

An Approach for Reducing Carbon-14 Stack Emissions via Optimal Use of Ion Exchange Resins at CANDU Plant

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Abstract

Relatively high carbon-14 emissions, which occurred at PHWR Plant during 1998 and 1999, made the site staff to implement several operational improvements: 1) the frequency and volume of the moderator cover gas purging were reduced through increased O₂ additions to the cover gas, 2) the 'old' resin columns were not used during re-start of the reactor from outage, 3) efforts were made to minimize air ingress, 4) the maximum service time of moderator ion-exchange columns were restricted to about 80 days. Through the improvements, the carbon-14 emission from each PHWR reactor returned to the normal levels during the remainder of 1999 and during 2000. We carried out a special surveillance at W-1 and W-3 from September 2001 to August 2002 to properly evaluate ways to optimize the use of moderator ion exchange resins from a C-14 perspective. The surveillance showed that only data that provided an operational marker for deciding when to remove the IX-resin column is an observed increase in the C-14 stack emissions themselves. Also, it is shown that any increase over the rate of 0.4 Ci month⁻¹ for two consecutive weeks may be the indication for an ion-exchange resin column change, especially if the IX-resin column has been in service for more than 80 days.

1. Introduction

A CANDU reactor is a pressurized heavy water reactor (PHWR) where heavy water (D₂O) is used as both moderator and coolant. One of problems that CANDU reactors are experiencing is its high stack emission of C-14. The main reason for this is that the large amount of heavy water is used as moderator.

In 1998, the site staff of PHWR plant installed an equipment at the stacks to monitor the radioactivity of C-14 from the stack because more than 99% of C-14 releases from a CANDU reactor occur as the stack emission of the cover gas in Moderator Cover Gas (MCG) system. Since ¹⁴CO₂ is the dominant species in airborne stack emission from reactor stacks under normal operation conditions, it is common practice to measure C-14 of ¹⁴CO₂ form only to minimize costs. The monitoring of C-14 emission is intended to ensure that the release levels of C-14 comply with regulatory limits.

During 1998 and 1999, relatively high C-14 emission rates were observed at PHWR plant. So we carried out the project to investigate the C-14 stack emission at PHWR plant from July 2000 to August 2002. This paper describes the results of the project with emphasis given to the optimization of the use of moderator ion IX resins to maintain low C-14 stack release with less volume of moderator IX resins sent to waste at PHWR plant.

2. Carbon-14 Source and Pathways to Emission

The dominant reactions leading to C-14 production in CANDU reactors are the (n,α) reaction on O-17, the (n,p) reaction on N-17, and (n,γ) reactions on C-13. The main C-14 production in a CANDU reactor comes from i) moderator system, ii) primary heat transport system, iii) annulus gas system, and iv) fuel elements.

Among the four systems, the moderator system is the largest contributor to C-14 production (94.8 % of the total C-14 production) because a large volume of heavy water is exposed to high thermal-neutron fluxes of the calandria where O-17 of heavy water is converted to C-14 by the $^{17}\text{O}(n,\alpha)^{14}\text{C}$ reaction. C-14 that is produced in the moderator system is present as a combination of $\text{D}_2^{14}\text{CO}_3/\text{D}^{14}\text{CO}_3/^{14}\text{CO}_3^{2-}$, among which the bicarbonate form is predominant because of moderator $\text{pH}_a \gg 7.0$. The anions ($\text{D}^{14}\text{CO}_3^-$ and $^{14}\text{CO}_3^{2-}$) are continuously removed on a mixed bed of strong-anion and strong-cation exchange resins in the moderator purification system, and end up with C-14 inventory. The amount of the C-14 inventory in the resin is about 93.3 % of the total C-14 production. On the other hand, C-14 whose amount corresponds to about 1.5 % of the total C-14 production is released to the moderator cover gas via equilibrium of $\text{D}_2^{14}\text{CO}_3$ with $^{14}\text{CO}_2$ in the cover gas phase at the water/cover gas interfaces under normal conditions. Frequent purging and venting of the moderator cover gas using make-up helium, primarily to control D_2 and N_2 in the cover gas system, is a main pathway leading to high releases of $^{14}\text{CO}_2$ in the gaseous emissions.

The second contributor to C-14 emission is the annulus gas system, but the production is only 0.2% of the total C-14 production. The primary heat transport system, with heavy water as coolant, also produces C-14. Its contribution is about 1.6% of the total C-14 produced by a CANDU 6 reactor. It has been recognized that the bulk of the C-14 in the primary heat transport system, present as carbonate ions at the prevailing pH_a of 10.2 to 10.8, is removed by the primary coolant purification system at removal efficiency of nearly 100%. Consequently, the primary heat transport system contribution to gaseous C-14 emission as $^{14}\text{CO}_2$ may be assumed to be negligible. The C-14 content in the CANDU fuel has been estimated to be represents 3.4% of the total C-14 production. C-14 release as a result of fuel failure is another pathway for C-14 emissions. It is estimated that for a fuel failure rate of 0.003%, C-14 released to the stack is insignificant.

In summary, under normal operating conditions 1.7% of the total C-14 produced in a CANDU reactor (1.5% from the moderator cover gas and 0.2% from the annulus gas system) is released to the reactor stack as gaseous emissions. On the other hand, 98.3% of the total C-14 production (94.9% retained by the liquid purification ion-exchange systems and 3.4% in the spent fuel) remains as inventory. The relations for productions and releases of C-14 in a CANDU reactor are presented schematically in Fig.1

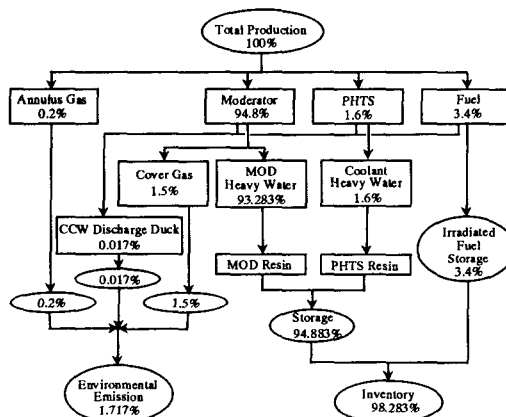


Fig. 1 Schematic for the production and emission of C-14 in a CANDU reactor

3. Review of PHWR Operating Chemistry and Carbon-14 Stack Emissions

3.1 Review of Data Received from PHWR Prior to 2000 December

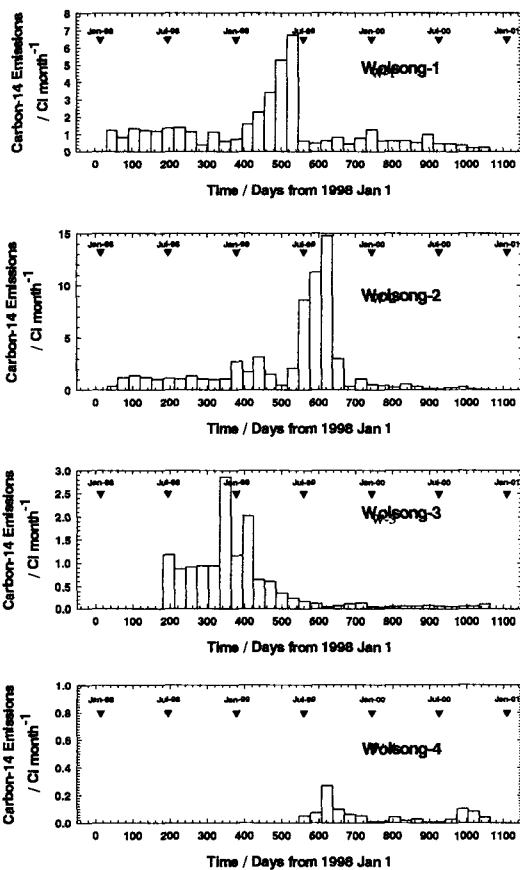


Fig. 2 C-14 stack emissions from PHWR reactors. Note different emission scale for each reactor.

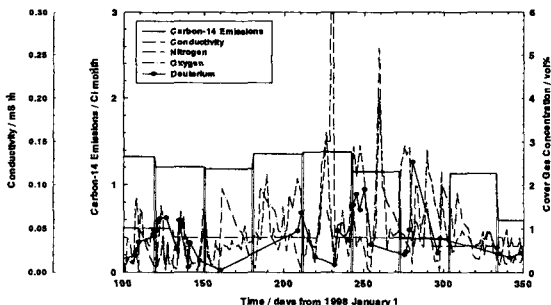


Fig. 3 Correlation of W-1 Unit C-14 emissions with chemistry data for 1998 April to December.

The C-14 stack emissions from the four PHWR reactors for the period 1998 January to 2000 December are summarized in Fig. 2. In 1999, the C-14 emissions from the plant site increased over the 1998 values, with Units 1 and 2 having values >5 Ci month⁻¹. After this excursion period, the C-14 emissions from all four reactors have been consistently low with values at the end of the review period at W-1 Unit $<$ about 1.0 Ci month⁻¹, W-2 Unit $<$ about 0.5 Ci month⁻¹, W-3 Unit $<$ about 0.1 Ci month⁻¹, and W-4 Unit $<$ about 0.1 Ci month⁻¹. These C-14 emission values for PHWR plant are consistent with, or lower than, those concurrently being reported from the Canadian Pt. Lepreau (0.3-1.0 Ci month⁻¹) and Gentilly-2 (0.3-0.5 month⁻¹) CANDU-6 NPPs.

(1) W-1 Unit

Prior to 1999 January, the C-14 emissions from W-1 Unit were slightly above about 1 Ci month⁻¹. Over the next six months, there was a general rise in emissions peaking after the start-up, in 1999 May, at near 7 Ci month⁻¹. Since then, the C-14 emissions decreased significantly and were generally lower than about 1 Ci month⁻¹. Detailed moderator chemistry data covers the beginning of 1998 April (day 90 on graphs) to 2000 March (day 814 on graphs). Some observations are made on this chemistry data.

First, over the period 1998 August-September in Fig. 3, based on the elevated nitrogen and deuterium concentrations in the cover gas and the large conductivity spike (day about 230), there appears to have been a significant chemistry perturbation with no impact on C-14 releases. This implies that, despite these

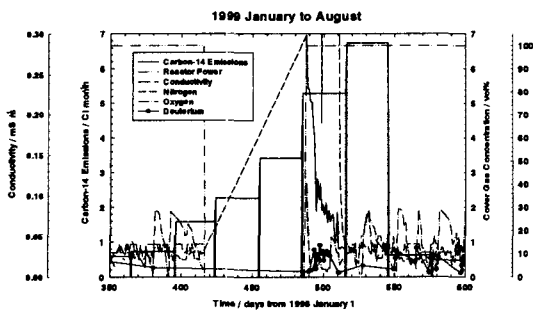


Fig. 4 Correlation of W-1 Unit C-14 emissions with chemistry data for 1998 January to August.

guaranteed shutdown state. It appears that the cover gas system may have been opened for maintenance during this period, judging by the high nitrogen concentration at the end of the shutdown (No chemistry data during the shutdown was supplied). These high C-14 releases may have been caused by purging associated with the maintenance activities. This implies that the C-14 in the bulk moderator water must have been elevated before the shutdown.

Thirdly, the high release rates immediately following the start-up are likely a direct consequence of re-using 'used' IX resin columns for the removal of the gadolinium nitrate: this practice at the site was discontinued after 1999. The $D_2^{14}CO_3 / D^{14}CO_3^-$ displaced from the 'used' resin will have equilibrated with the cover gas, and then the $^{14}CO_2$ will be released up the stack as a result of the venting/purging activities to establish cover gas chemistry and pressure during and after the start-up.

(2) W-2 Unit

Fig. 2 indicates that the pattern of C-14 stack emissions at W-2 Unit is similar to that of W-1 Unit. The stack emissions for C-14 were 1 to 2 Ci month⁻¹ in 1998 but rose in early 1999. Although the emission rates over the 1999 May outage were low, following the start-up in 1999 June, they rose to reach a maximum of 14-15 Ci month⁻¹ in 1999 September. After this peak emission, the values decreased below 1 Ci month⁻¹. A review was undertaken of the moderator chemistry data supplied for the period 1998 July (day 170) to 2000 August 9 (day 974). Some of this chemistry data is shown in Fig. 5. Listed below are some of our observations based on a review of this chemistry data.

First, for the period of time covered in Fig. 5, it appears that difficulties were experienced in controlling the chemistry. The values of conductivity of the moderator water, both before and after the moderator purification system, were elevated compared to normal operating levels of <0.05 mS/m. The deuterium (D_2) concentrations in the cover gas were also elevated. Normally deuterium concentrations are below 0.2 vol.%, and are generally undetectable.

Secondly, it appears that one purification column was in service in 1999 June (about day 525 in Fig. 5)

chemistry perturbations, C-14 was largely immobilised within the purification system over this period of time.

Secondly, around the outage 1999 February-May (around day 450, see Fig. 4), the C-14 stack emissions rose. This is unusual because the purification system would have been isolated from the main moderator system, as a requirement of the over-poisoned

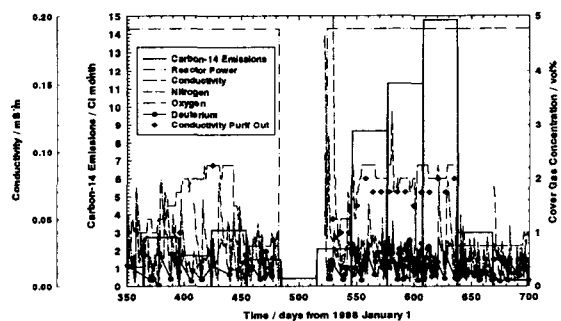


Fig. 5 Correlation of W-2 Unit C-14 emissions with chemistry data for 1998 Dec to 1999 Dec.

for the start-up after 1999 May outage. This column was removed from service in 1999 September and a fresh column was placed in service. The C-14 emissions that had peaked in 1999 September (day about 625), dropped to much lower values for the next month 1999 October, and then continued to drop further with time (see Fig. 2). Apparently the column had seen previous service before the 1999 May outage and consequently it released significant amounts of C-14 back into the moderator system following the

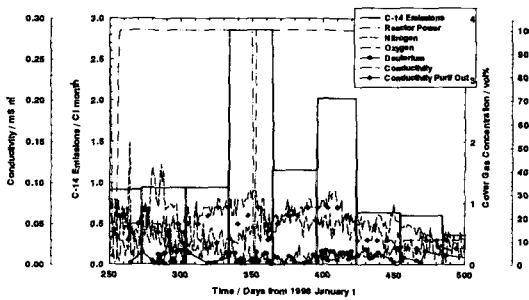


Fig. 7 Correlation of W-3 Unit C-14 emissions with chemistry data for 1998 September to 1999 May.

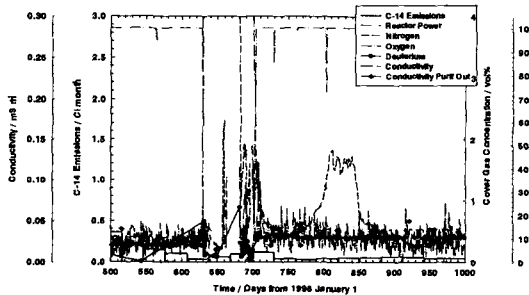


Fig. 6 Correlation of W-3 Unit C-14 emissions with chemistry data for 1999 May to 2000 Sept

conductivity were low, and deuterium was only detected in the cover gas prior to the start-up in 1999 December (day about 700 in Fig.7).

(4) W-4 Unit

The information in Fig. 8 essentially covers the operating life of W-4 Unit up until the end of 2000 September. As can be seen, following a small (about 0.3 Ci month⁻¹) spike in C-14 emissions initially, the emissions levels have been very low, below 0.1 Ci month⁻¹.

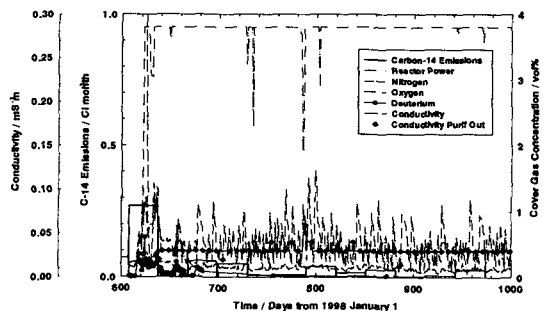


Fig. 8 Correlation of W-4 Unit C-14 emissions with chemistry data for 1999 Sept. to 2000 Oct.

3.2 Recommended Systematic Measurement Program to Generate Carbon Chemistry

In September 2001 we recommended that a period of special surveillance at one unit from each Plant Site (e.g., W-1 Unit and W-3 Unit) should be undertaken. During this period, we recommended a concentrated monitoring program involving i) measurement of C-14 stack emissions over one week (or

1999 June start-up.

(3) W-3 Unit

W-3 Unit began operation around 1998 March. In the initial operating period the C-14 emissions ranged from 1 to 3 Ci month⁻¹ until about 1999 July when the C-14 stack emissions dropped to very low values about 0.1 Ci month⁻¹ (Fig. 2). A review of the supplied moderator chemistry data suggests that up until 1999 May (day 500 in Fig.6), there were chemistry control difficulties as the values of conductivity, both before and after purification, were slightly elevated. As well, during this time period, deuterium was also detected in the cover gas. Fig. 7 summarizes the C-14 emissions and chemistry from 1999 May until 2000 September. As can be seen, the C-14 stack emissions were very low, the values of

shorter) periods, ii) measurement of Total Organic Carbon (TOC)/Total Inorganic Carbon (TIC) levels in the bulk moderator water and in the moderator purification return flow at least once a week, iii) measurement of C-14 levels in the bulk moderator water and in the moderator purification return flow at least once a week, iv) detailed chemistry measurements as currently done at PHWR plant, v) measurement of the dissolved deuterium concentration in the bulk moderator, vi) measurement of deuterium peroxide (D_2O_2) on a routine basis of about 1 week frequency, vii) detailed records of the purging, venting of the cover gas and any other moderator cover gas maintenance, and viii) detailed records of moderator purification IX column service.

3.3 Review of Data Collected for the Period 2001 September to 2002 August

The staff of PHWR plant supplied us with data from the 2001/2002 surveillance program that was conducted at W-2 & -3 Units. In each case, chemistry data from only one IX-column change was provided. The most extensive information was obtained for W-3 Unit. The 2001/2002 C-14 stack emissions for W-2 & -3 Units are given in Fig. 9; the time when the IX-resin columns were changed are also marked on the figure. Both W-2 & -3 Units operated continuously through this monitoring period.

(1) W-2 Unit

For W-2 Unit, the C-14 stack emissions (measured over a two week period) were consistently low (< 0.5 Ci month⁻¹) over the about 210 day period of time during which data was provided (Fig. 9); this is consistent with the emissions observed after 2000 January (Fig. 2). From Fig. 9, it

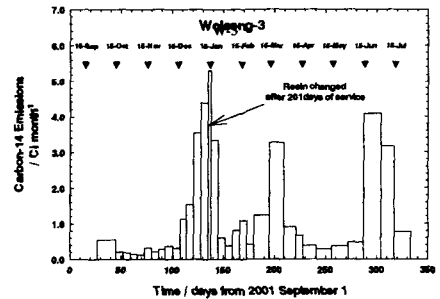
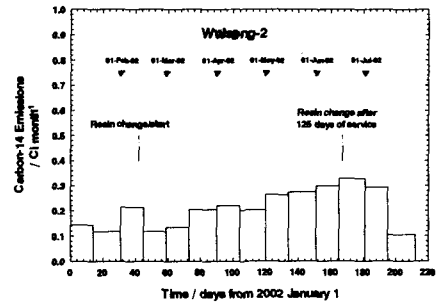


Fig. 9 C-14 stack emissions for W-2 & -3 Units.

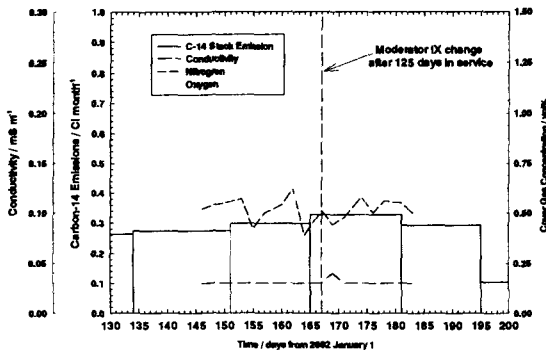


Fig. 10 Correlation of the C-14 emissions with cover gas concentrations and conductivity of moderator water in the calandria at W-2 Unit.

appears that the C-14 stack emissions for W-2 Unit are reduced after the first recorded column change at day 44 and then gradually increase until the resin is replaced again at 125 days later at day 165.

Chemistry data was supplied for the about 40 day period of time (2002 May 2 to July 3) around the IX-resin change as shown in Figs 10 and 11. Over this time period, no deuterium was observed in the moderator cover gas. This is due to the prudent practice of maintaining an excess of oxygen in the cover gas (Fig. 10) as mentioned before. This significantly reduced the number of helium purges of the cover gas system,

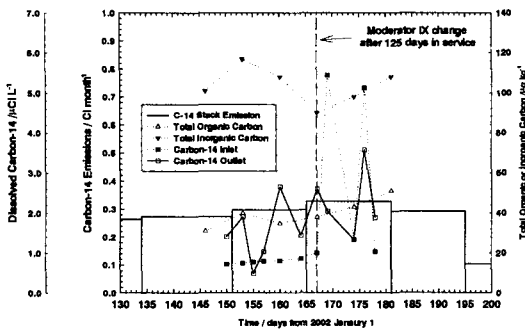


Fig. 11 Correlation of C-14 emissions with C-14, TIC and TOC concentrations in the moderator water in the calandria at W-2 Unit

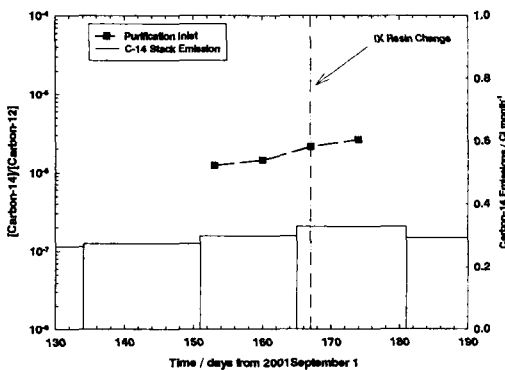


Fig. 12. Ratio of the concentration of C-14 to C-12 in the moderator water in the calandria for W-2 Unit.

μCiL^{-1} . The mole ratio of C-14 to C-12 in the moderator water had a value $1-3 \times 10^{-6}$ as shown in Fig. 12.

(2) W-3 Unit

For W-3 Unit, the C-14 stack emissions, for almost a year following 2001 September 1st, are shown in Fig. 9. Up to about day 100, the C-14 emission rate was low ($<0.4 \text{ Ci month}^{-1}$) and were comparable to the emission rates shown in Fig. 2 for the time period after 1999 July. As shown in Fig. 9, the rate of C-14 emissions increased significantly after day about 110 rising (mid 2002 December) to about 5 Ci month^{-1} which is higher than any of the C-14 emission rates at W-3 Unit in Fig. 2. It was reported that the IX-resin column that had been in-service to 201 days was replaced on day 135 (2002 January 14) as indicated in Fig. 9. Following the column replacement, the C-14 stack emissions from W-3 Unit decreased to a rate of $0.5-1.0 \text{ Ci month}^{-1}$ but then peaked to near $3-4 \text{ Ci month}^{-1}$ near day 200 and 300.

The site staff noted that difficulties were experienced with the Shut Down System-2 that required purges of the moderator cover gas 12 times between day 152 and 154; these purges did not have any significant impact on the C-14 stack emissions. The absence of any purging between day 100 to day 145 (Fig. 9) strongly suggests that the loss of C-14 from the moderator system to the stack occurred via leakage of moderator cover gas. This could be through the vent or purge valves or even through other areas such as the reactivity deck mechanism seals.

Detailed moderator chemistry information supplied from W-3 Unit for the period up to about day 175.

thereby reducing the transport of C-14 from the moderator gas to the stack. Fig. 11 provides data on the Total Organic Carbon (TOC) and the Total Inorganic Carbon (TIC) in the moderator. The concentrations of TOC and TIC remained relatively constant through the resin change period with TOC values in the $40-60 \text{ mg kg}^{-1}$ range and TIC in the $100-120 \text{ mg kg}^{-1}$ range.

The concentrations of dissolved C-14 in the moderator system and in the water leaving the purification were supplied (Fig. 11). Prior to the change of the resin after 125 days of resin service, the concentration of the dissolved C-14 entering the purification ($0.5-1.0 \mu\text{Ci L}^{-1}$) (i.e., the calandria concentration) was less than that exiting the purification system (about $1-4 \mu\text{Ci L}^{-1}$). Following the change of the IX-resin column, the dissolved C-14 concentration after purification remained unchanged while that before purification fluctuated between 1 and 6

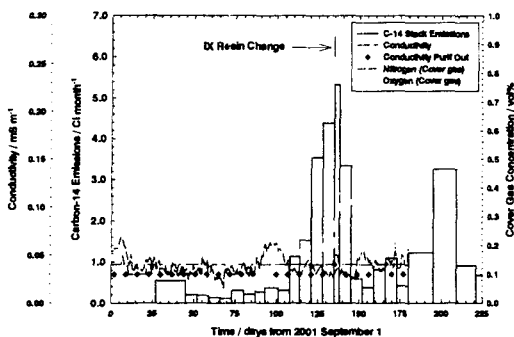


Fig. 13 Correlation of the C-14 emissions with moderator cover gas concentrations and with conductivity of the water in the calandria at W-2 Unit.

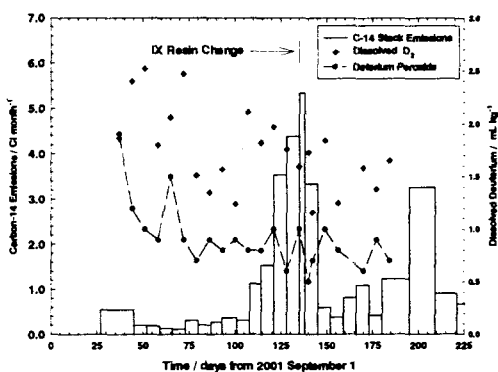


Fig. 14 Correlation of the C-14 emissions with moderator cover gas concentrations and with conductivity of the water in the calandria at W-2 Unit.

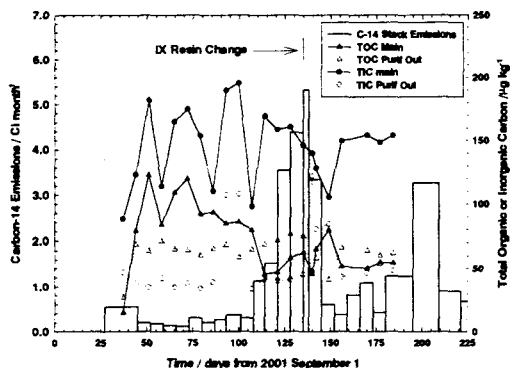


Fig. 15 Correlation of C-14 emissions with the moderator TIC/TOC concentrations at W-3 Unit.

From Fig. 13, it can be seen that the oxygen in the cover gas at W-3 Unit was maintained at a level so that no deuterium was observed, and the nitrogen concentrations indicated that no significant air ingress was occurring. The conductivity of the water, both in the moderator and at the purification system outlet, was consistently $<0.05 \text{ mS m}^{-1}$, which indicates that the good water purity was being maintained and thereby minimizing the radiolytic production of deuterium and oxygen. The dissolved deuterium and the deuterium peroxide concentration levels (Fig. 14) are consistent with values measured at other CANDU stations. None of the chemistry data in Figs 13 and 14 show any impact of the IX-resin column change at day 135 (after about 201 days of service).

For W-3 Unit, data was supplied on the concentration of TIC, TOC and dissolved C-14 at both the inlet and exit of the purification system (Figs 15 and 16). For TIC (Fig. 15), the concentration of 100-200 mg kg^{-1} was comparable to the levels observed for W-2 Unit (Fig. 11). The concentration of TIC at the outlet of purification was always less than that at the inlet, i.e., the IX-resin column was always removing TIC from the moderator water. The concentration of TOC in the main moderator water at W-3 Unit was also similar to that seen in W-2 Unit. The TOC concentration in the main moderator water decreased down to about 50 mg kg^{-1} until day about 115 and then remained constant through the IX-column

change at day 135. The TOC concentrations in the water exiting the purification system remained essentially constant over the whole reporting period (Fig. 15). Unlike the observations at W-2 Unit, the concentration of dissolved C-14 entering the W-3 Unit moderator purification system was always higher than that exiting the system, with the exception of the

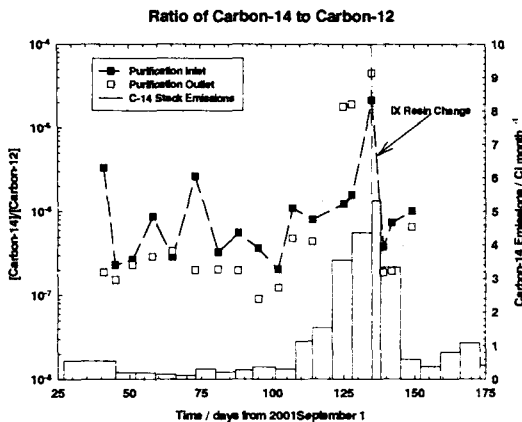


Fig. 16 Ratio of the concentration of C-14 to C-12 in the moderator water at W-3 Unit.

the dissolved C-14 concentration in the moderator up to $27 \mu\text{Ci kg}^{-1}$ from the very low concentrations of about $0.5 \mu\text{Ci kg}^{-1}$ prior to the excursions. Replacement of the IX-resin column had the immediate effect of returning the dissolved C-14 concentrations in the moderator back to the very low levels before the excursion.

The mole ratio of C-14 to C-12 in the circulating moderator water and that exiting from the purification system is shown in Fig. 17. While the data is somewhat scattered, the ratio for the main moderator water in W-3 Unit tended to be less than that observed for W-2 Unit (Fig. 12) with the

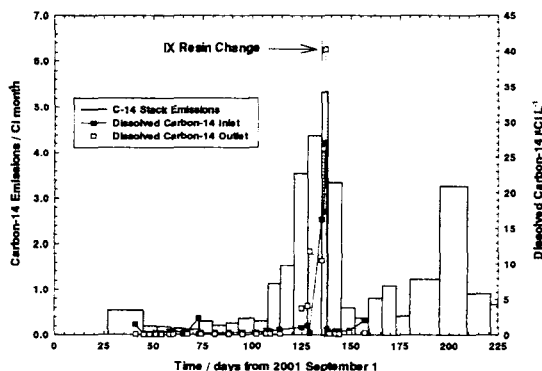


Fig. 17 Correlation of C-14 emissions with C-14 concentrations in the moderator water at W-3.

exception of the ratios calculated during the C-14 excursion. For water leaving the purification system (Fig. 17), the ratio tended to be $<2 \times 10^{-7}$ until the excursion began and then it increased by two orders of magnitude before returning to the original levels immediately after the IX-resin column was replaced in W-3 Unit. The TIC/TOC concentrations reported from the grab samples of the moderator did not reveal any upward trend before the IX-column was replaced.

time period day 115 to day 130 when the peak C-14 stack emissions occurred at W-3 Unit (Fig. 16). Outside the period from day 115 to day 130, the concentration of C-14 in the moderator water at W-3 Unit was less than that observed in W-2 Unit. During the time of the peak C-14 stack emissions from W-3 Unit, up to the point when the IX-column was changed, the dissolved C-14 concentrations at the exit of the purification system were always in excess of the concentration in the moderator. This drove

4. Overall Discussion/Evaluation of Plnat Data

There was a remarkable reduction in the C-14 emissions at the plant site during 2000 (see Fig. 2) and several factors have contributed to this reduction. One of the factors was the procedure that the maximum service time of acid-form mixed-bed IX resin in the purification columns was restricted to about 80 days to ensure that the weakly absorbing bicarbonate/carbonate anion was not displaced off the resin by other competing anions such as nitrate ions. This also minimizes the in-service peroxide degradation of the resin and the subsequent over loading of the IX column with C-12 carbonate/bicarbonate ions. The choice

of changing out the IX resin columns of the moderator purification system after about 80 days was based on practice which was initiated in the mid 1990's at Pt. Lepreau and Gentilly-2 NPPs which resulted in low C-14 stack emissions. The implications of this practice are that the moderator purification IX columns may be removed from service prematurely, leading to an increased production of radioactive IX resin waste. Therefore, for optimal use of the moderator resins from a C-14 emissions point of view, it is needed to estimate as exactly as possible the exhausting time of the resins with respect to C-14. The estimation can be made via chemical modeling and/or continuous (preferably on-line) monitoring of the chemical species in the moderator system that are directly involved in the C-14 releases. Only if the exhausting time is estimated, we may be able to remove moderator purification IX columns from service with a minimum production of resin wastes.

Furthermore, columns that had seen previous general purification service were no longer being used for the removal of gadolinium nitrate from the moderator during and following reactor start-up. It had been common practice at a number of CANDU sites to re-use IX columns, which had already seen normal operation service, for gadolinium nitrate removal at reactor start-up, as these columns were not "spent" as far as removal of gadolinium ions and nitrate ions were concerned. However, the IX columns were probably "spent" or close to being "spent" as far as carbonate/bicarbonate ions were concerned (both ^{12}C and ^{14}C forms). During the procedure to remove gadolinium nitrate at reactor start-up, the more strongly absorbing nitrate anions displace the carbonate/bicarbonate ions back into the moderator system.

At the PHWR plant, as a further measure to reduce releases from the moderator cover gas system, oxygen addition to the cover gas was also carried out to ensure that there is a stoichiometric excess of oxygen over deuterium. It should be noted that an oxygen concentration is now maintained in the moderator cover gas system at the plant site, so there is always a stoichiometric excess over deuterium. This allows for more efficient use of the catalytic recombiner to convert deuterium into heavy water, which has significantly reduced the frequency of purges needed to keep the cover gas deuterium concentration within specifications.

The IX-column in the W-3 Unit moderator purification system was reported to have been changed out after 201 days of service. The stack C-14 emissions over the last about 175 days of the IX-resin service life indicate that the emissions were acceptably low until about 25 days before the column was replaced. Of the moderator chemistry data available, the only chemistry parameter, which indicated that the C-14 stack emissions were going to increase and that the IX-column should be removed from service and replaced by a fresh column, was the increase in the C-14 to C-12 ratio for the purification outlet. However, this correlation could not be observed at W-2 Unit. Thus, it seems that the only data that provided an operational marker for deciding when to remove the IX-resin column is an observed increase in the C-14 stack emissions themselves. Furthermore, any increase over the rate of 0.4Ci month^{-1} for two consecutive weeks may be the indication for an IX-resin column change, especially if the IX-resin column has been in service for more than 80 days. For this, it is needed that the stack emissions continue to be measured on a weekly basis. This recommendation is predicated on there being no other source of higher emissions, such as excessive moderator cover gas purging or air ingresses, as we stated earlier. The data related to the concentrations of C-14 dissolved in the moderator did behave as expected around the stack emission peak

(Fig. 16). As the emission episode developed the C-14 levels in the moderator and at the exit of the purification system all significantly increased, indicating the moderator purification resin is no longer removing C-14 from solution. As well, the review of the special surveillance that were conducted at W-2 & -3 Units suggests that the moderator IX resins can probably be left in service for at least 100 days, provided that there have been no chemical upset events such as: i) air ingress into the moderator cover gas that may produce nitric acid in the moderator water; ii) excess use of gadolinium nitrate as reactivity shim during operation. The data we obtained from W-3 Unit (Fig. 15) revealed no significant change in the concentration levels of either TIC or TOC in the moderator system as the C-14 levels increased in the stack emissions.

5. Conclusions

The evolution of the moderator chemistry practices at PHWR plant has lead to a significant decrease in the C-14 stack emissions from 1999. These low C-14 emissions have been achieved through: i) changing out the moderator purification IX-resin column after about 80 days of service; 2) discontinuation of the practice of re-using IX-resin columns, which have seen previous service, for removing the gadolinium nitrate from the moderator water at start-up; iii) maintaining an excess of oxygen in the moderator cover gas to ensure the complete recombination of deuterium gas; iv) reducing the frequency of purges required to reduce the deuterium concentration of the moderator cover gas.

An evaluation of the moderator chemistry data we received from W-2 & -3 Units for 2001/2002 suggests that practices of changing the IX-resin column after 80 days may be extended slightly while still maintaining low C-14 emissions from the stack. The data we have received suggests that from a C-14 emissions perspective, the resin change out criterion can be based on weekly determinations of the stack C-14 emissions at PHWR plant, for instance if there is an increase in the recorded stack C-14 emissions ($>0.4 \text{ Ci month}^{-1}$) for two weeks in a row. The exact length of time for a resin column to be left in service may depend on the use of gadolinium nitrate for reactor shim, the rate of air ingress, and conductivity control.

Furthermore, there may be three approaches to minimize releases of $^{14}\text{CO}_2$ to the stack: i) immobilize the C-14 as carbonate/bicarbonate on the moderator purification IX resins; ii) minimize purging, venting and leakage of the moderator cover gas system, iii) use a scrubber to remove the $^{14}\text{CO}_2$ from either the moderator cover gas loop or from the purged gas flow that is released to the stack.