

CARBON-14 CHEMISTRY IN CANDU MODERATOR SYSTEM

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ABSTRACT

About 95% of the ^{14}C generated in CANDU reactors is produced in the heavy water moderator by neutron activation of the ^{17}O of the heavy water molecules. Most of this radioisotope, present as ^{14}C bicarbonate, is removed by ion exchange. If the ion exchange column is 100% efficient in the removal of ^{14}C , then a small predictable concentration of ^{14}C is expected in the moderator water and the helium-filled cover gas. The cover gas is in contact with the moderator water, where ^{14}C gaseous exchange occurs. Airborne release of ^{14}C takes place through venting and leakage of the cover gas.

Airborne releases of ^{14}C from stations are very low, much below the emission limits, but releases higher than expected have been observed from several CANDU reactors. Based on laboratory simulations, station data and other reactor information, the cause of this was related to the following sequence:

- deuterium peroxide, produced in-core, oxidizes and depolymerizes the resins;
- resin fragments released from the column are converted to inactive bicarbonate in-core;
- this additional bicarbonate saturates the column resulting in premature ^{14}C accumulation in-core.

Changes in awareness of the problem, resin management and other reactor operation, particularly related to the moderator, resulted in a reduction in ^{14}C emissions by a factor of approximately 6 from one CANDU reactor.

INTRODUCTION

Today's nuclear power plant designs, including CANDU, consistently exhibit low routine radioactivity emissions to the environment. Doses to the local population are a small fraction of regulatory limits, and represent a negligible health impact. Despite this, it is appropriate for plant operators and designers to seek efficient ways to reduce routine emissions as part of a continuous improvement process. This is consistent with the ALARA philosophy, and represents an application of safety culture in the nuclear community.

Recent work has led to a reduction of routine ^{14}C emissions at one CANDU station (Gentilly). A thorough survey of moderator ion exchange column operating practices at domestic CANDU stations has led to the understanding of the factors controlling the levels of ^{14}C in reactors [Torok et al, 1998; 1999a]. Following this, a carefully planned ion-exchange resin replacement strategy has resulted in significant reductions in emissions of ^{14}C at Gentilly. Recommendations on design and operations have now been developed to the point where specific changes and quantitative benefits can be defined. This approach can be applied to other CANDU stations.

CARBON-14 SOURCES AND SPECIATION

Approximately 95% of the ^{14}C produced in CANDU reactors originates from the moderator system by neutron absorption in the ^{17}O present in heavy water. Carbon-14 is present in the moderator mostly as $^{14}\text{CO}_2$ (gaseous form) in the cover gas, and $\text{D}^{14}\text{CO}_3^-$ (dissolved bicarbonate) in the moderator heavy water. Control of ^{14}C -bicarbonate levels in the moderator is done with an ion-exchange purification loop. The moderator water is in dynamic balance with the cover-gas circuit, which allows equilibration and exchange between gaseous $^{14}\text{CO}_2$ and dissolved $\text{D}^{14}\text{CO}_3^-$. Emissions of ^{14}C from reactors occur through venting or leakage of the moderator cover gas. Accordingly, the $^{14}\text{CO}_2$ concentration in the cover gas depends on the moderator chemistry, which, in turn, is controlled by the performance of the ion-exchange columns in the purification circuit.

RELEASE MECHANISM

A mass balance chemical equilibrium model was developed to predict the concentration of ^{14}C -bicarbonate and $^{14}\text{CO}_2$ in the moderator-water/ion-exchange resin/cover-gas system. Bicarbonate is the least strongly held of the anions removed by the ion-exchange column, and accordingly, it is released from a column that is close to saturation. If the ion-exchange column is replaced immediately after bicarbonate breakthrough is detected, the moderator water ^{14}C concentration should be maintained at a predictable steady-state value.

A review of available station historical measurements (mostly Bruce and Pickering) revealed that, prior to 1987, the measured ^{14}C of moderator water or cover gas agreed with calculations [Torok et al., 1999a]. This indicated that the ion-exchange columns were effectively controlling this nuclide, or they were not saturated. After this period, higher concentrations of ^{14}C than those expected have been measured. The elevated ^{14}C concentrations suggested that the anion-exchange resin was saturated during at least a portion of its service time.

A potential explanation suggested that polymer fragments, originating from resin debris and impurities in the resin and resin degradation products were carried into the moderator and converted to bicarbonate in the reactor core by the intense radiation. This *inactive* bicarbonate was then transported to the ion-exchange column, resulting in the premature saturation of the

ion-exchange resins. A resin prematurely saturated in this fashion has a diminished ability to remove ^{14}C .

The major factor in the reduction of the long-term capability of the ion exchange columns to remove ^{14}C is the degradation of the resin. Deuterium peroxide, generated in the reactor as a result of the radiolysis of heavy water, was identified as the main cause of resin degradation. Deuterium peroxide oxidizes the ion-exchange resin, which results in the depolymerization of the styrene-divinylbenzene copolymer structure of the cation-exchange resins. Degradation of ion exchange resins due to the action of peroxide was also identified in the Fugen reactor (Japan), which has a configuration and water chemistry conditions very similar to the CANDU moderator [Kitabata and Sakurai, 1986].

A comprehensive literature review indicated that the most important factors that affect the long-term resin degradation and the release of resin fragments are [Torok et al., 1999a; 1999b]:

- the degree of crosslinking of the ion-exchange resins with higher crosslinking favoring higher oxidation resistance; and
- the presence of oxidation catalysts, such as iron exchanged on the resins.

These factors were found to have a dominant affect on resin stability which impacts ^{14}C emissions, in a reactor where resin management is optimal. Carbon-14 excursions that are not necessarily related to the above can occur under non-optimal operations. (For example, there is at least one known occurrence of a saturated column, still in service, which was used with low pH moderator, and this eventually led to a ^{14}C excursion from this specific station.)

The gel-type resins commonly used are made of polystyrene-divinylbenzene chains. During resin manufacture, a nominal amount of divinylbenzene is added to provide links between the chains, or cross-links. The higher the degree of cross-linking, the more stable the resin is, structurally and chemically. The resistance to oxidation of the resin is directly related to the degree of cross-linking, as more electrons are needed to break the higher number of cross-links.

The resin degradation mechanism constitutes the backbone of the conceptual model that helped diagnose the higher-than-anticipated ^{14}C levels in CANDU reactors. Identifying the key element that affected resin degradation further refined the model: iron, acting as a catalyst for the peroxide-induced degradation of the polymer backbone of the resin. The mobilization of iron is possible under the acidic conditions that prevail in the moderator during shut-down, when the pH is intentionally low to keep gadolinium in solution, and during nitrogen ingress, when nitric acid is produced by radiolysis. The low pH promotes the dissolution of iron from system surfaces. The dissolved iron is then transported to the ion exchange column, where the cation exchange resin removes it. The presence of iron on resins is supported by analysis of Bruce A moderator resins [Moir et al., 1993; 1994].

SUPPORTING EXPERIMENTAL EVIDENCE

Supporting evidence was obtained in laboratory experiments simulating service conditions in the moderator ion-exchange columns: de-ionized water was recirculated through ion-exchange columns where the column temperature, the linear flow velocity, and the peroxide concentrations were matched to reactor conditions. Two types of ion-exchange resins, IRN-150 (manufactured by Rohm and Haas) and NRW-37 (manufactured by Purolite), currently used in reactors, were subjected to simulated reactor service conditions for four months. Identical ion-exchange columns were used as a control using oxygen as an oxidant, instead of peroxide.

A few experiments were also performed at elevated temperatures. These experiments confirmed that extensive deterioration of the resin was due to the presence of hydrogen peroxide at the 2- to 3-ppm concentration levels found in reactors. The presence of catalysts (Fe, etc.), pre-loaded on the resins before exposure to the peroxide solution, resulted in faster resin degradation, whereas the virgin resins (i.e., not pre-loaded with metals) showed no significant damage. The experiments showed that the cationic resins of the mixed bed were the most severely damaged. In all of the comparisons, IRN-150 was slightly less affected by the oxidation treatment than NRW-37. Elevated temperatures increased the rate of the degradation process.

RESIN SATURATION WITHOUT PEROXIDE-INDUCED DEGRADATION

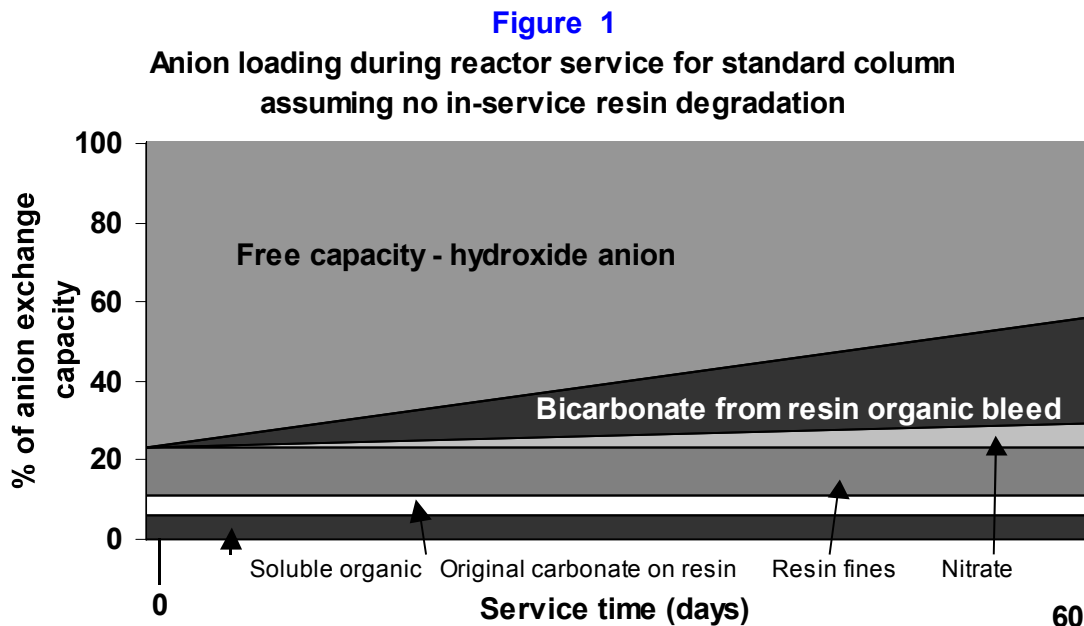
Some processes that consume the anion exchange capacity, and hence contributing to the saturation of the anion exchange resin, are independent of the oxidative degradation of the ion exchange column. Many of these processes that are responsible of anion exchange site consumption depend on resin quality:

- Resin debris released from the ion exchange resin in the form of:
 - resin fines (limited by resin specification);
 - soluble resin fragments, released during the first few hours of service;
 - soluble organic resin fragments, gradually released during reactor service;All of the debris from the above sources is subsequently converted to carbonate in the moderator, and then removed by ion exchange.
- Carbonate in as-received resin. During the manufacturing process, the anion exchange resin is converted from carbonate to hydroxide form, and hence there is some residual carbonate left on the resin. Maximum specification is 5% of the anion exchange capacity.
- Nitrate ions, the only significant quantity of anion that is not bicarbonate. Its dominant source is the radiolysis of trace quantities of dissolved nitrogen in the moderator water. In some reactors, GdNO₃ is used for shim, which has an effect on the anion loading of moderator resins.

An estimate of the change in anion load in the ion exchange column is illustrated in [Figure 1](#), for a simulated duration of 60 days of moderator service. It was arbitrarily assumed that sources other than the slow resin bleed and nitrate are introduced at the beginning of the reactor service. The estimates were made from the best available data, or based on the manufacturer's

specification (the specification limit was used). Since actual values are generally below specification limit, the data in Figure 1 is considered conservative.

Based on the data used in Figure 1, an ion exchange column would be saturated after about 5 months of service. Ion exchange resin replacement is, on average more frequent than this, and thus the oxidative degradation of the ion exchange resin must be a significant contributor to the frequent premature saturation of the anion exchange resin.



THE CANDU 6 EXPERIENCE

Close cooperation was developed with the staff at the Gentilly 2 reactor during the course of this investigation. Based on the findings outlined above, several interim recommendations were made to implement a ¹⁴C emission reduction program. The most important recommendations were:

- Ion exchange columns used for gadolinium removal should not be used in subsequent general purification, because these columns are likely to contain excessive iron contamination. (Iron has a detrimental long-term effect on resin degradation [Torok et al., 1999a; 1999b, Igarashi et al., 1999].)
- Limit the service time of columns used in general purification to 2, and at most 3 months, compared to over 4 months at most other reactors, because the release of debris increases with service time.

During the course of the cooperation with Gentilly 2 since early 1997, their emissions dropped by a factor of about 6.

The Pt. Lepreau data for the 1989-1997 period suggested that the station has maintained a six-fold ^{14}C emission reduction since approximately 1992. This coincided with an increase in the rate of column changeout [Torok et al., 1999a]. The station practice at Pt. Lepreau is very similar to the practice recommended for Gentilly mentioned above, however, it was done for other reasons, and this resulted in reduced ^{14}C emissions as an additional benefit. Since 1992, the Pt. Lepreau reactor has the lowest ^{14}C emission rate among the Canadian CANDU reactors.

FURTHER DEVELOPMENTS

The guidelines for resin change are conservative, because the direct monitoring of the carbon cycle in the moderator is currently not feasible. A recent development in instrumentation (TIC/TOC Analyzer Sampling Station or TASS) will allow the on-line measurement of the total organic carbon (TOC - mostly resin debris) and total inorganic carbon (TIC - bicarbonate) before and after the ion exchange columns used for purification. This TASS is scheduled for installation and testing at the Gentilly 2 reactor during the summer of 2000. The TASS should provide quantitative indications for optimum timing of resin changes, and thus help to reduce resin consumption.

Currently, the same resin composition is used for general purification and for gadolinium nitrate removal, following the Guaranteed Shutdown State. The required resin performance characteristics are opposite for these two applications. For gadolinium nitrate removal, high exchange kinetics are needed to ensure fast removal of this reactivity poison, which is achieved more effectively with low cross-linked resins. For general purification, oxidation resistance is important to maximize resin service life, which requires higher cross-linked resins. If separate columns are dedicated for each one of these uses, an oxidation-resistant, highly cross-linked resin would be best suited for minimum ^{14}C emission and maximum resin service time for general purification. Newer resins are available that have high oxidation resistance, and the fresh resin has minimum impurity content, such as resin fines and soluble polymers.

CONCLUSIONS

A conceptual model of premature resin saturation, impacting on airborne ^{14}C station emissions, was developed using laboratory experiments and a review of emissions and practices of domestic CANDU reactors. The model is based on the peroxide-induced degradation of the ion exchange resins of the moderator purification system, which contributes to the premature saturation of these resins by anion ingress. Calculations also indicated that anion saturation would occur after 5 months of resin use, even if premature degradation of the resins did not take place.

Close cooperation with one domestic CANDU station (Gentilly) led to two interim recommendations: i) columns used for Gadolinium removal should not be used for general purification; and ii) a maximum column service time of 2-3 months should be set for general purification, as a conservative measure to control ^{14}C levels in the moderator. During the course of the cooperation, the station ^{14}C emissions decreased by a factor of 6.

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