CARBON-14 MANAGEMENT: THE IMPLEMENTATION OF STACK EMISSIONS MONITORING AT ONTARIO HYDRO NUCLEAR

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ABSTRACT

The CANDU system generates higher levels of carbon-14 (^{14}C) than any other reactor type. More than 95% of this production occurs in the moderator and most of this is captured on the moderator ion exchange column resins with a small fraction being released to the environment.

In the past, OHN has depended mainly on environmental measurements of ^{14}C to assess the impact of its emissions. In 1995, the Advisory Committee on Radiological Protection published a report, ACRP-14, entitled: "The Management of Carbon-14 in Canadian Nuclear Facilities". The report recommended mandatory emissions monitoring at all OHN generating facilities along with reporting of ^{14}C inventory and the provision of information on the stability of stored ion exchange resins which retain the ^{14}C.

OHN has responded by committing to implement ^{14}C emissions monitoring by the end of 1999, reporting the OHN ^{14}C inventory and supporting research into resin and ^{14}C stability in storage.

'State-of-the-art' stack samplers, manufactured by a local company, BOT Engineering, have now been delivered to the various OHN locations and are either being installed or are awaiting installation.

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Introduction

Ontario Hydro Nuclear has made a commitment to the Atomic Energy Control Board to install stack emissions monitoring for carbon-14 (^{14}C) at all its nuclear generating facilities by the end of 1999.

This paper will:

a) Summarize the reasons behind the decision to implement a ^{14}C monitoring program at this particular time;

b) Briefly outline other ^{14}C related work that is going on or is planned, to complement the monitoring program,

c) Describe the stack sampler selected for installation.

^{14}C is a pure beta emitter with an energy level of 0.156 MeVs (just over 8 times that of tritium) and a half-life of 5,720 years. It is of concern in that it easily becomes airborne as $^{14}CO_2$ in which form it is readily incorporated into the food chain by photosynthesis and thence into the natural carbon cycle.

A consequence of this is that the contribution of ^{14}C to the total calculated dose commitment to the critical group can be quite high, though the dose itself is very small compared to natural background. For example, at Darlington, ^{14}C accounted for 71% of the total infant dose in 1995. Similarly, the contribution to the population collective dose due to ^{14}C from ingesting local produce around the Bruce Nuclear Power Development site in 1995 was 72%.

Production and Fate of ^{14}C in the CANDU System

It is no secret that the CANDU system generates higher levels of ^{14}C than any other reactor type.

Oxygen-17 (^{17}O), naturally occurring but increased by over 50% in the final polishing stages of heavy water enrichment, exists in the CANDU moderator water. Neutron activation of the ^{17}O produces ^{14}C by alpha decay. Production of ^{14}C in OHN's reactors is estimated to range from about 200 to 450 Ci per year (based on an 80% capacity factor), more than 95% of which is generated in the moderator.

What happens to this ^{14}C in the moderator? In CANDU reactors, moderator water is blanketed by a Helium cover gas. One of the functions of this cover gas is to maintain a positive pressure within the calandria so as to minimize air ingress and help maintain moderator water chemistry.

Most of the ^{14}C remains dissolved in the moderator water as carbonate and bicarbonate ions; some, however, will exchange with the cover gas in the form of $^{14}CO_2$, especially during conditions of low moderator pH. The cover gas system includes blowers, recombination units for D2 and O2 produced by radiolysis, and head tanks. Any intentional purging, or leakage from this system, will lead to ^{14}C emissions. It has been estimated that approximately 5% of chronic moderator production is released to the environment in this manner.

Moderator water is circulated through a purification loop containing filters and ion exchange (IX) columns. The main purpose of these IX columns is to remove ionic impurities from the moderator including poisons such as Gadolinium Nitrate, added to the moderator for reactivity control and reactor shutdown.

Carbonate and bicarbonate ions are captured by the IX columns and this is the main removal pathway for ^{14}C. Unfortunately, carbonate/bicarbonate ions are only weakly bound by IX resins and are easily displaced by nitrates. The columns can also saturate on ^{12}C carbonate ions created by, for example, radiolysis of organic matter in the moderator such as resin fines or lubricants from reactivity mechanism drives. This may be one of the explanations for acute releases, especially when coinciding with high cover gas purge rates which may typically occur during station outage maintenance work.

IX resins from the columns are slurried to resin storage tanks in the station via a dedeuteration process to retrieve the heavy water. The result is that the bulk of the ^{14}C ends up in station resin storage tanks awaiting periodic shipment to the Bruce Radwaste Storage Site.

It should be mentioned in passing that there used to be another significant source of ^{14}C - the annulus gas systems at Pickering 'A'. However, the conversion of the annulus gas from N_2 to CO_2 has virtually eliminated this as a ^{14}C source, reducing production by about half. All OHN's annulus gas systems now use CO_2.

Pickering 'A' is the only station that has been performing routine station-wide ^{14}C stack monitoring (in the O_2 form) on an ongoing basis. Since 1990 when the annulus gas changeover was nearly complete, the highest annual emission was in 1995 at 0.05% of the station Derived Emission Limit (DEL), and this was 2 to 3 times higher than the average due to 1 single emissions event that occurred during some outage maintenance work on the moderator system followed by cover gas purging. Non-routine measurements conducted at individual units of other OHN stations (either by OHN or by AECL Chalk River) tend to suggest emission of a similar magnitude.

In past years, OHN has depended on direct environmental measurements of ^{14}C to assess the impact of emissions on dose. Environmental measurements continue to be routinely conducted on milk samples, fish, vegetables and other foodstuffs.

ACRP-14

In 1995, a publication entitled: "ACRP-14, The Management of Carbon-14 in Canadian Nuclear Facilities" was published by the ACRP, an advisory committee of the Atomic Energy Control Board of Canada known as the Advisory Committee on Radiological Protection (ACRP).

Together with the Advisory Committee on Nuclear Safety, the ACRP is one of two senior level scientific committees of independent experts charged with providing the board with independent advice on general practices related to radiation protection (and nuclear safety).

The ACRP was concerned as to whether the practice of ensuring that the dose to a member of a critical group from 1 year's release does not exceed the limit on annual dose to a member of the public would provide adequate protection to members of the public, including future generations, for radionuclides such as ^{14}C which can accumulate in the environment and which can be dispersed, through environmental processes beyond the local region where the critical group is assumed to live.

Consequently, the ACRP established a working group consisting of 5 recognized experts in the field to review the production, release, environmental levels and waste management of ^{14}C arising in CANDU power reactors. The ACRP-14 report was published in July of 1995.

ACRP-14 Report Recommendations

The ACRP-14 report contained a number of recommendations for Ontario Hydro and the other Canadian nuclear utilities concerning ^{14}C, namely:

1) The AECB should require licensees of power reactors and waste management sites to estimate both maximum individual doses and local collective doses from ^{14}C on an annual basis, as part of the ALARA process.

2) The AECB should require power reactor licensees to demonstrate, on an ongoing basis, that releases of ^{14}C are maintained at a small fraction of the DELs.

   Appended to this recommendation was the statement that: "This is best done through mandatory emission monitoring. Environmental monitoring, as currently practised, is useful as an indicator of releases only in the active growing season when the samples are taken. It provides no information regarding emissions during the winter months."

3) The AECB should require power reactor licensees to provide an annual inventory of ^{14}C held within reactor buildings and waste management sites and also to provide information annually on the stability of the ion exchange resins and their continuing ability to retain the ^{14}C in storage.

Response of the AECB

1) ^{14}C Doses

"Licencees currently report annual doses to individuals and annual collective doses to the populations in the areas around Canadian nuclear power plants in their annual summaries and assessments of environmental data. Reporting of collective doses is not an AECB requirement, but AECB staff will consider the need during revision of C-129, The Requirements to Keep All Exposures as Low as Reasonably Achievable."

2) Emissions monitoring

"AECB staff agree with these conclusions. Currently, compliance with DELs for ^{14}C is demonstrated by licensees by either emission or environmental monitoring. So far AECB staff have not required mandatory emission monitoring of ^{14}C but will *initiate* discussions with the power reactor licensees as to the feasibility and benefits of mandatory emission monitoring at all stations."

3) ^{14}C Inventory

"AECB staff will undertake discussions with reactor licensees to obtain information about the inventory and physical condition of the ion exchange resins within the nuclear power stations to ensure doses from ^{14}C emissions are as low as reasonably achievable. The results of these discussions will be used to assess whether or not such information should be required to be submitted."

4) Resin and ^{14}C Stability

"The licensees are currently required to maintain an ongoing inventory of maximum quantities of significant radionuclides when the used resins are moved to the waste management sites. AECB staff will undertake further discussions with the licensees to verify that the stability of the resins is consistent with that assumed in the safety analysis."

Response of OHN

Ontario Hydro replied that the intent of the ACRP's recommendations may well be better addressed by means other than those proposed by the ACRP, and that time was required for an examination of the various options. The Board stated that they agreed with this request.

Because of the many areas of expertise (operating procedures, reactor chemistry, environment, research, etc.) encompassed by the ACRP-14 recommendations, a multidisciplinary team was formed to deal with the issues and formulate a response that would be acceptable to all the generating stations and the radwaste site. The team adopted the following mandate at its first meeting:

"To develop a strategy to demonstrate that ^{14}C is appropriately managed at nuclear stations and the waste management site".

The team was made up of representatives from each station and the waste management site, with expert advisers from OHT and AECL. One aspect that was not included in the team's mandate was ^{14}C in the workplace.

Recommendations of the ^{14}C Team

After considering many options, the team came out with a number of recommendations including the following:

- OHN should implement stack emissions monitoring for $^{14}CO_2$ and organic ^{14}C;
- OHN should perform composite sampling and analysis for waterborne ^{14}C emissions;
- OHN should maintain and report an inventory of ^{14}C arrived at by calculated production rates less measured emission rates;
- The RadWaste Operations Site monitoring program should be expanded to include ^{14}C in storage structures and in the environment;
- OHN should support research into areas related to resin and ^{14}C stability in storage.

All the above recommendations have been, or are being, acted upon. However, because of time constraints, I would like to focus on one area that I am actively involved in – the implementation of stack emissions monitoring for ^{14}C.

The next speaker, Dr Cornett, from AEC Chalk River is going to give a paper following this one on the final recommendation mentioned above - research related to resin and ^{14}C stability in storage.

Emissions Monitoring

The team decided to adopt the recommendation for permanent ^{14}C emission monitoring.

An alternative considered by the team to demonstrating that emissions are low is to demonstrate that retention of the ^{14}C is high. This would require a fairly accurate determination of the ^{14}C inventory in the calandria, IX resin and resin storage tanks, which would involve extensive sampling.

The difficulties of obtaining representative samples of IX resin are considerable. The resin consists of 2 fractions, anion and cation, with the ^{14}C being retained by the anionic fraction. ^{14}C distribution in resin is non-uniform and highly unpredictable. In addition, anion is smaller and less dense than cationic resin and this leads to a striation effect.

Measurements that have been obtained of ^{14}C activity on resin from an IX column have varied by 3 orders of magnitude. Sampling also involves significant implications for occupational dose. The 'demonstrating retention' option was not considered further by the team.

The advantages of emissions monitoring include:

- ^{14}C emissions from reactor operations and resin storage tanks (if any) will be included;
- Chronic and acute ^{14}C emissions will be included;
- Response time would normally be weekly but could be shortened as required (i.e. a measure of control could be introduced);
- Brings the other OHN stations into line with Pickering 'A' (and with Gentilly-2 and Point Lepreau);
- Emissions data should help to indicate where further efforts and expenditures can most effectively be made to reduce ^{14}C emissions further;
- The technology to perform stack monitoring is established and already used by OHN, i.e. minimal development is required.
- Satisfies the ACRP recommendations;
- Emissions data will allow a more accurate ^{14}C inventory calculation to be performed, satisfying another of the ACRP recommendations.

A concept for a stack sampler incorporating the required redundancy was sent out for tender for detailed design and mass production. The successful bidder was required to design, build and supply a total of 17 fully tested stack samplers by the end of 1997.

The samplers have now been delivered to the various OHN locations and are either being installed or awaiting installation.

Stack Samplers

Ontario Hydro has had experience in developing and installing ^{14}C samplers on a small scale in the past. However, on this occasion, as a larger number of samplers was required, it was decided to provide the conceptual design and go out to tender for the detailed design, construction, testing and delivery of the samplers.

In determining which stacks to monitor, the sources of potential ^{14}C emissions have to be considered. The most obvious source is the moderator/cover gas, followed by systems that handle moderator water (e.g. upgraders) and moderator resin storage tanks. As the resin storage tanks are associated with reactor units (Pickering's and Darlington's are unitized, Bruce 'A' tanks vent to Unit 2 and Bruce 'B' to Unit 6) the final number of samplers arrived at was initially 17 (this was prior to the decision to close Bruce 'A').

The Point Lepreau ^{14}C sampler was selected as a prototype as it incorporated a furnace-heated catalytic converter for the conversion of organic forms of carbon and CO thereby providing a measurement of total ^{14}C rather than just CO_2. However, an additional sampling train was incorporated, without a converter, to measure just CO_2.

It should be borne in mind that all OHN station ^{14}C Derived Emission Limits are based on $^{14}CO_2$. As stated in the introduction section, this is due to its rapid incorporation into the food chain via photosynthesis.

The reason for selecting the dual sampling train approach – $^{14}CO_2$ and total ^{14}C – was threefold:

1) In the event that providing total or organic ^{14}C emissions becomes a regulatory requirement at some stage in the future, the means to do so will be already available. The additional cost of providing a catalytic converter at the design stage is trivial compared to attempting to install it as a field retrofit at some time into the operating life of the samplers.

2) Reporting of ^{14}C inventory and of annual additions to it - one of the ACRP recommendations – requires a knowledge of total ^{14}C emissions, or alternatively a demonstration that the non-$^{14}CO_2$ component is insignificant. This information will be provided by having two sampling trains.

3) By utilizing separate components for each sampling train - separate pumps, separate flow controllers, separate alarms, etc, - the two sampling trains remain independent of one another thereby increasing redundancy.

Sampler Requirements

The principle of operation of the samplers was to be the conventional well-tried method of bubbling the dried sampler flow through two absorbant sodium hydroxide solutions in series. At the end of the sampling period – usually 1 week – aliquots of the solution are analyzed for ^{14}C by liquid scintillation counting.

However, there were several provisions that the manufacturer was required to meet. Unlike the Lepreau sampler, it was not acceptable to have the gas washing bottles or bubblers containing the NaOH made from glass or any material easily shattered. At the same time, the bottles should be transparent so that the bubbling in the gas washing bottles could be clearly observed.

Some other requirements were that the 4 bottles per sampling train (2 desiccant and 2 gas washing bottles) should be easily changeable in the field without use of tools or having to lubricate O-rings, etc., and still meet leak-tightness requirements. There was to be absolutely no handling of liquids in the field.

These and various other requirements were incorporated into a Technical Specification which was used in soliciting bids from companies on the bidder's list for the supply of the samplers. BOT Engineering of Campbellville, Ontario, was selected as the successful bidder. BOT has previously supplied a variety of equipment to OHN including radiation survey instruments, instrument power supplies for safety shutdown systems, OHN-designed tritium samplers and IAEA safeguards equipment and monitors.

BOT Engineering 'MS24C' ^{14}C Sampler Details

A prototype sampler was built and tested, and the remainder were completed by the end of last year. The samplers have now been delivered to the stations and are either undergoing or awaiting installation. According to OHN's commitment to the AECB, all the samplers are required to be in operation by the end of next year.

The material selected for the gas washing bottles and the desiccant containers (the 2 are interchangeable) was transparent cast acrylic polymer, unbreakable under normal usage, with high density polyethylene caps, combining excellent resistance to the NaOH solution with long-term clarity. The flow is bubbled through the gas washing bottles via 60 μm frits. Testing has validated the required CO_2 removal efficiency with the exit concentration not rising above 5 ppm over a 1-week sampling period.

The four sampling train bottles (2 desiccant holders and 2 gas washing bottles) are rack-mounted for ease of removal and replacement, with no fittings or quick-connects to undo. Rack and bottles are removed and replaced with caps still attached. The caps do not need to be removed until in the chemistry laboratory, making field spillage of the NaOH very unlikely.

Upon reracking, an eccentric cam presses the spring loaded bottles against the upper chassis providing a seal between the caps and silicone gaskets. The sampler then performs an automatic leak check that takes about 1 minute (if this option is selected) before resuming normal operation (provided that the leak check was successful).

There are no fittings or tubing except for the sampler inlet and outlet connections to the stack and for the oven mounted on top of the sampler.

Pumps: Despite the redundancy provided by having 2 sampling trains, dual pumps per sampling train are provided. The pumps are electromagnetic oscillating arm diaphragm pumps. In the event a problem prevents the flow from being maintained (either pump trouble or a flow blockage for example), the second pump will also start. If the problem clears, the first pump will stop and a local alarm will indicate which pump requires servicing. If the flow can not be maintained with both pumps running, a control room sampler trouble alarm will be generated.

The catalytic converter consists of a platinum-palladium catalyst maintained at $650^{O}C$ by a tube oven mounted above the sampler. This arrangement has demonstrated a conversion efficiency of better than 99%.

It is hoped that the samplers will prove rugged and reliable, as well as being easy for the station operating staff to use in terms of the weekly change-out of the collection solution and desiccant, and from the point of view of routine maintenance and calibration.

Should a high ^{14}C emission ever be anticipated or experienced, (for example opening up the moderator system for maintenance with unchanged resin still in service, or high cover gas purge rates), sampling periods could be reduced from weekly to, for example, daily, on one or both of the sampling trains. The flow rate can also be increased along with the alarm set-points, to increase sensitivity.

Information gained from the analysis of the ^{14}C emissions data, when correlated with station operating parameters such as moderator cover gas purge rates, moderator system maintenance, etc., and with the waterborne emissions data, may help in qualitatively associating such emissions with reactor operations and maintenance activities, or with possible leakage from resin in the station resin storage tanks. This, together with the planned research activities, will be useful in connection with another of the ACRP-14 recommendations concerning the security of ^{14}C held on the ion-exchange resins within the station resin storage tanks.
