Detection and Measurement of Carbon-14 in Nuclear Power Plants Gaseous Effluents

N. Sion
Ontario Power Generation, Toronto, M5G 1X6, Canada

INTRODUCTION

Carbon-14 (^{14}C) is an activation product in the nuclear fuel and is also produced in the heavy water moderator in CANDU systems, in the calandria and in the primary coolant. Most of the ^{14}C produced in the moderator is captured in the ion exchange columns but a small fraction finds its way to the environment via stack emissions.

The activation reactions producing ^{14}C are ^{14}N (n,p) and ^{17}O (n,α), and has been detected in several airborne forms, i.e. as a particulate, and as gaseous species of carbon monoxide and carbon dioxide (CO, CO_2), and as gaseous hydrocarbons of which ethylene C_2H_4 is the most significant. In the past, ^{14}C airborne emissions were routinely monitored at Ontario Power Generation's (OPG) nuclear sites. Having a very long half life of 5730 years, ^{14}C becomes a long term contaminant adding to the cumulative global inventory, or risk. Hence more recently, OPG made a commitment to the Atomic Energy Control Board (AECB) to implement continuous compliance monitoring of both $^{14}CO_2$ and the total ^{14}C as part of station stack emissions monitoring at the nuclear sites.

Quantification of the station releases, however minute is now a requirement. Sampling and monitoring instrumentation have just been installed and commissioned as part of the stack monitoring system.

A sampling instrument that can monitor both $^{14}CO_2$ and the total ^{14}C is described here.

THE STACK MONITORING SYSTEM

Fig 1 is a simplified schematic of the stack monitoring flow diagram. In essence, a representative isokinetic air sample is drawn from the stack conforming to ANSI 13.1 by a probe located in the upper end of the stack to minimise non-uniformity of the flow profile.

The stack monitoring system monitors for radioactive particulates, radioiodines, noble gases, and for tritium. The ^{14}C sampler is added to the loop by tapping off in parallel from the sampling line. After passing through the various samplers and monitors, the air is returned to the stack. A higher level than the targeted emission limit would induce "box-up", where the contaminated air is not emitted into the environment. This is done on signals from the particulate, radioiodines and noble gas monitors. The tritium and the ^{14}C samplers are collectors and do not provide box-up signals.

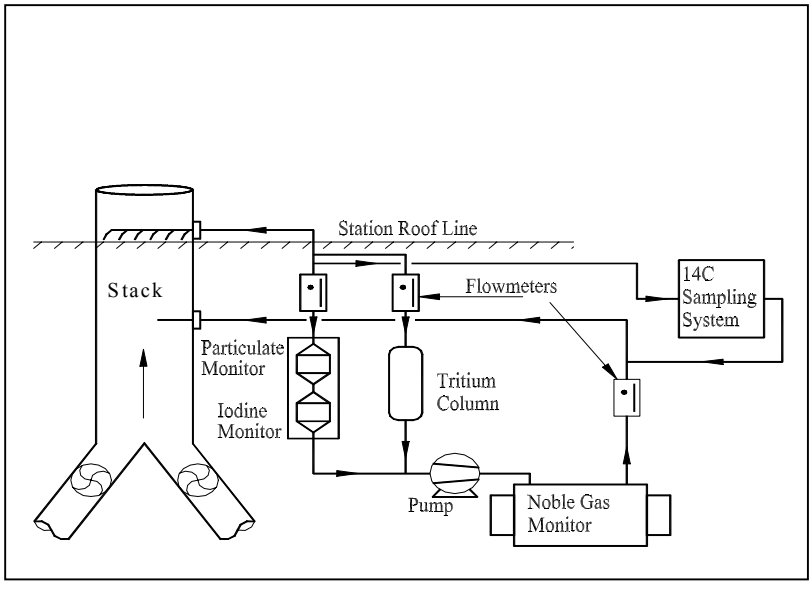

Fig.1 Schematic of Stack Monitoring System Including ^{14}C Sampler

REGULATORY REQUIREMENTS FOR AIRBORNE EMISSIONS

The regulatory requirements for ^{14}C emissions is shown as an OPG submission to the AECB as a standard, OHN-PROC-03480, which states that the range of monitoring shall be :

At the lower limit: Concentration of $\frac{0.01 \text{ of the weekly operating target}}{\text{mean weekly system flow}}$

At the Upper Limit: Concentration of $\frac{\text{100 times the weekly operating target}}{\text{mean weekly system flow}}$

both concentrations considered at the sampling point.

Therefore, the monitor's minimum collection levels, i.e. sensitivity, of hydrocarbons, and CO/CO_2 shall be better than 10 E^{-2} station weekly operating target. The operating target is an internal OPG target against which the performance of the nuclear facility, or site, is measured. Usually it is 0.01 of the regulatory requirement.

The stations' weekly operating targets are in Table 1. They are derived from the stations' Derived Emission Limits (DEL's) for that nuclear site.

TABLE 1
C-14 Station Weekly Operating Targets for Airborne Emissions

Darlington Site	Pickering Site	Bruce A	Bruce B
6.90 Ci/week	46 Ci/week	14.80 Ci/week	15.60 Ci/week

^{14}C SAMPLER'S FLOW RATES

From a purely design point of view, a regulated flow rate of 200 ml/min. was considered adequate. The flow is uni-directional, i.e. with non-return valves at strategic locations to prevent any flow reversal for any reason.

The ^{14}C sampling system is a stand alone instrument for the collection of ^{14}C in its oxide forms or in the hydrocarbon form.

^{14}C CONCENTRATIONS WITHIN THE SAMPLER

The concentration of ^{14}C within the sampler flow is derived from the concentration of ^{14}C in the Stack, scaled to the 200ml/m flow within the sampler. The concentration is itself derived from Weekly Operating Target (lower limit) shown in Table 1.

The concentration of ^{14}C within the sampler's flow is shown in Table 2.

TABLE 2
^{14}C Concentration Within Monitor (Lower Limit)

Unit Stack *	Flow Rate L/wk	Monitor Lower Limit of Concentration in Ci/wk	^{14}C Concentration Ci/l	Monitor Sampling Flow in ml/min	^{14}C in Monitor @ 200 ml/min flow in Ci/min
Darlington					
Units 1-4	24.2×10^{9}	0.069	2.85×10^{-12}	200	0.57×10^{-12}
HWMB/TRF	42.3×10^{9}	0.069	1.63×10^{-12}	200	0.326×10^{-12}
Pickering					
Units 5,6,8	2.23×10^{9}	0.46	0.206×10^{-9}	200	41.2×10^{-12}
Unit 7	6.79×10^{9}	0.46	0.068×10^{-9}	200	13.6×10^{-12}
Sulzer 1 Stack	1.179×10^{9}	0.46	0.390×10^{-9}	200	0.78×10^{-12}
Sulzer 2 Stack	1.712×10^{9}	0.46	0.269×10^{-9}	200	0.538×10^{-12}
Bruce A					
Units 1-4	17.9×10^{9}	0.148	8.27×10^{-12}	200	1.65×10^{-12}
Bruce B					
Units 5-8	21.7×10^{9}	0.156	7.19×10^{-12}	200	1.43×10^{-12}

* The stacks which are instrumented with ^{14}C Sampling systems.

HWMB - Heavy Water Management Building.

TRF - Tritium Removal Facility

Sulzer 1 & 2 - stacks where the ion exchange columns are located.

From Table 2, it is seen that the ^{14}C sampling instrument must be able to collect ^{14}C at the lowest concentrations as a minimum. i.e. collect less than $0.326x10^{-12}$ Ci/min of flow through the instrument.

THE CHEMICAL PROCESS

A chemical process is used to collect the CO_2 from the sample gas by chemical reaction with a sodium hydroxide (NaOH) solution to produce sodium carbonate (Na_2CO_3). This reaction occurs instantaneously as the sample gas is passed through the sodium hydroxide solution contained in a series of two gas washing bottles in series.

Fig.2 ^{14}C Sampler Front View This is achieved by bubbling (via a fine spray, e.g. via a porous plug), the gas through the solution of sodium hydroxide (NaOH) as in

$$2\ NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$
$$2\ moles + 1\ mole$$

Fig.2 ^{14}C Sampler Front View

A 200 ml solution of 0.5 Normal (moles/l) NaOH is considered sufficient to convert the normal CO_2 content of air (air being the major component of the stack gas) to sodium carbonate during a 1 week sampling period at a flow rate of 200 ml/min. For redundancy, a second gas washing bottle, in series with the first, is provided in each channel for protection against carryover from the first gas washing bottle, or in the event of elevated carbon dioxide levels. The range of flow should not exceed 350 ml/min lest the solution is depleted prior to the 1 week duration.

In the Total Carbon-14 channel, carbon monoxide and hydrocarbons are first converted to carbon dioxide by passage over a heated catalyst (or similar), before passing through the gas washing bottles.

THE CATALYTIC CONVERTER

The catalytic process consists of a furnace with a range above 650 °C. This temperature is considered adequate for converting the carbon monoxide and hydrocarbons into CO_2. The inner bore of the furnace and its length have been selected so as to bring the gas to at least 650 °C within the residence time the gas passes through the furnace. The furnace has temperature controllers and is fail-safe with annunciation should a malfunction occurs.

The catalyst itself consists of 50/50 % equal mix of pellets of Platinum coating on Alumina + Palladium coating on Alumina (½ % concentration in each case). The catalyst can be either in pellet form or spheres and is designed not to impede the flow.

Residence time of the gas through the catalytic converter is designed to be about 25 s. and a conversion efficiency of better than 99 % has been achieved.

Following the catalytic conversion, the gas is cooled and is passed through the NaOH solution bubblers.

THE DESIGN

The intent was to integrate the ^{14}C Sampler with the stack monitoring system which was already installed in each nuclear reactor site, yet operate independently drawing its own gas sample, with its own pumps, power supplies indicator's and local alarms. An alarm to the control room is integral with the other stack monitoring alarms in OR fashion.

The ^{14}C Sampler operates on a continuous basis and is attended weekly where an operator exchanges the NaOH solutions with a fresh batch is spare bottles for each of the Total channel and the CO_2 channel.

RESPONSE

The instrument response is almost instantaneous with the electronics and flow through. However, the total channel which has the catalytic furnace requires about 13 minutes to reach the optimum 650 °C for the most efficient conversion of the hydrocarbons to CO_2 .

ACCURACY

Qualification tests confirmed better than expected accuracies.

Flow accuracy is in the range of ± 0.2% for the CO_2 channel, and ± 0.4% for the Total channel for a flow of 200 ml/min.

Trapping efficiency of the CO_2 was somewhat difficult to achieve with a set acceptance limit of 5 ppm. It was attributed to contamination in the lines. The Sampler lines and the gas sampling bottles were thoroughly purged and the trapping efficiency was improved to less than 1 ppm. Normal content of CO_2 in air is about 450 ppm.

The catalytic converter efficiency was better than 99 % conversion. Testing for hydrocarbons (methane in air) showed a conversion to better than 0.1 ppm starting from 1600 ppm.

In leakage tests were conducted by inducing a vacuum in the Sampler. A vacuum of 205 mm Hg was sustainable for 20 s. This test was required to ensure that no in-leakage occurs after a change of NaOH bottles.

Fig.3 ^{14}C Sampler With Covers Removed

Fig.4 Assembly Line of 18 ^{14}C Samplers

Furnace controller accuracy was better than ± 5 ºC at the controlling temperature of 650 ºC.

CONTROLS, INDICATIONS, ALARMS AND INTERLOCKS

A second pump on each of the CO_2 and Total sampling trains was designed to be on redundant standby.

There were controls on the:

- Selection of vacuum, either manually and automatically after the change of chemical bottles.
- Selection of pumps.
- System reset.
- Initiate leak tests
- Alarm reset
- Timer reset
- Catalytic oven controls, indications and setting temperatures.

Indicators on:

- Flow
- Time

Status of:

- Leak tests in progress
- Test complete
- Bottles engaged

Alarms on:

- High oven temperature
- Temperature out of range
- Loss of power
- Single or dual pump failure
- Failure of leak tests
- Low flow/high flow
- Racks disengaged

The Sampler alarms were in an OR configuration with the Stack Monitoring System alarm which indicates in the station Control Room.

Power to the Sampler is provided by Class 2 uninterrupted power supply.

Fig.5 ^{14}C Sampler Installed and Integrated With the Stack Monitoring System at Darlington Nuclear Plant

EXPECTED PERFORMANCE

The above has been a description of a sampling instrument that would collect all species of carbon. The ultimate intent is to correlate that with the station operating targets shown in Table 1

After a week of collection and conversion of the carbons into sodium carbonate (Na_2CO_3), the solution is taken into the chemistry laboratory for analysis.

The solution is then mixed with a 1 ml sample of liquid scintillant. Calculations can then be made based on the station target DEL's, the stack flows, and hence the concentration of ^{14}C.

From these calculations, the expected performance, or output, for the target DEL's are shown in Table 3.

TABLE 3

STATION	SESITIVITY dpm/ml
Darlington	
Units 1-4	51.02
HWMB/TRF	28.90
Pickering	
Units 5,6, and 8	3687.83
Sulzer 1	6981.8
Sulzer 2	4815.7
Unit 7	1217.34
Bruce A	
Units 1-4	147.69
Bruce B	
Units 5-8	128.00

QUALITY ASSURANCE AND MANUFACTURE

The manufacture of the 18 ^{14}C Samplers was to Canadian Standards CSA Z299.3

Also, as an electrical piece of equipment, the Sampler complies with the Canadian CSA Electrical Safety Codes.

Covers