to 4% (F1 + F2) and 0.8% (F3) of the calculated ^{14}C production in the reactor water.

Table 4

Results Based on the Analysis of Spent Ion Exchange Resins (IX) from BWR-HWC Units

Sample ID	**Reactor**	**Origin**	**^{14}C concentration in spent IX sample** (kBq·kg^{-1} ww)		**$\sigma_{relative}$***	**Organic fraction**	**D.S. content**	**Total ^{14}C activity in spent resins** (GBq)	**Calculated ^{14}C production** (GBq·year^{-1})	**IX / Production**	**Correlation factor ^{14}C/^{60}Co**
			Inorganic **Organic**	**Total**							
IX B:1	B2	CCU	96.5 8.96	105	4%	8%	37%	1.47	342	0.43%	0.022
IX B:2	B2	CCU	110 19.3	130	36%	16%	47%	1.44	342	0.42%	0.039
IX B:3	B2	RWCU+ WPCU	70.3 4.75	75.0	4%	6%	36%	0.313	268	0.12%	7.3E-04
IX O:1	O1+O2	SFPCU	<0.842** <1.42**	<2.26	—	—	37%	<0.00146	542	<0.0003%	<2.6E-06

* Maximum standard deviation; based on the variation among analyzed subsamples OR the average standard deviation from the ^{14}C analysis of the subsamples (typically ~4%)
** Detection limit; derived values therefore upper limits

Table 5

Results Based on the Analysis of Spent Ion Exchange Resins (IX) from BWR-NWC Units

Sample ID	**Reactor**	**Origin**	**^{14}C concentration in spent IX sample** (kBq·kg^{-1} ww)		**$\sigma_{relative}$***	**Organic fraction**	**D.S. content**	**Total ^{14}C activity in spent resins** (GBq)	**Calculated ^{14}C production** (GBq·year^{-1})	**IX / Production**	**Correlation factor ^{14}C/^{60}Co**
			Inorganic **Organic**	**Total**							
IX F:1	F1+F2+F3	RWCU	53.8 5.60	59.4	5%	9%	44%	0.406	1640	0.025%	5.4E-04
IX F:2	F1+F2+F3	SFPCU	416 25.6	442	6%	6%	35%	0.998	1640	0.061%	0.074
IX F:3	F1+F2+F3	WPCU	68.3 3.27	71.6	26%	5%	39%	0.666	1640	0.041%	6.5E-04
IX F:4	F2	CCU**	1570 296	1870	4%	16%	43%	20.1	514	3.9%	1
IX F:5	F3	CCU***	278 88.7	367	4%	24%	37%	3.80	595	0.64%	0.2

* Maximum standard deviation; based on the variation among analyzed subsamples OR the average standard deviation from the ^{14}C analysis of the subsamples (typically ~4%)
** Carboxylate resins
*** Sulfonate resins

Process Water

The results from the ^{14}C analysis of process water from the PWR (R4), BWR-HWC (B2) and BWR-NWC (O3), collected in 2005, are presented in Table 6.

PWR. The activity concentration in the reactor water was found to be 28 kBq/kg; almost equally divided between the gas- and liquid phase, see Figure 3 for details. As expected, organic ^{14}C compounds are the dominant species in the water, with less than 1% present in inorganic form. In the gas phase, the dominant chemical species was most likely hydrocarbons and/or CO since these reduced forms are not absorbed by NaOH until oxidized by a catalyst. However, the organic ^{14}C compounds found in the liquid phase were found NOT to be volatile under the experimental conditions used. According to experiments performed during the optimization of the method, the presence of organic acids such as formic and acetic acid, could partly explain the findings. Moreover, the ^{14}C concentration in the liquid phase was the same (within experimental uncertainties) before (RW samples) and after (RWR samples) the RWCU (see Figure 3), indicating a very low uptake on the resins. Formic and acetic acid are expected to be present as anionic species and readily attach to the resins since the pH value over the RWCU resin is >6.5, which is well above the pKa-values of the acids. However, in the RWCU of a PWR the anion resin is saturated with boric acid, which may outcompete organic acids at low concentrations, resulting in slow movement of the acids through the ion exchange bed.

If the waste water sample (WPR_{Jun05}) is assumed to be representative of the year, the annual ^{14}C activity released as waterborne discharges from the PWR corresponds to 2.2‰ of the calculated production rate in the reactor water.

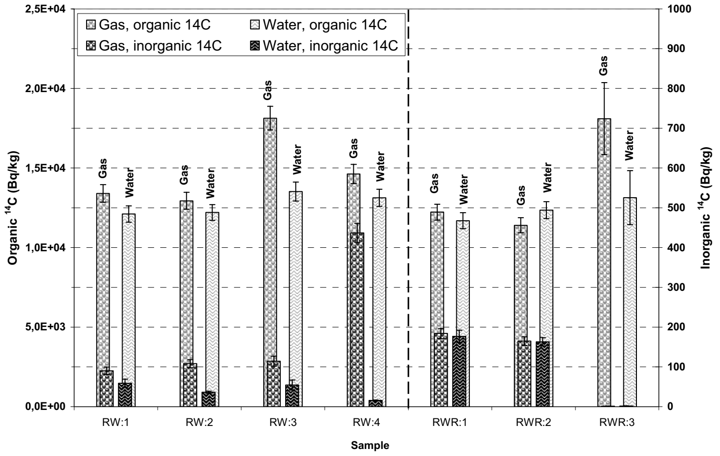


Figure 3. The organic and inorganic concentrations of ^{14}C found in the gas- and liquid phase of process water collected before (samples RW) and after (samples RWR) the RWCU in the PWR reactor R4, 2005. Note the different scales for organic and inorganic species.

BWR-HWC. The activity concentration in the reactor water of the BWR-HWC unit was found to be less than 3 Bq/kg.

If the waste water samples ($WPR_{Mar05–Jun05}$) are assumed to be representative of the year, the annual ^{14}C activity released as waterborne discharges from the BWR-HWC unit corresponds to 0.3‰ of the calculated production rate in the reactor water.

Table 6

Results from the ^{14}C Analysis of Process Water

Reactor type	Sample ID	Sampling date	Date of processing	Phase	Inorganic ^{14}C (Bq/kg)	$\sigma_{relative}$ (%)	Detection limit (Bq/kg)	Organic ^{14}C (Bq/kg)	$\sigma_{relative}$ (%)	Detection limit (Bq/kg)	Total ^{14}C (Bq/kg)	Organic fraction (%)
PWR (R4)	RW:1	27-Jun	5-Jul	Gas	90	10	13	13.4E+03	4.1	13	13.5E+03	99.3
				Liquid	59	17	18	12.1E+03	4.2	18	12.2E+03	99.5
	RW:2	27-Jun	6-Jul	Gas	108	9.2	14	12.9E+03	4.1	14	13.0E+03	99.2
				Liquid	36	6.7	0.74	12.2E+03	4.1	22	12.2E+03	99.7
	RW:3	5-Jul	8-Jul	Gas	114	11	18	18.1E+03	4.1	18	18.2E+03	99.4
				Liquid	55	23	22	13.5E+03	4.4	22	13.6E+03	99.6
	RW:4	8-Jul	22-Jul	Gas	437	5.5	18	14.6E+03	4.1	18	15.0E+03	97.3
				Liquid	16	6.7	0.54	13.1E+03	4.1	21	13.1E+03	99.9
	RWR:1	27-Jun	7-Jul	Gas	184	6.8	13	12.2E+03	4.1	13	12.4E+03	98.5
				Liquid	177	8.7	21	11.7E+03	4.3	22	11.9E+03	99.5
	RWR:2	5-Jul	22-Jul	Gas	165	6.5	0.95	11.4E+03	4.2	41	11.6E+03	98.6
				Liquid	163	6.5	0.95	12.4E+03	4.3	41	12.5E+03	98.7
	RWR:3	5-Jul	7-Jul	Gas	<1.1		<1.1	18.1E+03	13	50	18.1E+03	100
				Liquid	1.7	27	1.1	13.1E+03	13	50	13.1E+03	100
	BD*	20-Jul	21-Jul	Liquid	<0.34		<0.34	4.3	8.5	0.38	<4.6	>92.6
	BDR*	20-Jul	21-Jul	Liquid	0.60	51	0.36	2.5	11	0.37	3.1	80.4
	SFP	5-Jul	6-Jul	Liquid	39	6.6	0.47	7.6	7.6	0.85	46	16.4
	SFPR	5-Jul	8-Jul	Liquid	36	6.5	0.58	4.4	7.4	0.69	40	10.9
	WPR$_{\text{Jun05}}$	30-Jun	20-Jul	Liquid	135	6.5	0.52	56	6.5	0.44	191	29.4
BWR-HWC (B2)	RW:1	24-May	21-Jun	Liquid	0.36	46	0.39	1.0	17	0.39	1.4	>73
	RW:2	25-May	22-Jun	Gas	<0.29		0.29	<0.28		0.28	<0.57	
				Liquid	<0.45		0.45	<0.45		0.45	<0.90	
	RWR	24-May	21-Jun	Liquid	0.72	30	0.46	1.0	20	0.46	1.7	58
	COND	24-May	20-Jun	Liquid	<0.40		0.40	2.4	11	0.40	<2.8	>85
	FW	24-May	22-Jun	Liquid	<0.38		0.38	1.6	12	0.38	<2.0	>80
	WPR$_{\text{Mar05}}$	31-Mar	18-Jul	Liquid	1.5	15	0.40	4.5	7.4	0.4	5.9	76
	WPR$_{\text{Apr05}}$	30-Apr	18-Jul	Liquid								
	WPR$_{\text{May05}}$	31-May	18-Jul	Liquid								
BWR-NWC (O3)	RW:1	11-Jul	20-Jul	Liquid	0.36	47	0.30	2.7	8.5	0.32	3.1	88
	RW:2	11-Jul	20-Jul	Gas	0.79	17	0.23	0.39	29	0.22	1.2	33
				Liquid	<0.32		0.32	1.4	14	0.33	<1.7	>81
	RWR	11-Jul	19-Jul	Liquid	<0.29		1.1	1.1	17	0.32	<1.4	>79
	COND	11-Jul	19-Jul	Liquid	0.68	23	0.34	0.48	41	0.36	<1.2	41
	FW	11-Jul	19-Jul	Liquid	<0.33		0.33	2.4	9.2	0.36	<2.7	>88

* Primary-to-secondary leak rate 5 kg/h

BWR-NWC. The activity concentration in the reactor water of the BWC-NWC unit was found to be approximately 3 Bq/kg. No significant difference in chemical speciation between the HWC and NWC operated reactor could be seen. The sample collected after the CCU (FW) had an unexpectedly higher ^{14}C concentration than the sample collected before the purification system (COND). This may be because the CCU resin is bleeding ^{14}C at the end of its operation period.

Partial Mass Balance

The accumulated fraction (in terms of total and organic ^{14}C) in the resins may be calculated using the data from Tables 3–5 of total ^{14}C activities in spent ion exchange resins and the activity concentrations measured in process water (liquid phase). This has been done for the PWRs R2 and R3 and the BWR-HWC unit B2. B2 was the only reactor from which both spent resins and process water were analyzed; for R2 and R3 it was assumed that the ^{14}C concentration in the reactor water was the same as that in R4. The results are presented in Table 7.

Table 7

Calculated Fraction of Total and Organic ^{14}C From Process Water Accumulated in Spent Ion Exchange (IX) Resins

Reactor	Process water system	^{14}C fraction	^{14}C concentration in liquid phase (Bq·kg^{-1})	^{14}C activity in liquid phase passing through IX (Bq·year^{-1})	Accumulated ^{14}C activity in spent resins (Bq·year^{-1})	^{14}C activity in IX / ^{14}C activity in liquid phase
R3 PWR	RW	Total	13000	2.6E+12	2.7E+10	1%
	RW	Organic	13000	2.6E+12	7.8E+09	0.3%
R2 PWR	RW	Total	13000	2.6E+12	1.6E+10	0.6%
	RW	Organic	13000	2.6E+12	9.0E+09	0.2%
B2 BWR-HWC	RW	Total	1.4	6.7E+08	3.1E+08	50%
	RW	Organic	1.0	4.9E+08	1.9E+07	4%
	COND	Total	2.8	7.3E+10	1.5E+09	2%
	COND	Organic	2.4	6.2E+10	1.8E+08	0.3%

In the PWRs, only a small fraction of the ^{14}C in the reactor water is attached to the ion exchange resins, whereas the uptake in the resins from the BWR seems to be significantly higher. However, the calculated total uptake of 50% in RWCU (derived from the water concentration in RW) in B2 is based on the ^{14}C activity found in spent resins purifying both RW and WP water. It should also be noted that the activity concentrations in the process water from B2 are based on single measurements. The organic ^{14}C species seem less affected by resin uptake than the inorganic species in the water.

Estimation of the ^{14}C Inventory in SFR

The total activity accumulated annually (average accumulation rates over the period 1996–2004) in spent resins from all reactor units in Sweden (operational in 2004) was calculated based on the obtained correlation factors between ^{14}C activity in spent resins and the calculated ^{14}C production. The values from units not investigated were calculated using the system- or reactor-specific correlation factors in Tables 3–5. The results are presented in Table 8. System-specific production rates of ^{14}C in spent resins for each reactor unit are displayed in Figure 4. Since the ^{14}C activity in the SFPCU resin from the BWR-HWC unit was below the detection limit, the upper limits have been calculated. Since no system-specific correlation factors could be obtained from the PWR samples analyzed, only the total ^{14}C accumulation in spent resins from PWRs are shown (except the minor contributions from BTRS in R3 and R4 and BDCU in R4).

The total amount of ^{14}C accumulated annually in spent resins at Swedish reactors, was found to be 130 GBq, of which 24% is in organic form. The main contribution originates from the PWRs (56%), followed by the BWR-NWC units (40%), whereas BWR-HWC units contribute only a minor fraction (4%). It should be noted that the two BWR-NWC units operating with carboxylate CCU resins (F1 + F2) accumulate almost as much ^{14}C in their spent resins as a typical PWR. The higher fraction of ^{14}C on carboxylate resins may be explained as follows. The weakly acidic carboxylate resins have a higher pH than the strongly acidic sulfonate resins. The higher pH allows a larger fraction of the acidic species (hydrogen carbonate and simple organic acids) to attach to the resins. Furthermore, the degradation of sulfonate resins by hydrogen peroxide, forming sulfuric acid, may also lower the pH in the sulfonate resins. However, preliminary tests show that a large fraction of the ^{14}C in the spent resins from Forsmark (F1+F2+F3) never reaches the repository. Forsmark still uses bituminization to immobilize the spent resins, whereas all other Swedish power plants use cement immobilization. Prior to bituminization, the resins are dried at a temperature of 150°C. Preliminary tests on CCU resins (both carboxylate and sulfonate) from Forsmark show a loss of >50% during the heating process.

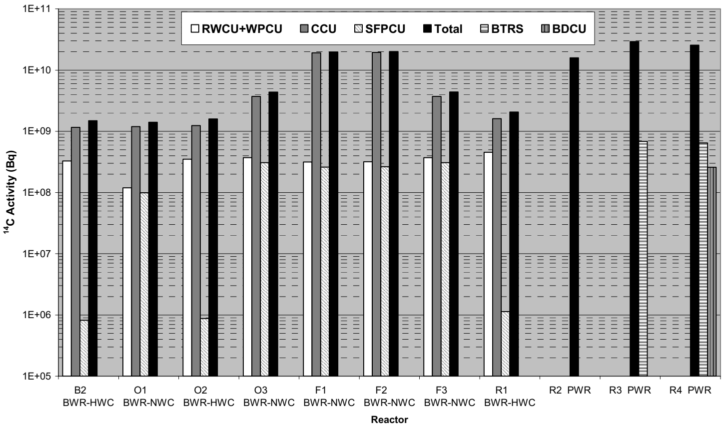


Figure 4. Calculated annual ^{14}C accumulation (average value over the years 1996–2004) in spent ion exchange resins from RWCU+WPCU, CCU, SFPCU, BTRS and BDCU originating from all Swedish reactors in operation during 2004. The activity in resins from SFPCU in BWR-HWC is the upper limit.

From Figure 4 it is evident that the CCU resins totally dominate the contribution from the BWRs. The spent resins from BDCU and BTRS do not contribute significantly to the total ^{14}C activity in resins arising from the PWRs R3 and R4. However, if deposited in less qualified repositories, e.g. shallow land burial, the contribution from BTRS and BDCU resins could be of importance.

Based on the data presented in Table 8, the total ^{14}C activity accumulated in spent resins during the life-time of the reactors has been calculated. This corresponds to the total theoretical amount of ^{14}C in spent resins that will be – or has been – deposited in the Swedish waste repository. Since the BWR B1 in Barsebäck was shut down in 1999, it was not included in Table 8 and Figure 4; however, it was included in these final calculations. The calculations assume a reactor life-time of 40 years (except for B1 and B2, where the actual life-times were used). The results are presented in Table 9. The total amount of ^{14}C in spent resins, generated by all power reactors in Sweden during their life-time, has been estimated to be 5.0 TBq, of which 24% will be in organic form. The derived value of the ^{14}C inventory in SFR was found to be within the conservative limits stated in the safety analysis report.

Table 8

Annual Accumulation of ^{14}C in Spent Ion Exchange Resins

Reactor type	**Reactor**	**Annual ^{14}C accumulation in spent resins** (GBq)	**Normalized ^{14}C accumulation in spent resins** ($GBq \cdot GW_e^{-1} \cdot year^{-1}$)
BWR-HWC	B2	1.5	3.4
	O2	1.6	3.3
	R1	2.1	3.5
BWR-NWC	O1	1.4	4.7
	O3	4.4	4.4
	F1	20	24
	F2	20	24
	F3	4.4	4.4
PWR	R2	16	21
	R3	29	36
	R4	26	33
Total		**130**	

Prior to this study, the ^{14}C inventory in SFR, stated in the safety analysis report, has been estimated using a correlation factor of $^{14}C/^{60}Co$ equal to 0.001. This factor has been derived from previous international experimental studies as well as national theoretical studies, and assumes a mixture of BWR and PWR resins in the repository.

By using the ratio 0.001 to estimate the ^{14}C activity in the batch samples collected in this study, the resulting estimation of the ^{14}C inventory would have been 150 GBq, which is a factor of 30 below the reported value in Table 9. The comparison shows that ^{14}C activities derived exclusively from the correlation factor seems to underestimate the accumulated activity in spent resins deposited in SFR for both PWRs and BWRs; the contribution from PWRs being most underestimated. The underestimation may be the result of the decrease in ^{60}Co production observed as a result of cobalt-reduction efforts. For example, the amount of ^{60}Co in spent ion exchange resins has decreased by a factor of 10 during the past 20 years in Swedish PWRs.

Conclusions

The largest uncertainties related to the calculated ^{14}C inventory of 5.0 TBq are considered to be whether the analyzed samples were representative of the system in question or not. For the PWRs investigated, the sampling procedure is considered to have been accomplished in the best possible way, considering the variety of systems represented in the sampled storage tanks. The samples should therefore reflect the average ^{14}C production in PWR resins over a complete fuel cycle. Whether this specific fuel cycle was representative of a longer period of operation remains uncertain.

Table 9

Total and Organic ^{14}C Activity Accumulated in Spent Resins by Swedish Power Reactors During their Life-time

Reactor type	**Reactor**	**Net Capacity** (MW_e)	**Total ^{14}C activity accumulated in spent resins during reactor life-time** (GBq)	**Organic ^{14}C activity** (GBq)
BWR-HWC	B1	600	36	3.8
	B2	600	42	4.4
	O2	602	64	6.8
	R1	830	83	8.8
BWR-NWC	O1	467	56	12
	O3	1160	180	37
	F1	1018	790	120
	F2	951	800	130
	F3	1190	176	37
PWR	R2	875	630	190
	R3	917	1200	340
	R4	908	1000	330
Total		**10000**	**5000**	**1200**

Since the analyzed BWR samples were all system specific, their contribution to the total inventory should be less uncertain than for the PWRs. However, due to the immobilization strategy (bituminization) – during which a substantial fraction of the ^{14}C activity might be lost – employed at the Forsmark and Barsebäck plants, their contributions could be overestimated by a factor 2.

Based on the above mentioned uncertainties, the total ^{14}C inventory calculated after 40 years of production is estimated to be within a factor of 2–3 of the value presented in Table 9. Despite this value (5 TBq) being within the limits stated in the safety analysis report, future repeated measurements or measuring campaigns should be considered to improve the method by which the ^{14}C inventory is assessed.

Estimating the ^{14}C activity in spent resins from correlation factors using ^{60}Co should be used with extreme care, since the accumulated amount of ^{60}Co may change over time due to cobalt reduction measures. Furthermore, the chemical properties of ^{14}C and ^{60}Co in the process systems and ion exchangers are also very different. This is reflected by the calculated correlation factors in Tables 3–5, covering more than three orders of magnitude.

Acknowledgements

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Paper V

^{14}C in spent ion-exchange resins and process water from nuclear reactors – A method for quantitative determination of organic and inorganic fractions

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A method of separately quantifying organic and inorganic ^{14}C compounds present in spent ion-exchange resins and process water from nuclear power reactors has been developed. Extraction of carbon compounds is accomplished by means of acid stripping (inorganic ^{14}C) and subsequent wet oxidation (organic ^{14}C) or by N_2 purging in combination with a catalytic furnace (oxidized and reduced gaseous compounds) with organic and inorganic ^{14}C species collected separately. Recovery experiments on simulated samples spiked with ^{14}C-labelled sodium carbonate, sodium acetate and sodium formate, showed extraction yields of 94–98%. The sample-specific procedures were also tested on authentic samples of spent resins and reactor water with good results. Validation and reliability of the procedures are presented and the method is compared to previous methods reported in the literature.

Introduction

Carbon-14 is a radionuclide of considerable concern in nuclear power production. According to UNSCEAR[1], the main contribution to the global collective dose (estimated over 10 000 years) from radionuclides released in various stages of the nuclear fuel cycle, is from globally dispersed ^{14}C. Furthermore, the collective effective dose from low- and intermediate-level waste (LILW) disposal is almost entirely due to ^{14}C.[1] Due to the potential impact on human health, minimizing waste and releases containing ^{14}C is recognised as being important. Carbon-14 waste minimization may also be economically beneficial due to its potential of being the inventory limiting nuclide in LILW disposal facilities.[2] It is also a critical nuclide in classifying waste and may therefore dictate the choice of disposal method.[3] In order to control the production and release rates of ^{14}C, the behaviour of ^{14}C inside the power plant (chemically and physically) must be known, as well as relative and absolute quantities within the different waste streams. Based on this knowledge, appropriate waste management strategies and practices may be implemented to reduce actual and potential releases to the environment.

The production of ^{14}C in nuclear reactors occurs through neutron-induced reactions with oxygen, nitrogen and carbon present in the fuel, fuel cladding, coolant, moderator and structural material of the reactor.[3] A variety of gaseous, solid and liquid waste containing ^{14}C is generated. In light water reactors (LWRs), the ^{14}C produced in the reactor coolant is almost solely responsible for the gaseous and liquid releases at the plant site. Most of this ^{14}C is discharged as gaseous releases, the rest being accumulated in ion-exchange resins or released as liquid discharges. Spent resins are today one of the largest sources of ^{14}C activity in LILW disposal facilities.[2]

Carbon-14 is a weak beta emitter (max. energy 156 keV) with a half-life of about 5730 years. When analysing ^{14}C in process media of nuclear reactors, it has to be isolated from dozens of other radionuclides. Because of the difficulty in measuring ^{14}C, published data on ^{14}C in process water and spent ion-exchange resins are limited. Most of the existing data on the quantification and characterization of ^{14}C in process water (generally reactor water) and spent ion-exchange resins from LWRs are from investigations performed in the 1980's and the beginning of the 1990's. The methods used for these analyses were generally intended to measure the total ^{14}C content, i.e. the chemical form of ^{14}C was not taken into consideration. However, the chemical form of ^{14}C (organic or inorganic) is an important factor when estimating doses arising from releases to the environment.

The chemical form of ^{14}C in process systems determines its behaviour (e.g. degree of adsorption on ion-exchange resins) and characterization is therefore important to be able to model and predict its fate. As is pointed out by YIM and CARON[3], the data used to characterize and quantify ^{14}C production in the reactor coolant are old, particularly in the case of LWRs. In the context of waste disposal, organic and inorganic carbon compounds are governed by different retention mechanisms during migration within the waste package as well as during transport outside the repository, if released. For example, in the case of ^{14}C released from a geological repository, only the organic ^{14}C compounds usually contribute to the total dose due to their high solubility and lack of retardation during transport.[4–6] In order to make reliable safety assessments, there is a need for more direct measurements of chemical forms of ^{14}C in some types of waste.[4,7,8]

This paper presents a method of quantifying organic and inorganic ^{14}C species separately in samples of various process media by sequential extraction. The method was optimized for ^{14}C analysis of spent ion-exchange resins and process water (gaseous and liquid phase), resulting in different procedures. A great variety of carbon compounds is expected in such samples (carbonates, organic acids, aldehydes, etc.[9,10]). Initial development of the method was therefore performed using ^{14}C-labelled compounds representing the most common organic and inorganic compounds found in process systems of Swedish pressurized water reactors (PWRs) and boiling water reactors (BWRs). Following recovery tests on simulated samples, the method was further optimized through series of tests on authentic samples of spent resins and reactor water.

Previous methods

Methods providing information on the chemical form of ^{14}C in different process media of nuclear reactors do exist, but are few, except for gaseous samples. Furthermore, they are generally based on measuring total and inorganic ^{14}C in separate subsamples, whereby the organic fraction is estimated by subtraction (i.e. indirect measurement). Separating the chemical forms of ^{14}C in the same sample allows direct measurements of both fractions within the sample to be made. Uncertainties related to taking differences, as in the former approach, are thereby excluded.

The basic principle of extracting ^{14}C from a medium is to convert the carbon compounds to CO_2 by either combustion or acidification. See Fig. 1 for a comparison of typical system set-ups. The purpose of combustion is to extract all the carbon compounds present, while acid treatment only extracts the inorganic fraction (i.e. carbonates). The carbon dioxide evolved in the process is led to an absorber (usually NaOH solution) by means of a carrier gas. If combustion is employed, a catalytic furnace is used to ensure complete oxidation prior to CO_2 absorption. The ^{14}C activity is determined by mixing a few millilitres of the absorber with a scintillation cocktail and measuring the activity with liquid scintillation counting (LSC). To avoid other radionuclides (e.g. ^{3}H) from reaching the absorber, a water trap may be utilized.

Methods previously used to determine the ^{14}C concentration in spent ion-exchange resins described in the literature[11–20] have been reviewed by STENSTRÖM and MAGNUSSON.[21,22] The majority of the ten methods reviewed were designed to quantify the total ^{14}C concentration or only the inorganic ^{14}C concentration. Methods providing information on both the organic and inorganic ^{14}C content include those presented by VANCE et al.,[20] PARK et al.[23] and SALONEN and SNELLMAN.[18] In the method described by VANCE et al.,[20] some of the resin samples were combusted for total ^{14}C determination and some treated with H_2SO_4 for inorganic ^{14}C determination. The fraction of organic ^{14}C was then estimated by subtracting the inorganic fraction from the total ^{14}C. A method developed by PARK et al.[23] resembles that of VANCE et al.[20] They used H_2SO_4 together with KOH to determine the inorganic fraction and wet oxidation-acid stripping (KOH followed by $K_2S_2O_8$, $AgNO_3$ and H_2SO_4) to determine the total ^{14}C concentration.

The only method designed to determine both fractions separately in spent resins by direct measurement is that reported by SALONEN and SNELLMAN[18]. Their method is designed to separate carbonates and CO_2 from hydrocarbons and CO using acid stripping for 90 minutes in combination with a catalytic furnace. Separation was achieved using two alkaline absorbers with the furnace located between them. With this arrangement, CO_2 was absorbed in the first absorber, while hydrocarbons and CO passing through it, were oxidized by the catalytic furnace and absorbed in the second absorber. The acid treatment procedure was conducted twice on the samples analysed, with a few days' interval, to assess the extraction efficiency.

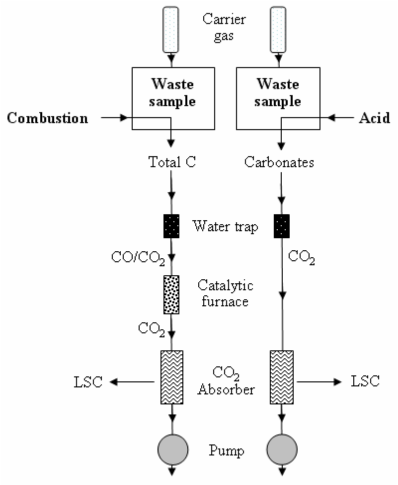

Fig. 1. Schematic comparison of system set-ups of the two basic analytical techniques used for ^{14}C determination in process media of nuclear reactors

Methods developed for ^{14}C extraction from process water (generally reactor water) have also been reported.[12,14,20,24–27] VANCE et al.[20] determined the inorganic ^{14}C fraction in reactor water by acidification (using H_2SO_4). They obtained the total ^{14}C activity by treating another sample with $K_2S_2O_8$ and $AgNO_3$ (i.e. wet oxidation). The organic fraction was then determined by subtraction. Two publications; BLEIER[12] and SALONEN and SNELLMAN,[24] report separate determination by direct measurements of organic and inorganic ^{14}C compounds in process water. The method used by SALONEN and SNELLMAN[24] is not described in the publication; instead they refer to their method developed for spent ion-exchange resins.[18] BLEIER[12] extracted the inorganic fraction by acid treatment for 5 hours, with simultaneous heating (70–80°C). The organic compounds were extracted by wet oxidation using H_2SO_4 + CrO_3 (duration not stated). A catalytic furnace located between two sets of CO_2 absorbers enabled chemical separation of the gases generated during the acid stripping process.

Experimental

Principle

To be able to extract the fractions of organic and inorganic ^{14}C in spent ion-exchange resins and process water, the approach suggested by STENSTRÖM and MAGNUSSON[22] was used as a starting point. This approach is based on a combination of the acid stripping techniques presented by CHANG et al.[13] and SALONEN and SNELLMAN[18] with slight modifications. In order to obtain complete extraction of the organic carbon compounds present, additional treatment involving wet oxidation by means of a strong oxidant and simultaneous heating, as described by e.g. VANCE et al.,[20] was also introduced.

The combination of acid stripping and subsequent wet oxidation allows separate extraction of the organic and inorganic carbon compounds in a single sample. The principle of the method developed (see Fig. 2) is to first extract the inorganic fraction by adding acid to the sample (acid stripping) and absorb the $^{14}CO_2$ generated in a pair of alkali gas washing bottles (bottles 2 and 3 in Fig. 2; the second one serves as a safety bottle which is monitored to verify complete CO_2 absorption). In the second step, the remaining carbon compounds (i.e. the organic fraction), are extracted by adding a strong oxidant (wet oxidation) and the $^{14}CO_2$ evolved is absorbed in a second pair of gas washing bottles (bottles 4 and 5). A catalytic furnace, located between the two sets of washing bottles, ensures oxidation of reduced compounds. This system set-up separates carbonates and CO_2 present in the sample (inorganic fraction) from CO, hydrocarbons, organic acids and other non- or semi-volatile organic carbon compounds (organic fraction). Tritium and other contaminants are trapped in a weakly acidified (to minimize CO_2 absorption) water trap (bottle no. 1 in Fig. 2) located immediately after the sample container (reaction vessel).

System set-up and Instrumentation

The system is schematically outlined in Fig. 2. Nitrogen, which is used as the carrier gas, is drawn through the system from a gas supply (at atmospheric pressure) by means of a

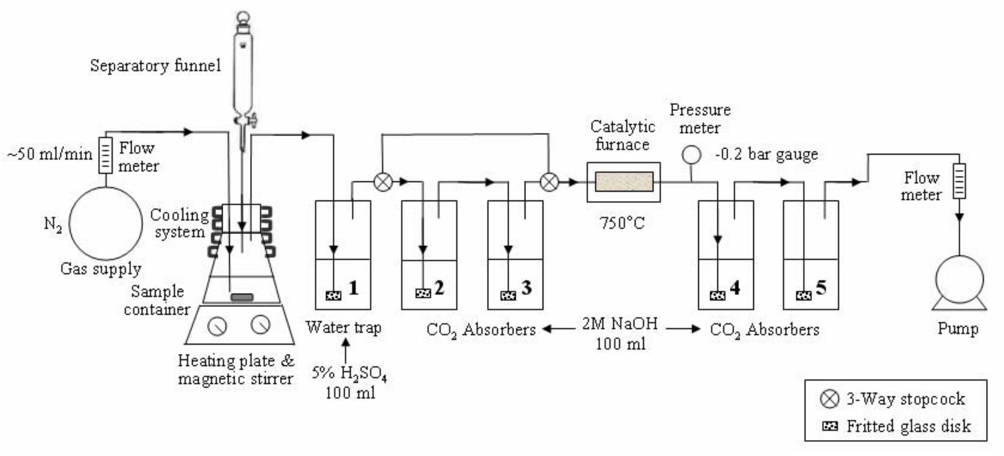

Fig. 2. System set-up used as a starting point for ^{14}C extraction from spent ion-exchange resins and process water. The gas washing bottles are referred to as 1–5 in the text

diaphragm vacuum pump (Air Cadet, Cole Parmer, max. pumping speed = 14 l/min). The gas supply is connected to a flow meter with a needle valve (max. flow = 522 ml/min; Cole Parmer) by silicone tubing. The system is operated slightly below atmospheric pressure to prevent losses in case of leakage.

The sample container consists of an Erlenmeyer flask (250 or 500 ml) with a three-hole rubber stopper (35×30×30 mm, 6 mm hole diameter) for gas and separatory funnel inlets and an outlet line. The container is placed on a magnetic stirrer with a heating plate. The three in- and outlet lines through the rubber stopper consist of PVC tubing (4 mm ID, 6 mm OD), connected to the rest of the system through polypropylene reducing connectors. The separatory funnel, (100 ml, Duran) is made of glass with a PTFE stopcock plug. To condense the water vapour generated, a tap-water cooling loop, made of copper tubing and manufactured to fit the outer side of the Erlenmeyer flask, is employed.

The five gas washing bottles (100 ml, Drechsel bottles, Brand) are all equipped with inserts with a fritted glass tip (porosity 1), which are secured to the bottles by stainless steel clips. Bottle no. 1 contains 100 ml 5% H_2SO_4 and nos. 2–5 100 ml 2M NaOH. The bottles are connected by silicone tubing (8 mm ID, 11 mm OD) with two polyethylene three-way stopcocks (T-shape) placed before and after the first set of CO_2 absorbers (nos. 2–3).

The catalytic furnace consists of a tube furnace (12 cm in length) surrounding a quartz tube (~ 200 mm, 9 mm ID, 12 mm OD) containing platinum (1 wt.%) on alumina pellets (3.2 mm, Aldrich Chemical Company, Inc.) and CuO (wire, 0.65 mm x 6 mm, pro analysi, Merck, Germany). The catalyst mixture (length of about 9 cm, mixing ratio: 30% platinum on alumina and 70% CuO by weight) is held in place by quartz wool inserted from both ends of the quartz tube. The silicone tubing is connected to the quartz tube by a Swagelok insert for tubing combined with a Swagelok tube fitting union. The pressure meter is a manometer (-1 to 0.6 bar), which is connected to the system by a Swagelok reducer combined with a Swagelok union tee.

Most of the devices are mounted on the system using an upper and lower Swagelok mounting rail together with appropriate metric rail nuts and tube support kits. Cork-lined clamps mounted on the rail with tube support kits are used to secure the gas washing bottles and Erlenmeyer flask.

Catalytic furnace efficiency

The decision to use an inert gas as carrier gas requires the catalytic furnace to be able to operate efficiently without any external oxygen supply. The efficiency of the catalyst mixture was tested using CH_4 demonstrating almost 100% oxidation (a catalyst of only wired CuO was also tested but did not provide the same degree of oxidation). The catalytic furnace has been proven to have an operation time of $\geq$200 hours, corresponding to 50 tests of 4 hours' duration.

Resin treatment procedure

A sample of ~1 g ww (wet weight) spent resin is placed in the sample container (250 ml Erlenmeyer flask; see Fig. 2). The system is evacuated to 0.2 bar below atmospheric pressure and the carrier gas (N_2) flow rate is set to 40 ml/min. A pressure of -0.2 bar gauge is maintained during the whole procedure. A volume of 17 ml 6M H_2SO_4 is added to the sample container through the separatory funnel. The solution in the container (pH close to 0) is purged for 30 minutes with N_2 and carefully mixed by magnetic stirring. Any reduced carbon compounds released from the sample during this time will pass through bottles 2 and 3 unaffected and be absorbed in bottle no. 4 after complete oxidation by means of the catalytic furnace. Following acid treatment of the resin, bottles 2 and 3 (the former now containing the inorganic ^{14}C fraction of the resin sample) are disconnected from the system by switching the three-way stopcocks, before and after the bottles.

In the second step, the now remaining organic ^{14}C fraction is oxidized using a strong oxidizing agent and subsequent heating (80–90°C) and magnetic stirring. Twenty ml 5% $K_2S_2O_8$ and 4 ml 4% $AgNO_3$ (as a catalyst to increase the reaction rate) are added to the sample container. The complete volume of $AgNO_3$ is flushed through the separatory funnel inlet line using 3 ml deionised water. After 1 hour, the same amounts of the same chemicals are added and again after 2 hours. After 3 hours (corresponding to three periods of wet oxidation) the extraction process is complete. Duplicate samples of 3 ml are collected from bottles 2 and 4. Single samples are taken from the other bottles to monitor the water trap (1) and the two safety bottles (3 and 5). The 3 ml samples are each mixed with scintillation cocktail, shaken and left to rest for 24 hours in darkness before measurement by LSC.

Process water treatment procedure

The three-step ^{14}C extraction procedure for process water is presented in Fig. 3. The basic system set-up is the same as for spent resins (see Fig. 2), with supplementary equipment illustrated in Fig. 4. The procedure allows quantification of organic and inorganic ^{14}C compounds in the gaseous phase as well as in the liquid phase. If separate data on the ^{14}C concentrations in the gaseous and liquid phases are not required, the initial gas phase extraction step is simply omitted.

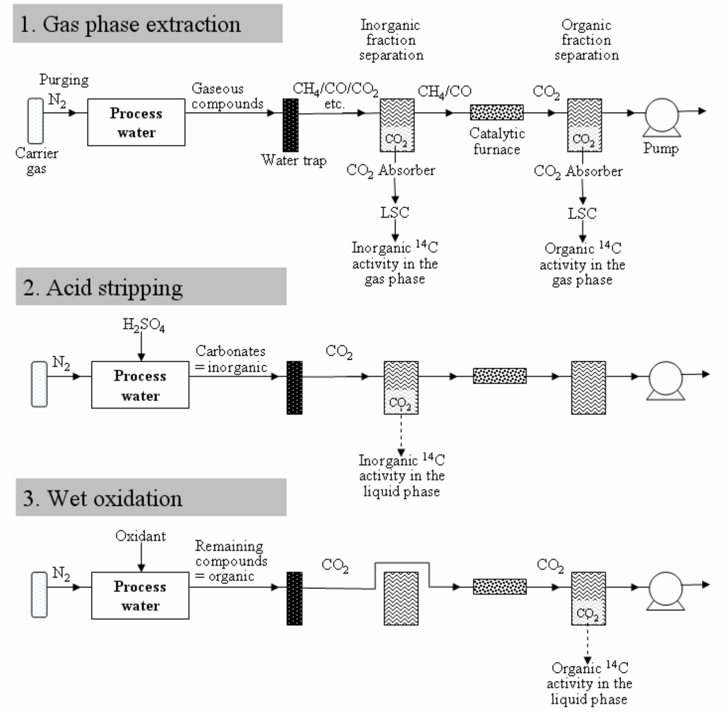

Fig. 3. The three-step ^{14}C extraction procedure for process water including gas phase analysis. Note that the alkaline gas washing bottles are replaced by new ones between steps 1 and 2

Sampling: The ^{14}C extraction procedure is optimized for a 100 ml water sample. Process water, including gas phase, is sampled using pre-evacuated 250 ml gas sampling tubes (Duran, with two capillary stopcocks, VWR) or 50 ml glass vials (Alltech Associates Inc., cat. no. 8607189), sealed with rubber bungs (Chromacol, 20-1FB3) and crimp caps (Chromacol, 20-MCB). The gas sampling tubes are intended for occasional sampling; the glass vials for frequent sampling. A volume of ~20 ml process water is drawn into the 50 ml glass vials, leaving 30 ml for the gas. A composite sample of 100 ml is achieved by combining five 20-ml samples, collected over a period of time, e.g. five weeks.

Gas phase extraction: For ^{14}C gas phase extraction from a 250 ml gas sampling tube (containing ~100 ml water; the rest being gas phase) the tube is mounted in the system as shown in Fig. 4a. The sample is purged from the bottom of the gas sampling tube, using a flow rate of N_2 high enough to avoid backflow, for 1 hour at slightly sub-atmospheric pressure. The gaseous carbon compounds are transported from the upper stopcock of the tube directly into bottle no. 1. Oxidized forms of carbon are then absorbed in bottle no. 2, while reduced forms are absorbed in bottle no. 4 after complete oxidation by means of the catalytic furnace. After complete gas phase extraction, duplicate samples of 3 ml are collected from gas washing bottles 2 and 4 and the bottles replaced by new ones before continuing the treatment procedure.

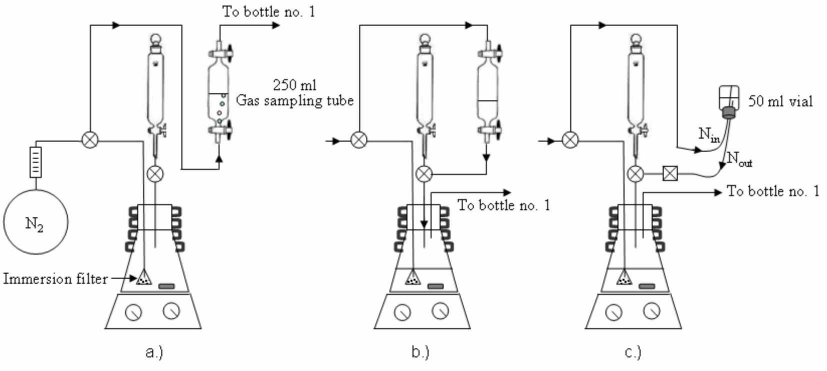

Fig. 4. Supplementary equipment used for process water treatment; a.) gas phase extraction from a 250 ml gas sampling tube, b.) transport of the water sample to the sample container prior to acid stripping, c.) transport of liquid and gas phase from a 50 ml vial to the sample container prior to gas phase extraction

Prior to acid stripping and subsequent wet oxidation of the carbon compounds in the liquid phase, the water sample is extracted from the bottom of the gas sampling tube into the sample container (500 ml Erlenmeyer flask). Sample transport is accomplished by reversing the flow of N_2 through the tube, according to Fig. 4b.

For gas phase extraction from the 50 ml glass vials (each containing ~20 ml water), the vial is mounted as shown in Fig. 4c and connected to the system with two needles (Sterican®, 14G×3⅛″, 80 mm length, B. Braun Melsungen AG), inserted through the rubber bung. With one needle connected to the N_2 gas supply (N_{in}) and the other to the reaction vessel (N_{out}), both the gas and liquid phase are transferred to the sample container by employing a flow rate of 60 ml/min for 5 minutes. The procedure is repeated until a composite sample of ~100 ml has been obtained. The sample is then purged for 1 hour in combination with magnetic stirring. Efficient purging of the container solution is accomplished by allowing the carrier gas to flow through an immersion filter (a glass filter normally used for reverse filtration; manufactured from a filter with a porosity of 1, 30 mm diameter), fully submerged in the water. After complete gas phase extraction, samples are collected from bottles 2 and 4 for inorganic and organic ^{14}C determination by LSC, respectively.

Acid stripping: After replacing bottles 2 and 4 (in the case of preceding gas phase extraction), the system is evacuated to 0.2 bar below atmospheric pressure and the carrier gas flow rate set to 60 ml/min. The inorganic ^{14}C fraction is extracted from the water by adding 50 ml 8M H_2SO_4 to the sample container through the separatory funnel. The acidified sample solution is purged for 1 hour using the immersion filter in combination with magnetic stirring. Following removal of the inorganic fraction, bottles 2 and 3 are disconnected from the system.

Wet oxidation: After acid treatment, the organic fraction in the water is oxidized by adding 50 ml 5% $K_2S_2O_8$ and 5 ml 4% $AgNO_3$ to the sample container during simultaneous heating (95°C) and magnetic stirring. After 1 hour, the same amounts of $K_2S_2O_8$ and $AgNO_3$ are added to the reaction vessel. The total time required for wet oxidation is 2 hours, corresponding to two periods of wet oxidation. Three-ml samples are then collected from the bottles and treated as described in the previous section. If necessary, the absorbed CO_2 can be precipitated as $BaCO_3$ and the precipitate measured by LSC, as this provides a lower detection limit.

Cleaning

All glassware is cleaned with concentrated HCl and rinsed with deionised water to avoid cross-contamination between different samples. Parts of the tubing, as well as the three-hole rubber stoppers, are used only once due to the risk of cross-contamination.

Results and Discussion

The initial development of the procedures described above were performed on inactive samples (Amberlite IRN-150L and deionised water, respectively) spiked with ^{14}C-labelled substances (simulated samples). Typically, an activity of 10 kBq of sodium carbonate (Na_2CO_3), acetic acid sodium salt (CH_3CO_2Na, sodium acetate) or formic acid sodium salt (HCO_2Na, sodium formate) (Amersham Biosciences UK Limited) was used. Acetate and formate have the highest concentrations among the organic compounds detected during routine analysis of reactor water in Swedish PWRs.[28] These organic acids are therefore not only expected to be found in samples of process water, but also possibly on spent resins. According to LUNDGREN et al.,[9] at least formate is believed to be present on spent resins. Following the initial optimization on simulated samples, the method was tested on authentic samples of spent resins and reactor water from PWRs and BWRs to evaluate the method and to establish the standard procedures presented above. The results from the numerous tests on simulated and authentic samples are presented and discussed below.

Ion-exchange resins

Tests on simulated resins

Recovery tests of ^{14}C: Recovery experiments were performed on 1 g (ww) Amberlite resin samples, to which 1–2 ml ^{14}C standard solution was added. Preparation of the simulated resin samples was followed by an adsorption period of 5–10 minutes prior to treatment.

The extraction efficiency of inorganic carbon compounds, using the standard procedure, was assessed using $Na_2{}^{14}CO_3$. The recovery obtained after 30 minutes of acid stripping was 98% (*n*=1)[a]. A similar result (96%) was achieved using 8M HCl. However, the presence of chloride ions during wet oxidation would significantly reduce the efficiency of the catalyst ($AgNO_3$) due to the precipitation of AgCl (see e.g. COOPER et al.[29]). The use of HCl may also damage the catalytic furnace, especially when the sample solution is heated, as this increases the volatility of HCl significantly.

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[a] Six recovery tests were performed using H_2SO_4 but with varying parameters (mean recovery 93%); only one of the tests was performed with the exact parameters defining the standard procedure.

The recovery obtained after 1 hour of wet oxidation using ^{14}C-labelled sodium formate and sodium acetate was 94% (*n*=1) and 97% (*n*=3), respectively. Upon excluding the Ag catalyst, the recovery fell to 3% or lower. The addition of 1 ml $AgNO_3$ solution resulted in half the recovery obtained with 2 ml $AgNO_3$ solution.

Additional tests: To ensure that all the activity added in the recovery tests of ^{14}C had been adsorbed on the resin prior to treatment, various adsorption experiments were performed to study the rate and degree of adsorption. Stripping experiments were also performed to investigate the behaviour of the adsorbed compounds when subjected to different kinds of treatment. The tests were performed using 1.0–1.5 g (ww) Amberlite resin and 1–2 ml of a standard solution containing 0.2–2.4 kBq ^{14}C-labelled sodium carbonate, sodium acetate or sodium formate.

Following an adsorption period of up to 3 days, the simulated resin samples were filtered and rinsed with deionised water. The degree of adsorption was then determined indirectly by measuring the ^{14}C activity recovered in the filtrate. The results obtained from the adsorption experiments are presented in Table 1. The experiments indicate that both organic and inorganic compounds are easily and relatively quickly adsorbed to the resin (acetate being the slowest). According to the results given in Table 1, >93% of the ^{14}C activity added, was adsorbed during the adsorption period employed in the recovery tests (5–10 min). Three additional samples, prepared at the same time with $Na_2{}^{14}CO_3$, were subjected to acid stripping after an adsorption period of 3, 4 and 30 days, giving recoveries of 92, 91 and 94%, respectively. The remaining activity was found neither in the container solution nor on the resin. The similar recoveries indicate that, without altering the chemical conditions, carbonate ions remained adsorbed to the resin for at least 30 days (i.e. there is no sign of progressive activity loss). When subjected to acid treatment, the carbonate ions were completely stripped from the resin (i.e. no remaining activity was found on the resin). The missing activity (6–9%) was attributed to microbial activity (verified by Agar cultivation).[30]

Stripping experiments including purging or heating of the sample, showed that the compounds remained adsorbed on the resin after N_2 purging (1 hour), as well as after being moderately heated (<100°C, 1 hour). However, at higher temperatures (~150°C) a substantial amount of the activity may be released,[24,31] almost exclusively associated with the inorganic fraction.[32] Numerous acid stripping tests were also carried out to investigate the effect of different parameters on the recovery of $Na_2{}^{14}CO_3$. The parameters varied included type of acid and acid concentration, duration and carrier gas. An important finding was that the activity remaining on the resin after the treatment was generally insignificant, as was the activity found in the container solution.[30] This indicates overall high extraction efficiencies (>99%).

Table 1. Degree of adsorption (%) of sodium carbonate, sodium formate and sodium acetate to inactive Amberlite resin, obtained after an adsorption period of 5 minutes, 24 hours and 3 days

	Degree of adsorption (%) of ^{14}C-labelled compounds		
Adsorption period	Carbonate	Formate	Acetate
5 min	>95	96.5	93.5
24 h	–	99.9	99.7
3 days	>99.9	–	–

During the acid treatment (30 minutes), acetate and formate ions were completely removed from the resin into the container solution, from which a slight loss of ^{14}C activity occurred. The lost organic ^{14}C activity was found in bottle no. 2, i.e. the bottle intended for selective absorption of $^{14}CO_2$ originating from the inorganic fraction of the sample. The loss was initially assumed to be the result of increased volatility of the organic acids[31,33,34] as the pH of the container solution is drastically reduced by the addition of H_2SO_4. However, the activity released from the container solution (0.5–8.5%) was almost completely recovered in bottle no. 2, while the activity found in the acidified water trap (bottle no. 1) was insignificant (<0.05%). This situation is expected for absorption of $^{14}CO_2$, but would have been the opposite if the loss were associated with volatilized organic acids. Agar cultivation of the organic standard solutions showed microbial activity, through which ^{14}C-labelled sodium formate and acetate are gradually converted into inorganic ^{14}C species, released upon acidification. The effect of the acid treatment on these organic acids was therefore considered to be negligible, i.e. the losses caused by increased volatility were <0.05%.

Tests on spent resins

Tests, as well as determination of ^{14}C concentrations were performed on 24 subsamples taken from 9 batch samples of spent resins from Swedish PWRs and BWRs. The batch samples were collected from different storage tanks containing spent resins. Different types of resins (sulphonate and carboxylate resins) from various cleaning systems were studied. From each batch sample, 2–6 subsamples were taken and analysed separately. Most of the results from the ^{14}C analysis have been presented in MAGNUSSON et al.[31] and MAGNUSSON and STENSTRÖM.[33] The tests conducted on the samples to evaluate and further optimize the method are described below, and the results and reliability of the final treatment procedure discussed. A summary and comparison of the results from ^{14}C extraction tests on simulated and spent resins are presented in Table 2. The potential introduction of organic ^{14}C into bottle no. 2 (i.e. the inorganic fraction), shown in Table 2, is further discussed in section "Separation capability" below.

Tests on spent PWR resins confirmed that 30 minutes of acid stripping was sufficient (n=3). Extending the time to 90 minutes did not release any additional detectable activity. However, the addition of more acid (8 ml) slightly increased the recovery of ^{14}C (n=3), i.e. the

Table 2. Extraction yields (%) of organic and inorganic ^{14}C in simulated resins, spiked with ^{14}C-labelled compounds (determined yields), and spent resins (estimated yields)

		Bottle no. 2		Bottle no. 4	
Sample	Treatment	Inorganic	Organic	Inorganic	Organic
Simulated resin	Acid stripping	98	1.8[a]	ND	ND
	Wet oxidation	–	–	–	94-97
Spent resin	Acid stripping	~100	<2.5	–	>95[b]
	Wet oxidation	–	–	–	

[a] Mean value (n=5) for acetic and formic acid from tests conducted according to the standard procedure (t= 30 min; acid = H_2SO_4)

[b] Total extraction yield of organic ^{14}C obtained after acid stripping and wet oxidation

ND = Not detected (corresponding to <0.03 %)

additional activity recovered from bottle no. 2 was ≥1σ (1σ ±4%) of the amount obtained following the standard procedure. The test was performed on three samples referred to as IX1:5, IX2:4 and IX3:4. This means that they were taken from three different batches (IX1–3), from which 3-4 subsamples already had been analysed according to the standard procedure (IX1:1–4, IX2:1–3 and IX3:1–3). By comparing the result obtained from IX2:4 and IX3:4 to the other three subsamples from the same batch (IX2:1–3 and IX3:1–3, respectively) it was found that the additionally released activity probably originated from organic compounds. The organic ^{14}C content of IX2:4 and IX3:4 was found to be 90% below the mean value of the organic content in IX2:1–3 and IX3:1–3, respectively (standard error of the mean was 45% and 8%, respectively). No conclusions could be drawn from the test performed on IX1:5 (IX1 was also of a different resin type than IX2 and IX3). These tests show that there is a potential risk of cross-contamination between the two fractions. However, when employing the standard procedure, the amount of organic ^{14}C introduced into the inorganic fraction (i.e. into bottle no. 2) should be minimal (<2.5%). This was deduced from recent ^{14}C analyses of spent resins, which were found to contain almost exclusively organic compounds.[32]

The effect of wet oxidation was investigated by combusting some of the resin samples after one or two periods of oxidation (referred to as Wet 1 and Wet 2). Combustion was performed in a long, vertical quartz tube in a flow of oxygen using a Bunsen burner. The filtered resin sample was placed in the bottom part of the tube on top of quartz wool. The combustion gas was passed through a set of three gas washing bottles: one slightly acidified to trap contaminants, and the other two both containing 100 ml 2M NaOH. The time required for complete combustion was 5–10 minutes. The combustion rate was controlled by adjusting the flow of oxygen in order to decompose the resin sample slowly without any visible flames. The combustion efficiency was assumed to be 100% since only traces of the resin samples were left after combustion. The results are presented in Table 3. After Wet 1, 69–94% of the total activity had been extracted from the sample. After Wet 2, the corresponding values were was 94–96%.

Apart from the samples combusted, 20 samples of spent resins were subjected to 1–3 periods of wet oxidation. Samples were collected from bottles 2 and 4 after each period for analysis by LSC. None of these samples showed the same poor extraction efficiency during Wet 1 as sample no. 3 in Table 3. As the standard procedure for ^{14}C extraction from spent resins includes three periods of wet oxidation, the organic ^{14}C activity remaining on the resin after the treatment is considered to be <5% (i.e. the total extracted organic fraction after Wet 2, presented in Table 3, is regarded as minimum value).

Table 3. The percentage of total organic activity extracted after one period of wet oxidation (Wet 1) or two (Wet 2) of the resin sample. The total organic activity was determined from combustion

Sample	Fraction extracted (%) of total organic ^{14}C activity		
	Wet 1	Wet 2	Combustion
1	94	–	100
2	82	–	100
3	69	94	100
4	94	–	100
5	78	96	100
6	75	–	100

The efficiency of wet oxidation seemed to depend on the type of resin (i.e. sulphonate or carboxylate resin). Carboxylate resins generally required only one period of wet oxidation for complete extraction of organic ^{14}C, while sulphonate resins were generally more demanding. To certify complete ^{14}C extraction (i.e. >95%) combustion is required. Combustion after acid stripping is not a reliable alternative to the 3 hours' wet oxidation, since most of the organic compounds are expected to be present in the sample container solution after acid treatment (see section, "Additional tests", above) and would therefore escape detection.

Separation capability

Minimal cross-contamination between the absorbed organic and inorganic fraction (i.e. between bottles 2 and 4; see Table 2) is essential for the reliability of the determination of ^{14}C concentrations. The potential introduction of organic ^{14}C into the inorganic fraction (absorbed in bottle no. 2; see above) is believed to be less than 2.5%, based on recent ^{14}C analyses.[32] The resulting underestimation of the organic ^{14}C content should normally be insignificant (i.e. within 1σ employing the standard treatment procedure), as should the overestimation of the inorganic ^{14}C content. The latter is due to the generally low fraction of organic ^{14}C in spent resins.[33] One explanation of the cross-contamination apparently observed in the tests described above, could be decarboxylation of organic acids. Decarboxylation involves removal of the carboxyl group, resulting in the release of CO_2.

The introduction of inorganic ^{14}C into the organic fraction (absorbed in bottle no. 4) is considered to be insignificant. Such cross-contamination can occur by incomplete removal of carbonates prior to wet oxidation. However, based on the low pH value obtained during acid treatment (pH ~0), results obtained from the prolonged acid stripping tests on spent resins and the overall high recoveries obtained for $Na_2{}^{14}CO_3$, the removal of inorganic ^{14}C is considered to be ~100%. Another potential cause of unintended introduction of inorganic ^{14}C into the organic fraction is incomplete CO_2 absorption in the first set of gas washing bottles (bottles 2 and 3). However, no detectable activity was found in the safety flask (bottle no. 3).

Interference of other nuclides

Gamma-emitting nuclides present on the resin were also efficiently stripped during the treatment procedure. The gamma activity of treated resin samples (determined after filtering the resin and rinsing with water) corresponded to only 4% of the activity of the untreated samples (n=2). After being stripped into the sample container solution, gamma-emitting nuclides remained in the sample container during sample processing, i.e. no further transport occurred. This was verified by gamma spectroscopy of solutions from bottles 1 and 2. Beta spectrum analysis of solutions from all gas washing bottles confirmed that any ^{3}H released from the container solution, was completely absorbed in the water trap (bottle 1) and not transferred to the rest of the system.

^{14}C analysis

The 3 ml samples from the gas washing bottles were mixed with 18 ml scintillation cocktail (Hionic Fluor, PerkinElmer), shaken and left to rest in darkness for 24 hours. The samples were then measured by LSC for a maximum of 3×60 minutes, using a Beckman LS6500 counter. Background was determined by processing blank samples regularly, using 1 g (ww) of Amberlite resin, and measuring the sample solutions in duplicate by for LSC 5×60 minutes. The detection limit of the resin samples analysed (1.0 g ww) was 840 Bq/kg. The total propagated error was typically of the order of ±4% (includes errors associated with LSC measurement, background determination and determinations of mass and volumes).

The system was regularly (after every five sample treatments) checked for memory effects, however no such effects were found. Furthermore, no activity was ever found in the safety bottles, verifying a complete $^{14}CO_2$ absorption in the dedicated bottles.

Comparison with previous methods

Extraction of carbonates from spent resins by acid stripping is usually reported as being successful. The acid stripping method developed by SALONEN and SNELLMAN[18] was reported to have an efficiency of 93% (n=3), determined from recovery tests using $NaH^{14}CO_3$. Other similar methods reviewed by STENSTRÖM and MAGNUSSON[21,22] were reported to have mean recoveries ranging from 49% to 97% (median value 93%). PARK et al.[23] report recoveries of 82–99% using H_2SO_4 and KOH on resins spiked with $Na_2{}^{14}CO_3$.

The only study found in the literature, employing ^{14}C-labelled organic substances was performed by PARK et al.[23] Their wet oxidation-acid stripping method resulted in recoveries of 93% and 91% for ^{14}C-labelled alcohol and toluene, respectively. However, PARK et al.,[23] as well as VANCE et al.,[20] estimated the organic ^{14}C fraction by calculating the difference between the total and inorganic ^{14}C, determined from two different subsamples. To minimize the uncertainties related to this approach, high batch sample homogeneity and/or representative subsampling is necessary but might be difficult to achieve. The method used by VANCE et al.[20] was found to be unreliable when applied to resin samples from BWRs, containing low fractions of organic ^{14}C. The inorganic concentrations in such cases were generally higher than the total ^{14}C activity, probably due to poor combustion efficiency or unrepresentative subsampling. The method is not reported to have been validated.

The ^{14}C extraction method developed by SALONEN and SNELLMAN[18] was used to analyse spent resins from Finnish PWRs and BWRs. To check the efficiency of their method, they compared the results obtained in the second extraction with those obtained in the first extraction of the treated resin samples (n=7). As expected, the acid stripping was highly efficient in extracting the inorganic fraction of the sample; an activity corresponding to 0.03–3.4% of the result obtained in the first extraction was additionally released. However, for the organic compounds, the corresponding values were 0.1–100%. For the PWR resins, which had the highest organic ^{14}C activity concentrations, the mean value was 68%, i.e. the removal of organic compounds obtained after the first extraction was far from complete. Furthermore, according to the results obtained in the tests presented in this paper, the method of SALONEN and SNELLMAN[18] may not be reliable if organic acids are present, since these are not significantly affected by the acid treatment. Therefore, SALONEN and SNELLMAN[18] probably underestimated the organic fraction of the spent resins from Finnish PWRs and BWRs.

Process water

Recovery tests of ^{14}C on simulated process water

The efficiency of the acid stripping process was tested using $Na_2{}^{14}CO_3$ added to 100 ml deionised water. The mean recovery obtained was 95% (n=4) using the standard procedure. The efficiency of 1 hour wet oxidation was investigated using ^{14}C-labelled sodium acetate, yielding a recovery of 95% (n=5). The final standard procedure of 2 hours wet oxidation was a result of tests on reactor water (see below).

Tests on reactor water

Final optimization of the method was accomplished through various tests conducted on samples of reactor water from two Swedish BWRs and one PWR. Forty samples, generally containing both liquid and gas phase, were analysed with respect to organic and inorganic ^{14}C concentrations. The results from the initial part of this study have been presented in MAGNUSSON and STENSTRÖM.[33] The tests conducted on the samples are described below. A summary and comparison of the results from ^{14}C extraction tests on simulated process water and reactor water are presented in Table 4. The potential introduction of organic ^{14}C into bottle no. 2 (i.e. the inorganic fraction), shown in Table 4, is discussed in section "Separation capability" below.

Complete extraction of the gas phase was achieved when purging was employed directly in the gas pipette as well as in the sample container solution using the immersion filter. No detectable additional activity was released after purging the gas pipette for 1 hour (n=1), or the container solution for 45 minutes (n=3). For simplicity, one hour was chosen to be the standard procedure using both approaches.

The efficiency of the acid treatment could only be assessed in one out of three tests on reactor water due to the low concentration of inorganic ^{14}C. In this test, no additional detectable activity was absorbed in bottle 2 following the initial 30 minutes of acid stripping.

Complete wet oxidation using the standard procedure (2 hours) was also verified on reactor water (n=3). Tests of the wet oxidation treatment showed that 1 hour and one batch of chemicals was generally sufficient (n=4 out of n=6) to completely extract the organic fraction of reactor water, i.e. no additional activity was released when adding another batch of

Table 4. Extraction yields (%) of organic and inorganic ^{14}C in simulated process water, spiked with ^{14}C-labelled compounds (determined yields), and reactor water (estimated yields)

		Bottle no. 2		Bottle no. 4	
Sample	Treatment	Inorganic	Organic	Inorganic	Organic
Simulated process water	Acid stripping	95	<1.2	ND	ND
	Wet oxidation	–	–	–	95
Reactor water (PWR)	Gas phase extraction	~100	–	–	~100
	Acid stripping	~100	<1	–	~100[a]
	Wet oxidation	–	–	–	

[a] Total extraction yield of organic ^{14}C obtained after acid stripping and wet oxidation
ND = Not detected (corresponding to <0.02%)

chemicals. However, due to the incomplete extraction in two of the tests, it was decided that two batches of chemicals added one hour after each other should be the standard procedure. During wet oxidation, the catalytic furnace proved to be unnecessary since the organic compounds were fully oxidized by the strong oxidant in the sample container (*n*=1). The catalytic furnace is therefore only required in the initial phase of the sample treatment, i.e. the gas phase extraction step where hydrocarbons and CO are extracted.

Separation capability

The degree of cross-contamination between the organic and inorganic fractions was investigated by adding 8 kBq ^{14}C-labelled sodium carbonate and sodium acetate to 100 ml of deionised water. The sample was then subjected to acid stripping and subsequent wet oxidation according to the standard procedure. The recoveries obtained from bottles 2 and 4 were both 95% (mean value; *n*=3), indicating a low degree of cross-contamination. Therefore, high separation capability of the method is also expected for authentic samples of process water. Based on these tests and the demonstrated high recoveries obtained for $Na_2{}^{14}CO_3$, the introduction of inorganic ^{14}C into the organic fraction is considered to be insignificant.

The potential introduction of organic ^{14}C into the inorganic fraction was determined to be less than 1% based on ^{14}C concentrations in reactor water.[32,33] Even so, this potential contribution to the recovered inorganic activity will be of significance when analysing reactor water from PWRs, containing low concentrations of inorganic ^{14}C. From analyses of the liquid phase of the reactor water it was found that a substantial part (~50%) of the organic fraction was neither volatile hydrocarbons nor CO, and therefore could possibly consist of organic acids (in agreement with ion chromatographic analyses at the power plant).[28] Despite this, no ^{14}C activity was detected in bottle no. 1, demonstrating insignificant introduction of organic ^{14}C into bottle no. 2 (<0.1%), due to volatilization of organic acids during acid stripping.

Interference of other nuclides

Potential interference was regularly checked by analysing spectra obtained from the LSC. Spectra of samples obtained from bottle no. 1 confirmed efficient absorption of tritium. Spectra of samples obtained from bottles 2–5 showed no interference from other radionuclides.

^{14}C analysis

A volume of 3 ml was usually collected from the gas washing bottles and mixed with 18 ml Hionic Fluor, shaken and left to rest for 24 hours prior to LSC measurements. The detection limit for a water sample of 100 ml was 8 Bq/kg, measured by the Beckman LS6500 within the energy range of 0–E_{max}. The background was determined regularly by processing blanks. The total error in the analysis of reactor water was typically of the order of ±4% (includes errors associated with LSC measurement, background determination and determinations of mass and volumes). Samples with ^{14}C concentration below the detection limit were precipitated as $BaCO_3$ and the precipitate (mixed with Insta-Gel Plus, PerkinElmer) measured by LSC giving a detection limit of ~0.4 Bq/kg. The precipitated samples were corrected for losses in precipitation and counting (determined by precipitating sample solutions of known activity). The resulting total propagated error was typically of the order of ±7–10%. The system was regularly checked for memory effects; however, none was found.

Comparison with previous methods

Neither BLEIER,[12] nor SALONEN and SNELLMAN[24] reported validation of the methods used for ^{14}C extraction from process water. However, SALONEN and SNELLMAN[24] refer to the method they developed for spent ion-exchange resins,[18] which was partly validated using a carbonate standard (see above). From the analysis of reactor water from the Swedish PWR,[32,33] referred to above, it was found that ~50% of the organic ^{14}C compounds were affected neither by purging nor by acid stripping; they were, however, released when subjected to wet oxidation. Since the method developed by SALONEN and SNELLMAN[18] is based solely on acid stripping, it is not likely that they achieved complete extraction of organic carbon compounds.

The method developed by BLEIER[12] should be capable of high extraction efficiencies of both inorganic and organic ^{14}C compounds present in process water. However, the procedure presented is time consuming and neither validation nor reliability assessments were reported. VANCE et al.[20] estimated the organic fraction based on determinations of the inorganic and total ^{14}C concentration in different aliquots of a batch sample of water. The method is not reported to have been validated but should have acceptable accuracy as long as the batch sample is homogeneous (this assumption is generally not applicable to spent ion-exchange resins).

Conclusions

The method developed for samples of spent ion-exchange resins was optimized and assessed using simulated resins, as well as authentic samples. The degree of adsorption to the resin, following an adsorption period of 5 minutes, was found to be 94–97% for the three ^{14}C-labelled substances tested. Upon acid treatment, the adsorbed substances were found to be completely removed from the resin. The inorganic substance was recovered in the dedicated CO_2 absorber (yield 98%), while the organic substances remained in the sample container solution. During subsequent wet oxidation, the organic substances were found to be efficiently oxidized and separately recovered with yields of 94–97%. Tests on spent resins showed that the organic ^{14}C activity remaining on the resin after the treatment was less than 5%. Complete separation of organic and inorganic ^{14}C compounds present on spent resins can not be guaranteed. However, the degree of cross-contamination between the two fractions is believed to be insignificant when employing the standard procedure. Possible decarboxylation of organic acids during acid stripping may pose a problem, which should be borne in mind.

Other methods developed for ^{14}C determination on spent resins have been reported to have overall high extraction efficiencies for carbonates, but verification was only reported in one case, using ^{14}C-labelled organic substances. The only method reported that allows separate determination by direct measurements of organic and inorganic ^{14}C[18] is believed to underestimate the organic fraction. This is due to the reported inadequate extraction of organic ^{14}C, and the generally insignificant effect of acid stripping on organic acids, believed to be present on spent resins.

The ^{14}C extraction procedure developed for process water was shown to achieve a recovery of 95% for both ^{14}C-labelled substances tested. Experiments on reactor water verified complete extraction of oxidized and reduced gaseous compounds, as well as complete extraction of organic ^{14}C compounds in the liquid phase. Introduction of organic ^{14}C into the recovered inorganic fraction was determined to be less than 1%. Although small, this potential contribution will be of significance when analysing samples of process water containing low fractions of inorganic ^{14}C.

Similar methods described in the literature for ^{14}C extraction from process water, appear not to have been validated, although the method developed by BLEIER [12] should achieve high extraction efficiencies of both ^{14}C fractions.

Acknowledgements

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Paper VI

CHARACTERIZATION OF ^{14}C IN SWEDISH LIGHT WATER REACTORS

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Abstract

This paper presents the results of a 4-year investigation of ^{14}C in different waste streams of both boiling water reactors (BWRs) and pressurized water reactors (PWRs). Due to the potential impact of ^{14}C on human health, minimizing waste and releases from the nuclear power industry is of considerable interest. The experimental data and conclusions may be implemented to select appropriate waste management strategies and practices at reactor units and disposal facilities. Organic and inorganic ^{14}C in spent ion exchange resins, process water systems, ejector off-gas and replaced steam generator tubes were analyzed using a recently developed extraction method. Separate analysis of the chemical species is of importance in order to model and predict the fate of ^{14}C within process systems as well as in dose calculations for disposal facilities. By combining the results of this investigation with newly calculated production rates, mass balance assessments were made of the ^{14}C originating from production in the coolant. Of the ^{14}C formed in the coolant of BWRs, 0.6–0.8% was found to be accumulated in the ion exchange resins (core-specific production rate in the coolant of a 2500 MW_{th} BWR calculated to be 580 GBq GW_e^{-1} y^{-1}). The corresponding value for PWRs was 6–10% (production rate in a 2775 MW_{th} PWR calculated to be 350 GBq GW_e^{-1} y^{-1}). The ^{14}C released with liquid discharges was found to be insignificant, constituting less than 0.5% of the production in the coolant. The stack releases, routinely measured at the power plants, were found to correspond to 60–155% of the coolant production, with large variations between the BWR units.

Key words: ^{14}C, low-level waste, process water, nuclear power plant

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INTRODUCTION

The operation of nuclear power reactors produces a wide range of undesirable radioactive by-products. One of considerable concern is ^{14}C. Because of its long half-life (5730 y), environmental mobility, and ease of assimilation into living matter, it is necessary to control the production in, as well as the release from, nuclear facilities.

Carbon-14 is a weak beta emitter (maximum energy 156 keV) with both natural and anthropogenic source terms. Natural production occurs continuously in the upper atmosphere, through the irradiation of ^{14}N by neutrons of cosmic ray origin, at an estimated rate of 1.5×10^{15} Bq y^{-1} (UNSCEAR 2000). The operation of nuclear power reactors releases an additional amount of 1.1×10^{14} Bq y^{-1} into the biosphere (estimated value for the period 1995–1997; UNSCEAR 2000). In light water reactors (LWRs), comprising boiling and pressurized water reactors (BWRs and PWRs), ^{14}C is produced mainly through neutron-induced reactions with ^{17}O and ^{14}N. These nuclides are present in the fuel, fuel cladding, coolant and structural material of the reactor (IAEA 2004). Therefore, a variety of gaseous, solid and liquid waste containing ^{14}C is generated during reactor operation. The production of ^{14}C in the reactor coolant is almost entirely responsible for the releases from BWRs and PWRs at the power plant site. Gaseous releases constitute the main release path from this production source; the rest being accumulated in ion exchange resins or released as liquid discharges. Spent ion exchange resins are today one of the largest sources of ^{14}C activity in low- and intermediate-level waste (LILW) disposal facilities (Yim and Caron 2006). According to UNSCEAR (2000), ^{14}C is the main contributor to the global collective dose (estimated for 10,000 y) arising from the radionuclides released during various stages of the nuclear fuel cycle. The collective effective dose from LILW disposal is also almost entirely due to ^{14}C (UNSCEAR 2000). Due to the potential impact on human health, minimizing waste and releases containing ^{14}C is recognized as being important. Minimization of ^{14}C in waste may also be economically beneficial due to its potential of being the inventory-limiting nuclide at LILW disposal facilities (Yim and Caron 2006).

In order to implement appropriate waste management strategies, knowledge concerning the activity released from or accumulated in various waste streams, as well as the production rates of ^{14}C, is of considerable interest. However, existing data are limited and often outdated. IAEA (2004), referring to Bush et al. (1984), listed ranges of production rates calculated in 1975–1980. Vance et al. (1995) used data from 1974 (Bonka et al. 1974) to obtain updated values of the production rates; these values are also those listed by Yim and Caron (2006). Because of the difficulty in measuring ^{14}C, experimental data on ^{14}C in process water systems and spent ion exchange resins, for example, are also limited. Furthermore, existing data often lack information on the chemical form of ^{14}C (organic or inorganic), which is an important factor, for example, when estimating doses arising from the release to the environment.

This paper presents the results of an extensive investigation initiated by the Swedish Nuclear Fuel and Waste Management Company (SKB), with the general aim of obtaining new experimental data on ^{14}C in terms of concentration and distribution in different waste streams. The investigation included the following:

1. The development of a method for separate quantification of organic and inorganic forms[§] of ^{14}C in process media (Magnusson et al. 2007c).
2. Analyses of ^{14}C in spent ion exchange resins from PWRs and BWRs (major parts presented in Magnusson et al. 2005, 2007a).
3. Grab sample analysis of ^{14}C in process water from BWRs and PWRs (reported in Magnusson et al. 2005, 2007a).
4. A 10-month survey of all process water systems in a PWR unit with respect to ^{14}C concentrations and characterization.
5. Analyses of oxides from replaced steam generator tubes, and analyses of sampling filters from the reactor coolant of a PWR.
6. Ejector off-gas measurements on a BWR operating with charcoal columns.
7. Carbon-14 mass balance assessments for BWRs and PWRs.

The last-mentioned study (7) was performed using recently developed calculation models[**] of the ^{14}C production rate in LWRs. The fate of the ^{14}C produced in the reactor coolant was then assessed by comparing the results of the ^{14}C analyses (2–6 above) with the production rate in the coolant.

This paper focuses on the results obtained from the 10-month survey of ^{14}C in process water (mainly the primary circuit), but also presents the results of the calculation of production rates, and the mass balance assessment. Updated results from the analysis of spent resins, and important conclusions with respect to e.g. LILW waste disposal are also included in the paper.

MATERIALS AND METHODS

Sampling

Process water

Sampling and analysis of process water were carried out in 2005 and 2006. The first study (Magnusson et al. 2005, 2007a) included both BWRs and PWRs but was based on only a limited number of grab samples. Interesting findings in this preliminary study caused a more comprehensive study to be carried out on the PWRs. This second study was conducted on the PWR unit 4 at Ringhals (referred to as R4; 2775 MW_{th}) for 10 months in 2006. This period covered all stages of reactor operation: power operation, shutdown, outage and startup. Besides the primary circuit, samples were also taken from the secondary circuit and auxiliary systems, including the spent fuel pool, waste water releases, ejector condensate and steam generator blow-down. The process water systems sampled are shown in Fig. 1. The samples of ejector condensate and steam generator blow-down water were taken due to a primary-to-secondary leakage through the steam generator tubes on R4[††]. The liquid and gaseous phases from most of the process water systems sampled were analyzed separately with respect to ^{14}C concentrations. This allowed chemical (organic or inorganic) as well as physical (volatile or

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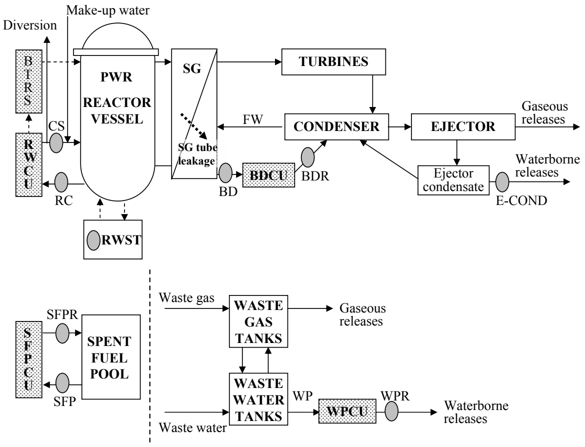
[§] Inorganic ^{14}C species here refers to carbonates and carbon dioxide; organic species refers to hydrocarbons and carbon monoxide (in the text also referred to as reduced compounds), and all other organic compounds.

[**] ALARA Engineering AB (www.alara.se)

[††] Total leakage rate 7 kg h^{-1}



ABBREVIATIONS	
BD	Steam generator blow-down water
BDR	Steam generator blow-down water return after cleanup
BDCU	Steam generator blow-down cleanup system
BTRS	Boron thermal regeneration system
CS	Reactor coolant after cleanup
E-COND	Ejector condensate
FW	Feedwater
RC	Reactor coolant before cleanup
RWCU	Reactor water cleanup system
RWST	Refueling water storage tank
SFP	Spent fuel pool water
SFPR	Spent fuel pool water return after cleanup
SFPCU	Spent fuel pool cleanup system
SG	Steam generator
WP	Waste processing water
WPR	Waste processing water after cleanup
WPCU	Waste processing cleanup system

Fig. 1. Schematic of the PWR unit R4, showing process water systems and cleanup systems of interest. Abbreviations are explained in the list. Sampling points relevant for the collection of process water in 2006 are indicated by shaded ovals.

non-volatile) characterization of the ^{14}C, yielding four different fractions.

Most of the systems were sampled once a week using pre-evacuated sampling vessels (50 mL glass vials with a septum) filled with process water to about 1/3 of the total volume (referred to as subsampling). Sampling was performed in a closed system without atmospheric contact. To minimize the laboratory work and cost, a number of subsamples were combined prior to ^{14}C extraction to give a composite sample (~100 mL), representing a certain period of time (generally six weeks during the operation phase). This allowed a high subsampling frequency. The composite sample analyzed should therefore be representative of the process water system for the period of interest. Additional details can be found in Magnusson et al. (2007b).

In systems where ^{14}C was not expected to be present in the gas phase, sampling was carried out using ordinary glass bottles. A summary of collected and analyzed samples of process water is presented in Table 1.

The sampling approach used in the preliminary study in 2005 was slightly different from the one described here and included only grab samples collected during a period of ≤3 weeks.

Spent resins

Spent resin samples of 20–1,000 mL (referred to as batch samples) were collected in plastic containers or sealed glass vials during 2004–2006 from various storage tanks at seven Swedish reactor units. The study covered all cleanup systems (see Table 2) and three types of reactors: PWR, BWR-HWC (hydrogen water chemistry) and BWR-NWC (neutral water chemistry). The batch samples collected represented three PWR units, three BWR-NWC units and one BWR-HWC unit. A number of subsamples were taken from each batch sample for ^{14}C analysis; additional subsamples were taken for gamma analysis and determination of the fraction of dry solids (D.S. = dry weight/wet weight). A summary of the batch samples

Table 1. Number of samples collected (i.e. subsamples) and analyzed (i.e. composite samples of ~100 mL) from various process water systems in the PWR unit R4 during 2006. The abbreviations are the same as those in Fig. 1.

	Phase analyzed		Operation (9 months)		Shutdown (4.5 days)		Outage (20 days)		Startup (5.5 days)		Total no. of composite samples analyzed
System	Gas	Liquid	Subsamples	Composite samples	Subsamples	Composite samples	Subsamples	Composite samples	Subsamples	Composite samples	
RC	X	X	33	7	18	4	12	2 [a]	13	2	15
CS	X	X	33	6	18	4	4	1	12	2	13
SFP	X	X	32	6			12	2			8
SFPR	X	X	31	6			12	2			8
WPR		X	–	9			–	1			10
RWST [b]		X	–	2							2
BD	X	X	33	5							5
BDR	X	X	33	5							5
E-COND		X	33	4							4

[a] For one of the samples, organic and inorganic ^{14}C could only be determined in the liquid phase due to sampling from the reactor cavity.

[b] The two samples collected from the RWST constituted grab samples of ~100 mL.

collected, together with the number of subsamples taken for ^{14}C analysis (shown in brackets), is presented in Table 2. Cleanup systems in the PWR units are shown in Fig. 1. Additional details can be found in Magnusson et al. (2005, 2007b).

The analyses of spent resins from the boron thermal regeneration system (BTRS) and the steam generator blow-down cleanup system (BDCU) were performed in order to verify that the ^{14}C activity concentrations were within the limits stated for disposal at the shallow land burial site at Ringhals.

^{14}C extraction and analysis

A method of separately quantifying organic and inorganic ^{14}C compounds present in spent resins and process water was developed. The method is based on acid stripping followed by wet oxidation, in combination with nitrogen purging and magnetic stirring. Slightly different

Table 2. System-specific overview of batch samples of spent ion exchange resins. The number of subsamples analyzed with respect to ^{14}C is given in brackets. Abbreviations are explained in Fig. 1; CCU = condensate cleanup system. Carb. = carboxylate resins; Sulf. = sulfonate resins.

	CCU						
Reactor type	Carb.	Sulf.	SFPCU	RWCU	WPCU	BTRS	BDCU
BWR-NWC	1^{a} (4)	1^{a} (3)	1^{b} (2)	1^{c} (2)	1^{c} (2)		
BWR-HWC		2^{a} (4)	1^{b} (2)	1^{c} (2)			
PWR [d]				4^{c} (22)		2^{e} (6)	1^{f} (2)

[a] Mixed bed (2:1; ratio given as cation:anion), powdered resins.

[b] Mixed bed (3:1), powdered resins.

[c] Mixed bed (1:1), bead resins.

[d] The storage tanks in the PWR units generally contained spent resins from a variety of process systems; to ensure good representativeness, the majority of the batch samples collected were composite samples constituting ≥10 subsamples.

[e] Anion, bead resins; intermittent operation.

[f] Mixed bed (29:1), bead resins.

approaches and procedures were developed for the two types of samples (~1.0 g resin and ~100 mL process water) using both simulated and authentic samples. Both inorganic and organic ^{14}C-labeled compounds (sodium carbonate, sodium formate and sodium acetate) were utilized during optimization of the procedures. The basic system setup used as a starting point for ^{14}C extraction from process water and from spent resins, is schematically outlined in Fig. 2. Detailed information on the set-up, validation and reliability of the method is presented in Magnusson et al. (2007c).

The basic procedure (used principally for the resin samples) consists of two steps: acid stripping and wet oxidation. The inorganic carbon fraction of a sample is extracted by the addition of sulfuric acid (H_2SO_4) and the carbon dioxide generated is absorbed in a pair of alkali gas washing bottles (nos. 2–3 in Fig. 2, where no. 3 serves as safety flask). Following acid stripping, the remaining carbon compounds (i.e. the organic fraction), are extracted by the addition of potassium peroxodisulphate ($K_2S_2O_8$) and silver nitrate ($AgNO_3$) with simultaneous heating. The carbon dioxide evolved is absorbed in a second pair of gas washing bottles (nos. 4–5, where no. 5 serves as safety flask). A catalytic furnace, located between the two sets of washing bottles, ensures oxidation of reduced compounds. A water trap (no. 1) is utilized to avoid interfering radionuclides (e.g. ^{3}H) from reaching the absorbers. The basic procedure results in two separate fractions: inorganic and organic ^{14}C.

The ^{14}C extraction from process water generally follows a three-step procedure: gas phase extraction, acid stripping and wet oxidation. The procedure allows quantification of organic and inorganic ^{14}C compounds in the gaseous phase (where applicable), as well as in the liquid phase, resulting in four fractions.

Duplicate samples of a few milliliters were collected from the gas washing bottles, mixed with scintillation cocktail and measured using liquid scintillation counting (LSC). The background was determined by regularly processing blank samples. The detection limit (calculated with a confidence interval of 95%) of the LSC analysis was on the order of 12 Bq kg^{-1} water (assuming a volume of 100 mL) and 1,000 Bq kg^{-1} resin (assuming a wet weight of

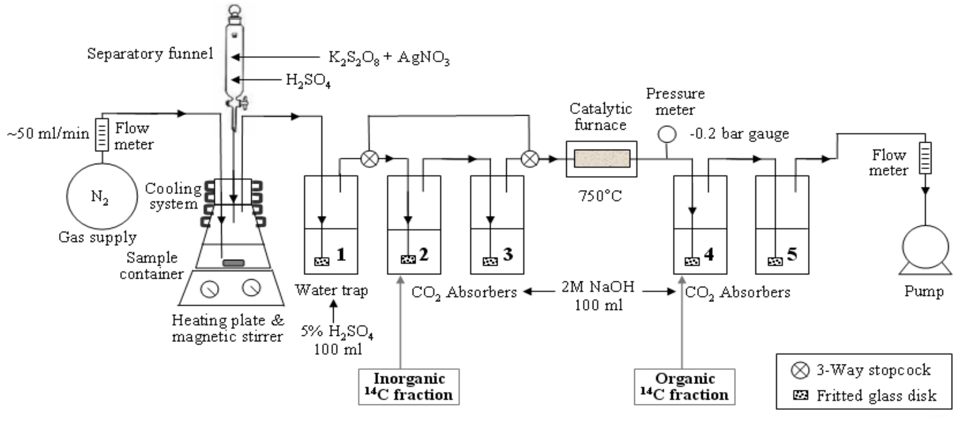


Fig. 2. System setup used as a starting point for ^{14}C extraction from process water and spent ion exchange resins. The gas washing bottles are referred to as 1–5 in the text; bottles 3 and 5 serve as safety flasks.

1.0 g). The total propagated error was typically on the order of ± 5% and included errors associated with LSC measurement, background determination and determinations of mass and volume. A few selected samples of process water, with a ^{14}C concentration below the detection limit, were further processed by precipitating the NaOH solutions obtained. Measurements of the precipitates yielded an improved detection limit of ~0.4 Bq kg^{-1}.

RESULTS AND DISCUSSION

Calculation of production rates

The production of radionuclides by neutron activation of the reactor coolant and the containment atmosphere has recently been calculated in connection with updates of the Safety Analysis Report for a BWR unit (R1, 2500 MW_{th}; ASEA Atom); and a PWR unit (R4, 2775 MW_{th}; Westinghouse). The calculations were performed using the previously developed calculation models, BwrCoolAct and PwrCoolAct[‡‡]. The models are designed as a number of compartments, each divided into a number of cells to account for differences in e.g. neutron flux and temperature. The models also consider different flow paths through the reactor core, the steam void profile as a function of reactor power (only BWR) and core flow, the effect of impurities in the reactor coolant, the effect of water chemistry and cleanup systems, etc. The thermal neutron fluence rates were calculated for each reactor core, considering the enrichment and burnup level for the equilibrium core, using the ORIGEN-S code (Hermann and Westfall 2000). The neutron spectrum for higher energies was determined based on input from different in-core fuel management calculations. Therefore, the equation used to calculate the neutron activation rate (Bq s^{-1}) is core-specific; furthermore, it accounts for neutron-induced reactions over the whole energy range (i.e. thermal, epithermal and fission neutrons). The cross sections used in the calculation of the production rates of ^{14}C are given in Table 3. A summary of the results of the calculation of ^{14}C production rates (realistic scenario) is presented in Table 4.

From Table 4 it is evident that activation of ^{17}O is the main source term of ^{14}C in the reactor coolant of LWRs, accounting for more than 99% of the total production rate. In the BWR unit, the thermal neutrons were found to induce the majority of the reactions, whereas in the PWR, fission neutrons gave the highest production rate. The difference is due to the harder neutron spectrum in the PWR core (the average flux of fission neutrons being roughly double that in the BWR). The conservative production rates calculated for the BWR and the

Table 3. Neutron activation reactions and cross sections used in the calculation of the production rate of ^{14}C in Swedish LWRs (RI = Resonance Integral). Data from JEF-PC 2.2 (OECD Nuclear Energy Agency 1997).

Neutron-induced reaction	Cross section (barn)		
	Thermal	RI	Fission
^{17}O (n, α) ^{14}C	0.235	0.106	0.095
^{14}N (n, p) ^{14}C	1.82	0.818	0.0355

[‡‡] Calculation models developed by ALARA Engineering AB (www.alara.se)

Table 4. Calculated production rates of ^{14}C (Bq s^{-1}) in the reactor coolant of a BWR (2500 MW_{th}, ASEA Atom) and a PWR (2775 MW_{th}, Westinghouse) unit from neutron-induced reactions with ^{17}O and ^{14}N. A realistic case scenario is presented [a].

	BWR, 2500 MW_{th}			PWR, 2775 MW_{th}		
	Production rate (Bq s^{-1})			Production rate (Bq s^{-1})		
	Thermal	Epithermal	Fission	Thermal	Epithermal	Fission
^{17}O	8.4×10^3	770	6.5×10^3	3.4×10^3	1.1×10^3	5.8×10^3
^{14}N [b]	2.7	0.25	0.10	47	16	4.0
Sum	8.4×10^3	770	6.5×10^3	3.4×10^3	1.1×10^3	5.8×10^3
Fraction	53%	5%	42%	33%	11%	56%
Total	1.6×10^4			1.0×10^4		
Fraction from ^{14}N	0.02%			0.65%		

[a] Conservative values: 2.4×10^4 Bq s^{-1} (33%) and 1.1×10^4 Bq s^{-1} (6.1%) for the BWR and PWR, respectively; fraction from activation of ^{14}N in brackets. The conservative case scenario for the BWR assumes introduction of N_2 through the scram system into the reactor, equivalent to a feedwater concentration of 100 ppm nitrogen. Conservative value for the PWR based on a nitrogen concentration of 5.4 ppm in the reactor coolant.

[b] For the BWR, a concentration of 0.1 ppm N_2 in the feedwater was used; for the PWR, a concentration of 0.54 ppm N_2 in the reactor coolant was used.

PWR were 50% and 6% higher than the realistic values presented, respectively. The uncertainty in the values for the BWR is due to the possibility of N_2 being introduced into the reactor through the scram system (see Lundgren et al. 2002). The overall uncertainty in the calculation of the production rates is estimated to be ± 20%.

The production rates presented in Table 4 correspond to 580 and 350 GBq GW_e^{-1} y^{-1} for the BWR and the PWR unit, respectively. The generic production rate of ^{14}C in Nordic BWRs has previously been calculated to be 23–24 kBq MWh_{th}^{-1} (Lundgren et al. 2002), corresponding to 590–620 GBq GW_e^{-1} y^{-1}. Off-gas measurements conducted on a BWR (Oskarshamn 3, O3) showed that the activity flow rate from the turbines was 98% of the calculated generic production rate, i.e. strongly supporting the results of the previous, as well as the present, calculations. Vance et al. (1995) reported production rates of 540–570 GBq GW_e^{-1} y^{-1} and 270–410 GBq GW_e^{-1} y^{-1} for BWRs and PWRs, respectively, i.e. similar values to those presented here.

Process water

The variation and distribution of ^{14}C in the reactor coolant of the PWR unit R4 are shown in Fig. 3 (RC samples, before cleanup) and Fig. 4 (CS samples, after cleanup). The different lines represent the four fractions (organic and inorganic ^{14}C in gas phase; and organic and inorganic ^{14}C in liquid phase) analyzed separately for each composite sample. Each point represents one composite sample, which corresponds to a certain period of time. The points are located in the middle of the period they represent, and thus the lines are only to guide the eye (this applies to Figs. 3, 4, 5, 6 and 8). Periods of shutdown, outage and startup are indicated in Fig. 5.

From Figs. 3 and 4 it can be seen that the concentration and the distribution of different ^{14}C species in the primary circuit show large variations during the fuel cycle. The

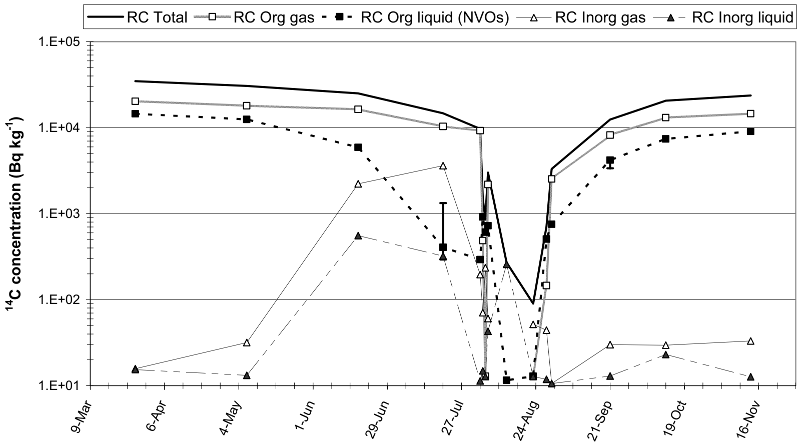


Fig. 3. Distribution of ^{14}C in RC samples (reactor coolant before cleanup), collected in 2006 from the PWR unit R4; NVOs here refers to non-volatile organic compounds. Refueling outage in August. Most of the plotted concentrations ≤43 Bq kg^{-1} are not statistically significant. Median standard deviation (SD) for values >43 Bq kg^{-1} = 5%; anomalous SD:s for NVOs on 20 July and 21 September are plotted in the figure. Note the logarithmic scale.

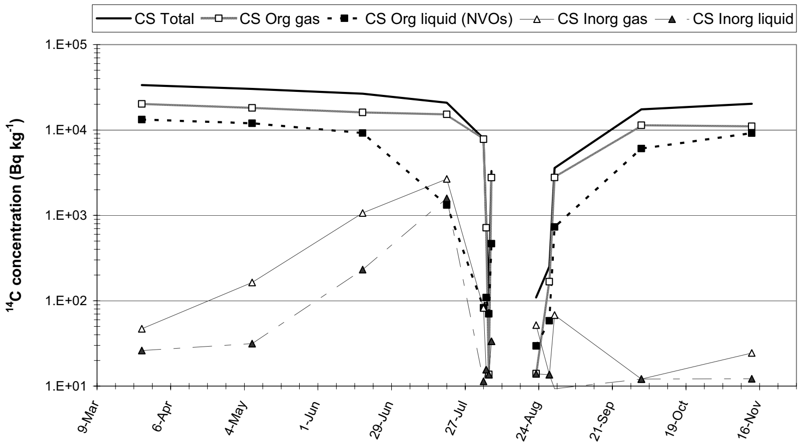


Fig. 4. Distribution of ^{14}C in CS samples (reactor coolant after cleanup), collected in 2006 from the PWR unit R4; NVOs here refers to non-volatile organic compounds. Refueling outage in August. Most of the plotted concentrations ≤34 Bq kg^{-1} are not statistically significant. Median standard deviation for values >34 Bq kg^{-1} = 6%. Note the logarithmic scale.

maximum total concentration, $3.5 \pm 0.1 \times 10^4$ Bq kg^{-1}, was obtained for the first sampling period (March–April), after which it steadily decreased towards the outage period (in August). An unambiguous explanation of this observation has not yet been found.

For most of the power operation period, the chemical composition of the RC samples was: ~99.7% organic ^{14}C and ~0.3% inorganic ^{14}C. A high fraction of organic carbon compounds is expected due to the prevailing reducing conditions. However, during the end of the fuel cycle (June–July in Figs. 3 and 4), the inorganic fraction increased to 27% of the total ^{14}C. This shift from organic species to inorganic species in June and July was unexpected, and an unambiguous explanation has not been found. The period coincided with an increase in pH value after the reactor water cleanup system (RWCU; caused by the low boron concentration at the end of the fuel cycle) and operation of the BTRS resin.

The majority of the organic ^{14}C compounds in the reactor coolant (~60%) were found to be reduced gaseous compounds, probably methane. The remaining part (~40%) was recovered in the liquid phase and classified as non-volatile organic ^{14}C compounds (here referred to as NVOs). Consequently, the NVOs were not affected by either purging or acid stripping, but were converted to CO_2 upon wet oxidation. Based on simulations and the prevailing chemistry conditions (see Lundgren et al. 2002), and on routine analyses of organic compounds at the Ringhals units, the NVOs are believed to be comprised mainly of formate and acetate.

The ^{14}C concentration, distribution and trends were found to be similar before and after the RWCU (compare Figs. 3 and 4). Similar concentrations are expected, given that gaseous ^{14}C compounds are the dominating species and are not adsorbed on the RWCU resins. The absorbed fraction of NVOs in the RWCU [(Bq kg$^{-1}{}_{RC}$ – Bq kg$^{-1}{}_{CS}$) / Bq kg$^{-1}{}_{RC}$] was generally low during power operation; about 4%. However, the absorbed fraction increased significantly when using fresh ion exchanger material (at the start of the shutdown period and at the beginning of the startup period). Within three days, the absorbed fraction decreased significantly, indicating breakthrough.

A close-up of the time period comprising the shutdown, refueling outage and startup is shown in Fig. 5. A list of important events (a–o) related to the period is also included in the figure. The sharp fall in the concentration of gaseous organic compounds seen in Fig. 5 between 3 and 5 August is the result of: (1) venting of the volume control tank (VCT); (2) decreased reactor power; and (3) the shift to oxidizing conditions (i.e. reduction of the hydrogen concentration followed by forced oxygenation through the addition of hydrogen peroxide). This decrease was followed by an unexpected peak in organic ^{14}C on 6 August, where the major part was gaseous compounds. This peak was probably due to the collapse of the steam bubble in the pressurizer, which introduced preserved organic ^{14}C (shielded from the oxidizing conditions) into the reactor coolant. During startup, the concentration of organic ^{14}C in the liquid phase (i.e. NVOs) initially dominated. This may have been due to the introduction of trace amounts of various organic chemicals, used for cleaning etc., during the outage period, as well as organic compounds present in the make-up water.

Fig. 6 summarizes the results from direct and indirect measurements of ^{14}C in the reactor coolant (before cleanup) from samplings performed in 2003[§§], 2005 (Magnusson et al. 2005, 2007a) and 2006. Due to the similarity between the fuel cycles, the results should be directly comparable. The results shown for 2003 (January–March) were calculated based on ^{14}C analyses of ejector off-gas from the turbines. The concentration in the reactor coolant was

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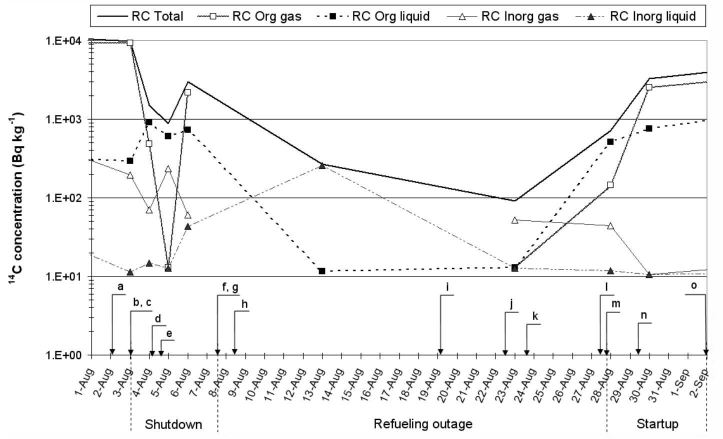
[§§] Unpublished results



Details of events

a.	Reactor power 96%
b.	Switch to RWCU shutdown resin bed
c.	Start reduction of reactor power
d.	Reactor power 0%
e.	Addition of H_2O_2 (forced oxygenation)
f.	Opening of reactor vessel head
g.	Filling of reactor cavity (from RWST)
h.	Start refueling operations
i.	Stop refueling operations
j.	Emptying of reactor cavity (to RWST)
k.	Closure of reactor vessel head
l.	Addition of hydrazine (deoxygenation)
m.	Switch to RWCU power operation resin bed
n.	Reactor critical
o.	Reactor power 99%

Fig. 5. Close-up of Fig. 3 showing the shutdown (3 August to 7 August), outage (7 August to 27 August) and startup (27 August to 2 September) periods, including a list of important events (a–o) indicated in the figure. The duration of the fuel unloading and fuel loading operations was ~48 h each. Note the logarithmic scale.

derived by combining the off-gas data with the total steam generator leak rate (i.e. backwards calculation). As can be seen in Fig. 6, the total concentrations are similar, but the distribution of chemical species (organic versus inorganic species) shows variations between the fuel cycles as well as within the same cycle. The relatively high inorganic fraction obtained in 2003 may be the result of effects on the secondary side where the samples of ejector off-gas were collected. One such effect may be chemical decomposition of organic non-volatile

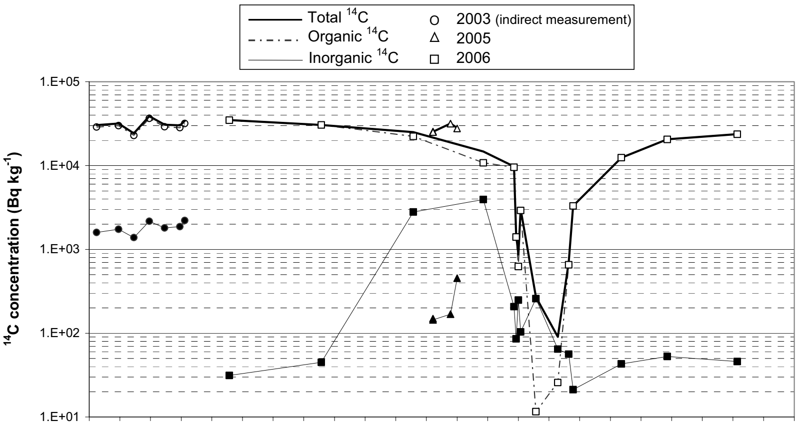


Fig. 6. Compilation of results obtained by direct and indirect measurements of ^{14}C in the reactor coolant in 2003 (indirect measurement), 2005 (RC grab samples) and 2006 (RC composite samples). Concentrations in 2003 were calculated based on analyses of ejector off-gas and measured steam generator leakage rates. Organic ^{14}C (gas + liquid phase) open symbols, inorganic ^{14}C (gas + liquid phase) filled symbols. Note the logarithmic scale.

compounds into inorganic compounds, caused by the difference in prevailing chemical and physical conditions.

Using the concentrations and distributions obtained from the RC samples, the removal rate (Bq s^{-1}) of ^{14}C from the reactor coolant system was calculated. Individual removal rates from the system were calculated based on the venting rate of the VCT (gaseous compounds only), the degassing of the charging pumps (gaseous compounds only), and the make-up water (total concentration) added to the reactor coolant during the period of interest. The total removal rate obtained for each sampling period in 2006, as well as for a few separate days in 2005, is shown in Fig. 7. In this figure, the removal rates are compared to the calculated production rate, revealing some interesting features. At the beginning of the fuel cycle (i.e. autumn 2006), the production rates are found to exceed the removal rates, implying that ^{14}C is accumulated somewhere in the reactor coolant system. Towards the end of the fuel cycle, here March–July 2006 (i.e. the end of the preceding fuel cycle), the removal rates significantly exceed the production rates (similar results were obtained from the grab samples collected at the end of the fuel cycle in 2005). This observed excess of ^{14}C, suggests the presence of a second source, supplying the reactor coolant system with additional ^{14}C at the end of the fuel cycle. This source is believed to be the ion exchange resins in the RWCU, which seem to release accumulated ^{14}C towards the end of their operational period. Deposition on, and release from, system surfaces does not seem to be a realistic explanation based on the measurements of replaced steam generator tubes (see Table 7).

Fig. 8 shows the net accumulation rate on the ion exchange resins (IX), assumed to be the difference between the production rate and the removal rate (data plotted as if all the 2006 samples originated from the same fuel cycle). The data from 2005, also included in Fig. 8, fit well with the exception of the outlier on 5 July.

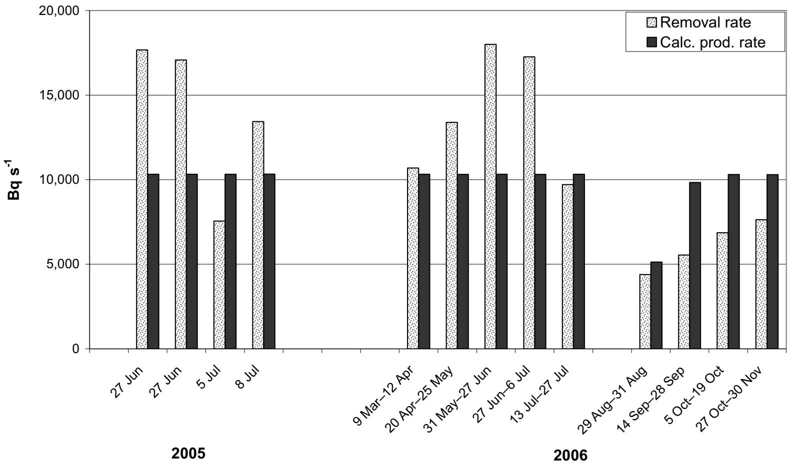


Fig. 7. ^{14}C removal rate (Bq s^{-1}) from the reactor coolant system versus calculated production rate (Bq s^{-1}). Removal rates calculated from analyses of RC samples in 2005 (grab samples) and 2006 (composite samples) and by using the venting rate of the VCT, the degassing of the charging pumps and the make-up water added to the reactor coolant.

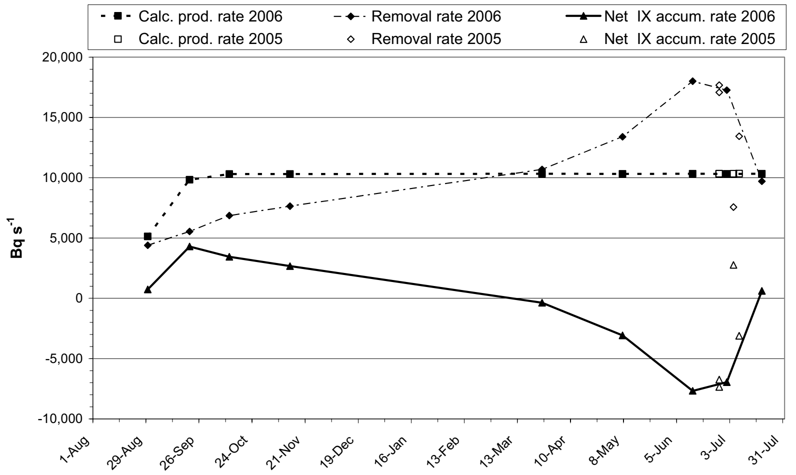


Fig. 8. Net accumulation rate on the ion exchange resins (IX) in the RWCU during a hypothetical fuel cycle. The net IX accumulation rate is assumed to be the difference between the calculated production rate and the removal rate.

Process water collected from the secondary circuit and auxiliary systems was found to contain small amounts of ^{14}C; one exception being the waste processing system (annual discharge rate calculated to be 0.8 GBq). The majority of the samples from the spent fuel pool (SFP and SFPR) and the steam generator blow-down system (BD and BDR) were found to be below the detection limit (being $\leq$ 16 Bq kg^{-1} and $\leq$ 25 Bq kg^{-1}, respectively). However, following the refueling operations, the total concentration in the SFP was found to increase by a factor of ~4 (from 12 ± 1 Bq kg^{-1} to 53 ± 19 Bq kg^{-1}).

Spent resins

Updated results from the analyses of spent resins are presented in Table 5. Based on the concentrations obtained for the different batch samples (MBq kg^{-1} wet weight), some interesting observations were made.

1. The condensate cleanup (CCU) resins contained the highest concentrations in the BWRs; the main reason is believed to be the significantly higher flow rate through the system.
2. A significant difference, in terms of concentration and accumulation rate, was found between the sulfonate CCU resins and the carboxylate CCU resins (see discussion below).
3. A significantly higher concentration was obtained for the SFPCU batch sample originating from BWR-NWC units (compare sample ID IX:$5_{\mathrm{BWR\text{-}NWC}}$ with IX:$4_{\mathrm{BWR\text{-}HWC}}$ in Table 5). This is thought to be the result of spill-over from a storage tank containing a mixture of carboxylate and sulfonate CCU resins into the tank containing SFPCU resins.

Table 5. Summary of the results obtained from the ^{14}C analyses of spent resins from BWR-HWC, BWR-NWC and PWR units.

		^{14}C in batch sample			Accumulation in spent resins		Normalized accumulation in spent resins [c]
Sample ID	Reactor type / Batch sample content	Total conc. [a] (MBq kg^{-1} ww)	SD [b]	Org. fraction [a]	Total (GBq y^{-1})	Org. fraction	(GBq GW$_e^{-1}$ y^{-1})
	BWR-HWC				1.8	11%	3.4
IX:1$_{\text{BWR-HWC}}$	RWCU+WPCU	0.075	±4%	6%			
IX:2$_{\text{BWR-HWC}}$	CCU	0.13	±36%	16%			
IX:3$_{\text{BWR-HWC}}$	CCU	0.10	±4%	8%			
IX:4$_{\text{BWR-HWC}}$	SFPCU	1.3×10^{-3}	±60%	~80%			
	BWR-NWC				5.3 (22) [d]	21% (16%) [d]	4.7 (24) [d, e]
IX:1$_{\text{BWR-NWC}}$	RWCU	0.059	±5%	9%			
IX:2$_{\text{BWR-NWC}}$	WPCU	0.072	±26%	5%			
IX:3$_{\text{BWR-NWC}}$	CCU Sulfonate	0.37	±4%	24%			
IX:4$_{\text{BWR-NWC}}$	CCU Carboxylate	1.9	±4%	16%			
IX:5$_{\text{BWR-NWC}}$	SFPCU	0.44	±6%	6%			
	PWR				16–27	29–31%	20–33 [f]
IX:1$_{\text{PWR}}$	RWCU operation	20	±16%	29%			
IX:2$_{\text{PWR}}$	RWCU shutdown, SFPCU, WPCU	1.6	±10%	35%			
IX:3$_{\text{PWR}}$	RWCU shutdown, SFPCU, WPCU	1.4	±14%	30%			
IX:4$_{\text{PWR}}$	RWCU operation, RWCU shutdown, SFPCU	8.3	±23%	28%			
IX:5$_{\text{PWR}}$	BTRS	0.36	±7%	98%			
IX:6$_{\text{PWR}}$	BTRS	0.32	±5%	88%			
IX:7$_{\text{PWR}}$	BDCU [g]	3.3×10^{-3}	±60%	44%			

[a] Reported as the average value from analyses of 2–6 subsamples; ww = wet weight.
[b] Maximum standard deviation; based on the variation between analyzed subsamples or the average total propagated error from the analyses of the subsamples.
[c] Normalized to the energy production during the year(s) of operation of the resin(s) in the batch sample.
[d] BWR-NWC unit operating with carboxylate CCU resins within brackets.
[e] Assuming that IX:5$_{\text{BWR-NWC}}$ was unrepresentative (see item 3 in the text), but similar to IX:4$_{\text{BWR-HWC}}$, a normalized accumulation rate of 4.2 GBq GW$_e^{-1}$ y^{-1}, instead of 4.7, was obtained.
[f] The lower value, 20 GBq GW$_e^{-1}$ y^{-1}, probably underestimates the accumulation rate in PWRs since it was calculated based on IX:4$_{\text{PWR}}$ (believed to be unrepresentative; see item 5 in the text). A more realistic range would be 30–33 GBq GW$_e^{-1}$ y^{-1}.
[g] Primary-to-secondary leakage rate during the period of operation 7 kg h^{-1}.

4. The concentration in the BTRS resins was above the limit for disposal at the shallow land burial site at Ringhals[***].
5. A significant discrepancy was found between the two PWR samples containing spent resins from the RWCU during power operation (referred to as RWCU operation; compare samples ID:s IX:1_{PWR} and IX:4_{PWR}). The lower concentration (as well as normalized accumulation rate) of sample IX:4_{PWR} might be an effect of the longer operation period of the RWCU resin (two fuel cycles) compared to sample IX:1_{PWR} (one fuel cycle; standard period of resin operation). As discussed in the section above, a release of ^{14}C from the resin seems to be taking place towards the end of the fuel cycle.

The annual accumulation in spent resins, presented for each reactor type in Table 5, was calculated based on system-specific, as well as reactor-specific, consumption rates of spent resins (kg dry weight y^{-1}) and the D.S. fraction determined for each batch sample. The normalized accumulation rates (GBq GW_e^{-1} y^{-1}) show similar results for the BWR-HWC and the BWR-NWC reactors. However, a BWR unit operating with carboxylate CCU resins (values shown in brackets) may show as high an accumulation rate as a PWR unit. The organic fraction in spent resins annually generated from a PWR was found to be ~30%, as shown in Table 5. The corresponding value for BWR-HWC and BWR-NWC units was 11% and 21%, respectively.

Fig. 9 shows system-specific accumulation rates for the reactor types investigated, where the three PWR units investigated are shown individually. Due to the often mixed origin of spent resins in the storage tanks in the PWR units (batch samples IX:2_{PWR}–IX:4_{PWR} in Table 5), system-specific data were generally not available. However, for the PWR unit R3 in Fig. 9, the RWCU operation (sample IX:1_{PWR} in Table 5) was found to constitute 74% of the total annual accumulation. For the BWRs, Fig. 9 clearly shows that the accumulation in the CCU resins is the totally dominating source of ^{14}C in operational solid LILW waste, both from HWC and NWC units. Furthermore, the normalized accumulation rate in carboxylate CCU resins was found to be a factor of 6 higher than that obtained for sulfonate CCU resins. The higher uptake of ^{14}C on the carboxylate resins is believed to be due to their higher pH, allowing a larger fraction of acidic species (hydrogen carbonate and simple organic acids) to adsorb to the resins. Most of the carbon compounds adsorbed on the resins are expected to be in the form of anionic species (e.g. HCO_3^-, acetate and formate ions). Therefore, the difference in accumulation is not expected to be directly correlated to the functional groups of the cation resin (i.e. carboxylate and sulfonate), but due to the differences in the chemical characteristics of the two types of resins. The carboxylate resins are only weakly acidic, whereas the sulfonate resins are strongly acidic. The degradation of sulfonate resins by hydrogen peroxide, forming sulfuric acid, may also lower the pH in this type of resin.

The results presented in Table 5 indicate that the batch samples collected were representative of the waste stream in question (with two exceptions discussed earlier). This was concluded by comparing batch sample IX:$2_{BWR\text{-}HWC}$ with IX:$3_{BWR\text{-}HWC}$, IX:2_{PWR} with IX:3_{PWR}, and IX:5_{PWR} with IX:6_{PWR}. Each pair of batch samples contains the same type of resin(s) but the batch samples were collected either on different occasions or from different

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[***] Average allowable ^{14}C concentration in the waste according to the Swedish Radiation Protection Authority (SSI): 0.01 MBq kg^{-1} ww; individual waste packages: up to 0.1 MBq kg^{-1} ww (SSI 2007).

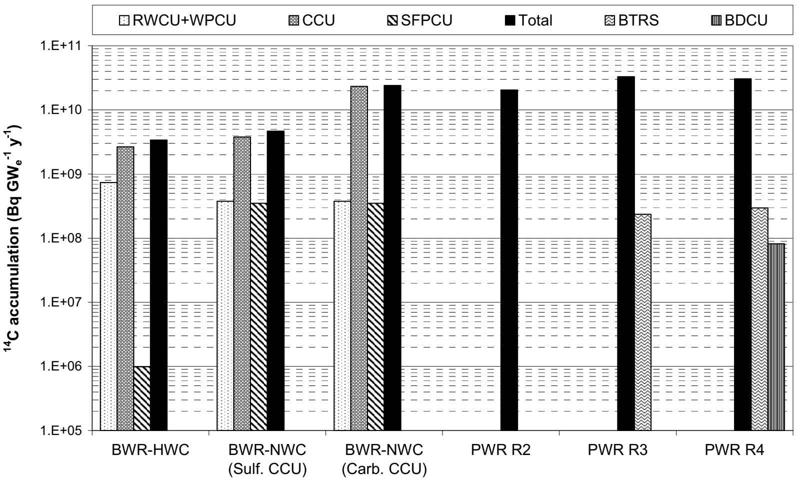

Fig. 9. Normalized annual ^{14}C accumulation (Bq GW$_e^{-1}$ y^{-1}) in spent ion exchange resins from the RWCU+WPCU, CCU, SFPCU, BTRS and BDCU in BWR-HWC, BWR-NWC and PWR units.

storage tanks. Even so, the concentrations obtained (as well as the normalized accumulation) were similar. Furthermore, the samples IX:1$_{PWR}$–IX:4$_{PWR}$ were considered to have been collected in the best possible way (see footnote d in Table 2).

Previously reported data on accumulation rates of ^{14}C in spent resins are very limited. Table 6 shows a comparison between the values presented in this paper and values calculated from or reported by Salonen and Snellman (1985), Vance et al. (1995) and Miller (2006)[†††]. Good agreement was found with the accumulation rates derived from Salonen and Snellman (BWR) and from Miller (PWR). The high accumulation rates reported by Vance and colleagues may be partly explained by other forms of low-level waste included in the values reported (i.e. ^{14}C in waste originating from sources other than spent resins). These values correspond to approximately 8% and 21% of the production rate Vance and colleagues presented for BWRs and PWRs, respectively, which are relatively high fractions (compare with fractions presented in Table 7).

Mass balance assessment

A mass balance assessment of the ^{14}C produced in Swedish LWRs was performed based on the results obtained in the investigation. The assessment shows the fate of the ^{14}C produced in the coolant and includes gaseous, liquid and solid waste streams, as well as potential sinks. The results of the mass balance assessment of ^{14}C are presented in Table 7 for two BWR-NWC units (Oskarshamn 3, O3, and Forsmark 3, F3), one BWR-HWC unit (Ringhals 1, R1), and two PWRs (Ringhals 3 and 4, R3 and R4). In the table, all fractions are related to the calculated ^{14}C production in the coolant (O3 and F3 calculated from the generic production

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[†††] Miller C. Principal radwaste engineer at Diablo Canyon power plant. Personal communication; 2006.

Table 6. Comparison between accumulation rates in spent ion exchange resins calculated in this investigation and those calculated from or reported by others (Salonen and Snellman 1985; Vance et al. 1995; Miller 2006 [a]). BWR operating with carboxylate CCU resins shown in brackets. VVER = PWR of Soviet design.

	Normalized ^{14}C accumulation in spent resins ($GBq\ GW_e^{-1}\ y^{-1}$)			
Reactor type	This paper	Salonen [b]	Vance [c]	Miller [d]
BWR	3.4–4.7 (24)	1.5–4.8	46	
PWR	20–33		70	24
VVER		5.1–7.9		

[a] Miller C. Principal radwaste engineer at Diablo Canyon power plant. Personal communication; 2006.

[b] Reported values ($MBq\ y^{-1}$) normalized using the energy production stated in the IAEA Power Reactor Information System (PRIS) database (PRIS 2007), averaged over the two years of sampling.

[c] Values based on shipping manifests for "low-level solid waste"; according to Yim and Caron (2006), irradiated hardware was not included. Depending on the amount of other solid waste forms shipped, ^{14}C in spent resins may have been responsible for 65–100% of the values reported (estimated based on distribution data of ^{14}C in various low-level waste streams in LWRs reported by Yim and Caron 2006).

[d] Value calculated based on the average annual ^{14}C activity in spent resins (i.e. does not include spent filter cartridges) reported buried from Diablo Canyon 1 and 2 over the years 2001–2005 and normalized using energy production data from the PRIS database (PRIS 2007).

rate, taken as 24 kBq MWh_{th}^{-1}, given by Lundgren et al. (2002); R1, R3 and R4 calculated from the core-specific production rates).

The proportion of ^{14}C ending up as liquid waste discharged to the sea was found to be 0.3% for PWRs and 0.04% for BWRs. However, the value derived for BWRs is highly uncertain. The solid waste streams account for 0.6–0.8% in BWRs and 6–10% in PWRs (6% was calculated for R2, not included in Table 7, and is believed to be unrepresentative for the PWRs due to the specific batch sample, IX:4_{PWR}, on which the calculation was based; see item 5 in previous section). However, for a BWR-NWC unit operating with carboxylate CCU resins (F2, not presented in Table 7), the solid waste stream was found to constitute 3.8% of the production. The assessment shows significant variations in the fraction released as gaseous waste (routinely measured in the stack), depending not only on reactor type but also on the power plant site. For BWRs, the expected fraction would be ~100%. However, all three BWRs at Oskarshamn nuclear power plant (only O3 shown here) had lower fractions than expected (92%, 59% and 63%), whereas the three BWRs at Forsmark nuclear power plant (only F3 shown here) had higher fractions than expected (146%, 155% and 128%). Since the calculated production rate in O3 was verified by off-gas measurements (see the section on production rates above), the underestimated release rates are probably an effect caused by the installed monitoring equipment (a subject under current investigation). The cause of the consistently high fractions of gaseous releases reported from the Forsmark units has not yet been investigated. The uncertainty in the calculation of the production rates, estimated to be ± 20%, is not considered to affect the conclusions made for the Oskarshamn and the Forsmark units.

The assessment for the PWRs showed that the total ^{14}C content of the waste streams accounts for 80–97% of the ^{14}C production on the three units (the result for R2, not shown here, was 89%). Although the proportions obtained are within the uncertainty estimated for the calculated production rates, yet undiscovered sinks of ^{14}C can not be completely ruled out. However, system surfaces, such as the steam generators, are not considered to constitute a significant sink, indicated by the low fraction presented in Table 7. Furthermore, any deposited ^{14}C on system or fuel surfaces in R4 would have caused transient releases into the reactor coolant at shutdown; a phenomenon not observed in the survey. Remaining potential sinks of ^{14}C, yet to be investigated, include reactor coolant filter cartridges.

CONCLUSIONS

Core-specific calculations for a PWR (2775 MW_{th}; Westinghouse) yielded a production rate of 350 GBq GW_e^{-1} y^{-1}, of which fission neutrons were responsible for the major part. The corresponding value calculated for a BWR (2500 MW_{th}, ASEA Atom) was 580 GBq GW_e^{-1} y^{-1}. For both reactor types, production from ^{14}N constituted less than 1%.

Of the ^{14}C formed in the coolant, 0.6–0.8% ended up in spent resins on BWRs; with an exception for units operating with carboxylate CCU resins where 3.8% was recovered in the resins. The corresponding value for PWRs was 6–10%. The results from individual batch samples of spent resins indicate that the major part of ^{14}C in PWRs seems to be accumulated during power operation and not during shutdown. Furthermore, the uptake appears to be highest at the beginning of the fuel cycle, with the release of accumulated ^{14}C towards the end of the fuel cycle. For BWRs it should be noted that the accumulation rate in carboxylate CCU resins seemed to be a factor of 6 higher than for the corresponding sulfonate resins. Therefore, due consideration should be taken before replacing the sulfonate resins with carboxylate resins on units with high sulfate concentrations in the reactor coolant.

The ^{14}C released with liquid discharges was found to be insignificant, constituting less than 0.5% of the calculated production in the coolant. Based on the ^{14}C recovered in the solid and liquid waste streams, the gaseous releases should account for the remaining 90–99%. However, according to the routine measurements of stack releases at the power plants, gaseous releases constituted 60–155% of the production. The large variations and uncertainties in the reported release rates limit the usefulness of the mass balance assessment, especially in the case of BWRs.

From the survey of ^{14}C in the reactor coolant of a PWR, it was found that the concentration as well as the distribution of different ^{14}C species showed large variations during the fuel cycle. Organic species generally constituted ~100% of the total ^{14}C during power operation. Reduced organic compounds (probably methane) accounted for ~60%; the remaining part being non-volatile organic compounds, believed to consist of compounds such as formate and acetate. Nevertheless, it should be noted that organic compounds only constituted some 30% of the total ^{14}C activity on spent resins from the PWR units.

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Table 7. Mass balance assessment of ^{14}C originating from production in the coolant and its fate in different waste streams (presented as percentage of the calculated production). Results from five different reactor units are presented.

	BWR-NWC (O3)		BWR-NWC (F3)		BWR-HWC (R1)		PWR (R3)		PWR (R4)	
	Basic data	Fraction	Basic data	Fraction	Basic data	Fraction	Basic data	Fraction	Basic data	Fraction
Thermal power (MW)	3300		3300		2500		2775		2775	
Energy production ($TW_eh\ y^{-1}$) [a]	9.17		9.65		6.24		7.35		7.24	
Calculated ^{14}C production ($Bq\ y^{-1}$) [a]	6.15×10^{11}		6.43×10^{11}		4.11×10^{11}		2.83×10^{11}		2.84×10^{11}	
Gaseous waste										
Stack releases [a, b]		63%		128%		118%		86%		70% [c]
Accumulation in off-gas system [d]		2%		2%						
Solid waste										
Accumulation in spent resins		0.77%		0.77%		0.55%		9.8%		9.0%
Accumulation in filter cartridges [e]								0.02%		0.02%
Deposition on steam generator tubes [f]								0.04%		0.04%
Liquid waste										
Waste water tanks [g]		0.04%		0.04%		0.04%		0.26%		0.26%
Ejector condensate [h]										0.08%
Accumulation in RWST [i]								<0.02%		<0.02%
Accumulation in spent fuel pool [j]								0.01%		0.01%
TOTAL		66%		131%		119%		97%		80%

[a] Reported as average value over the years 2002–2006.

[b] Based on the reported values from the power plants, at which ^{14}C in stack releases are routinely measured.

[c] Minimum value since the stack sampling equipment was periodically unavailable. A more correct value is estimated to be 78%.

[d] Rough estimate based on six ejector off-gas measurements on one BWR-NWC unit (O3) operating with charcoal columns in recirculation mode.

[e] Based on the maximum result (5.4×10^7 $Bq\ y^{-1}$) obtained from ^{14}C analysis of four sampling filters in R4, i.e. not authentic reactor coolant filters.

[f] Based on three measurements of oxides from tubes in a replaced steam generator from R3, 1995. Average concentration corresponds to 2×10^5 $Bq\ m^{-2}$.

[g] Value for BWRs (see Stenström et al. 2006) considered to be uncertain (based on 3 samples, i.e. three months of discharges, collected from one BWR-HWC unit, B2; presented in Magnusson et al. 2005, 2007a).

[h] Primary-to-secondary leakage rate 7 kg h^{-1} (average value for the period of interest).

[i] Rough estimate based on two grab samples from R4.

[j] Rough estimate based on the analyses of spent fuel pool water from R4 and a total water volume of 2×606 m^3.

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