To:
Dr. S. Swanson, Panel Chair
Deep Geologic Repository Project
Canadian Environmental Assessment Agency
160 Elgin St., 22nd Floor
Ottawa, ON
K1A 0H3

From:
Dr. F. R. Greening
OPG (Retired)

<personal information removed>

January 6th, 2014

Dear Dr. Swanson,

Please find herein a copy of a letter I have sent to Mr. Ken Nash, President and CEO of the Nuclear Waste Management Organization. I trust you will support my call for a substantial revision to some of the published radionuclide inventory data for certain types of CANDU waste.

Sincerely,

<original signed by>

Dr. F. R. Greening

To:

Mr. Ken Nash
President and CEO
Nuclear Waste Management Organization
22 St. Clair Avenue East
Toronto, Ontario
M4T 2S3

From:

Dr. Frank Greening

<personal information removed>

January 6th, 2014

Dear President Nash,

I have worked as a research scientist for the Canadian nuclear industry since 1978, first for Ontario Hydro and its successor company OPG, and subsequently for Bruce Power in Kincardine. As a radioanalytical chemist, my work has been mainly focussed on the characterization of reactor components such as pressure tubes and feeder pipes removed from Pickering and Bruce Units. Thus, over the past 35 years, I have compiled a large body of data on the radionuclide content of components that are now slated for long-term disposal as refurbishment or decommissioning waste.

I have reviewed published information pertaining to the disposal of radioactive waste from OPG and Bruce Power's reactors, and have been especially interested in publications such as:

1. "*Reference Low and Intermediate Level Waste Inventory for the Deep Geological Repository*" OPG Report 00216-REP-03902-00003, issued in December 2010
2. "*New Nuclear Darlington Environmental Assessment – Nuclear Waste Management Technical Support Document*" OPG Report NK054-REP-07730-00027, issued August 2009
3. "*Disposal Aspects of Low and Intermediate Level Decommissioning Waste*" IAEA-TECDOC-1572, issued December 2007.

These reports contain tables of data on the specific activities of radionuclides in CANDU reactor refurbishment wastes. What is notable about these tables is the fact that much of the data are <u>not</u> based on direct measurements at all but rather on "*scaling factors, used fuel ratios and neutron activation calculations*". Indeed, <u>none</u> of the data for pressure tubes, end fittings and calandria tubes is based on direct measurements and only a handful of radionuclides are reported to have been directly measured for steam generator waste.

It is therefore appropriate to ask a number of questions about the NWMO's waste inventories:

(i) How were the scaling factors, used-fuel ratios and neutron activation calculations implemented?

(ii) How do the theoretical/calculated activities compare with measured values when such empirical data are available?

(iii) When measured data are unavailable, how are the calculated values verified?

I have attempted to answer these questions using published information on scaling factors, well-established neutron activation computational procedures and radionuclide measurements that I have made, or radionuclide data reported in the literature. I have focussed mainly on three radionuclides in pressure tube and steam generator waste – H-3, Nb-94 and Cm-244 – because these species exemplify troublesome issues I wish to address in this letter. I am providing this information to you for comment before I submit my findings to a journal for publication since I firmly believe this type of information belongs in the public domain.

I shall begin with a discussion of values of Nb-94 activities in pressure tube waste that are given in the three documents noted previously. These values, converted to units of Bq/kg are as follows:

Reference 1, generic OPG pressure tube:	7.58×10^{9} Bq/kg
Reference 2, Darlington pressure tube:	1.06×10^{10} Bq/kg
Reference 3, Darlington pressure tube:	9.74×10^{9} Bq/kg
Reference 3, Bruce pressure tube:	3.36×10^{8} Bq/kg
Reference 3, Pickering pressure tube:	2.19×10^{7} Bq/kg

Reference 3, which is based on calculations carried out by Kinectrics on behalf of the NWMO, has this comment on its own reported values:

The estimated level of Nb-94 in Darlington NGS decommissioning waste appears to be a factor of 29 greater than the corresponding level at Bruce NGS-A, which in turn appears to be a factor of 19 greater than the level in Pickering NGS-A waste. Considering that pressure tubes are the principal source of Nb-94 and that each Pickering, Bruce and Darlington reactor has 390, 480 and 480 pressure tubes, respectively, with each pressure tube being of approximately similar mass, it is not evident why the Nb-94 levels at the three stations differ so significantly.

What is remarkable about this statement regarding the calculated activities of Nb-94 in pressure tube waste is that no consideration is given to measured values for these activities. This is all the more puzzling because measured values of Nb-94 activities in irradiated pressure tube are readily available – See for example:

- A. W. Tarr et al. "*Measurement of Carbon-14 and Other Long-Lived Radionuclides in Irradiated Zr-2.5 % Nb Pressure Tubes*". Proceedings of the *Waste Management '94* Conference held in Tucson, Arizona, February 1994.

- E. L. Cooper et al. "*Characterization of Radionuclides in Primary Heat Transport System Crud Samples and Pressure Tube Scrapes Samples from CANDU Reactors*". COG Technical Note TN-05-3053, April 2006.

Nb-94 has a 20,000 year half life and is produced in irradiated Zr-2.5% Nb pressure tubes by neutron activation of Nb-93. The Nb-94 activities in the eleven pressure tube samples measured in the previously noted references are shown in Table 1 in units of GBq/kg of Zr-Nb, ($= 1 \times 10^9$ Bq/kg). The pressure tubes in question were removed from Pickering and Bruce Units after about 10 EFPY of operation. Because of the long half life of Nb-94, (20,000 y), decay corrections are not an issue.

Table 1: Nb-94 Activities Measured in Pressure Tube Samples

Pressure Tube Sample ID	Axial Location (meters)	Nb-94 (GBq/kg ZrNb)
P3J09	2.9	7.6
P3F13	0.5	3.8
	5.8	3.7
P4K10	0.5	4.1
	3.2	7.7
P4N16	3.2	6.7
	5.8	3.5
B5B16	1.5	7.8
	4.0	9.6
B7T02	1.5	6.3
	4.0	8.0

Tritium in Irradiated Pressure Tube Material

To date the NWMO has relied solely on calculated values to estimate inventories of individual radionuclides in pressure tube waste even though measured values of many species are readily available. What is more, as explained below, measured tritium concentrations are orders of magnitude *higher* than the values predicted by the first-order neutron activation calculations used by the NWMO to estimate radioactive waste inventories. The term "first-order calculations" refers to theoretical estimates involving only *one* tritium production pathway, namely neutron activation of deuterium impurities in pressure tubes via the D-2(n,γ)T-3 reaction. As-installed in a CANDU reactor, pressure tubes are specified to contain less than 20 mg/kg of hydrogen. It follows that the initial concentration of deuterium in a pressure tube is very low because the natural abundance of deuterium relative to hydrogen is only 0.016 %. Nevertheless, deuterium is produced by neutron activation of hydrogen at a significant rate because of the moderate, (0.33 barn), cross section of the H-1(n,γ)D-2 reaction. This leads to a slow build up of deuterium in operating pressure tubes.

A pressure tube containing an initial hydrogen concentration of 10 mg/kg hydrogen will attain a deuterium concentration of 0.625 mg/kg deuterium after 30 years of irradiation in a neutron flux of 1×10^{14} neutrons/cm^2/s. This deuterium will itself undergo further irradiation to produce tritium which may be calculated to attain an activity of 5.2×10^6 Bq/kg at the end of 30 years. OPG/NWMO reports its pressure tube waste activities after a 5 year decay period to account for cooling of waste before transfer to a DGR. With 5 years decay, first-order calculations predict a tritium activity of 3.90×10^6 Bq/k. This compares well with the OPG/NWMO reported value of 3.63×10^6 Bq/kg.

This level of agreement is encouraging; however, it becomes a moot point when we look at actual measurements of tritium in irradiated pressure tubes such as the data found in:

- A. W. Tarr et al. "*Measurement of Carbon-14 and Other Long-Lived Radionuclides in Irradiated Zr-2.5 % Nb Pressure Tubes*". Proceedings of the *Waste Management '94* Conference held in Tucson, Arizona, February 1994.

- G. R. Grant et al. "*Measurement of C-14 and other Long-Lived Radionuclides in CANDU Pressure Tubes*" Whiteshell Laboratory Report RC-697, November 1991

- D. L. Moir et al. "*Activities of Carbon-14 and Other Long-Lived Radionuclides on the Surface and in the Metal of Irradiated Zr-2.5Nb Pressure Tubes from the Pickering Unit 4 Reactor*" CANDU Owners Group Report No. COG-94-105, June 1994

Examples of measured tritium activities taken from these reports are presented in Table 2 below. For consistency with other radionuclide data in this letter, tritium activities are reported in GBq/kg, (= 1×10^9 Bq/kg).

Table 2: Tritium Activities Measured in Pressure Tube Samples

Pressure Tube Sample ID	Axial Location (meters)	Tritium Activity (GBq/kg ZrNb)
P3J09	2.9	2.8
P3F13	3.2	2.9
P4K10	3.2	1.7
P4N16	3.2	1.5
P4B17	3.0	1.6
P4M11	3.0	2.9
P4V13	3.0	2.2
B1L08	5.5	2.3
B1S04	5.5	2.1

The average of the tritium activities reported in Table 2 is 2.2×10^9 Bq/kg which is about *600 times higher* than the OPG/NWMO reported value of 3.63×10^6 Bq/kg. The main reason for this significant under-estimation of tritium is that pressure tubes operate in high temperature and pressure D_2O and pick up deuterium during operation as a result of the corrosion reaction:

$$Zr + 2D_2O = ZrO_2 + 2D_2$$

This ingress of deuterium overwhelms the small production of deuterium from the H-1(n,γ)D-2 reaction, which as we have seen is less than 1 mg/kg after 30 years. By comparison, values of deuterium concentrations measured in irradiated pressure tubes show that up to 100 mg/kg of deuterium can build up in a pressure tube after 30 years of reactor operation due to the proposed corrosion mechanism. (See for example: B. Warr "*Review and Predictions of Corrosion and Deuterium Uptake in the Body of Operating Pressure Tubes*" Ontario Hydro Nuclear Report No. OH A-FC-97-113-P, July 1998).

Significantly, however, a calculation of the tritium activity expected in a pressure tube that picks up 3 mg/kg deuterium per year for 30 years results in a value of 0.8×10^9 Bq/kg, which is less than half of the observed value of 2.2×10^9 Bq/kg, suggesting that there is another, unidentified source of tritium production in irradiated pressure tubes. Lithium, which is added to a PHTS for pH control, appears to be the source of this "missing" tritium via the high cross section, (940 barns), thermal neutron reaction $^6Li(n,\alpha)^3H$ reaction.

It is well documented that lithium isotopes are incorporated into pressure tube oxides by ion-exchange of Li^+ for protons on the hydroxylated surfaces of ZrO_2 crystallites:

$$\text{-Zr-OH} + Li^+ OH^- \leftrightarrow \text{-Zr-OLi} + H_2O$$

(See for example: B. Cox et al. "*Mechanisms of LiOH Degradation and H_3BO_3 Repair of ZrO_2 Films*" Eleventh International Symposium on Zirconium in the Nuclear Industry, September 1995).

Secondary Ion Mass Spectrometry (SIMS) depth-profiling of isotopes of H, Li and Be has been carried out on the inside surface oxides of samples of irradiated pressure tube from high flux mid-channel locations. These consistently show evidence for neutron induced processes involving the transmutation sequence:

$$^9Be \rightarrow {}^6Li \rightarrow {}^3H$$

Where the underlying nuclear reactions are:

$$^9Be(n,\alpha)^6He \xrightarrow{\beta} {}^6Li$$

And,

$$^6Li(n,\alpha)^3H$$

Beryllium is found at significant concentrations in the oxide scales of irradiated pressure tubes and is undoubtedly derived from the braze used to attach bearing pads to the fuel sheathing. (See for example: F.R. Greening. "*The Characterization of Thick Oxide Patches on Removed Pressure Tubes: New Results for B3U11*" OHT Memorandum to: P. Ellis, OHN, February 1999)

From available SIMS data it is possible to estimate the tritium activity in the B3U11 pressure tube oxide as a result of neutron activation of ^6Li:

Average $[^6Li] \approx 5 \times 10^{17}$ atoms/cm^3 in an oxide of thickness ≈ 35 μm

Hence, the surface concentration of ^6Li in B3U11 is 1.75×10^{15} at/cm^2.

25-year activation of ^6Li via the $^6Li(n,\alpha)^3H$ reaction $\rightarrow$ ^3H surface activity of 6.7×10^6 Bq /cm^2

1 cm^2 of oxide covers ~ 2.6 g of pressure tube so the effective tritium activity is 2.5×10^9 Bq/kg

This predicted level of tritium in the B3U11 pressure tube confirms that tritium production from ^6Li significantly exceeds its production from deuterium even allowing for deuterium ingress from the zirconium corrosion reaction. Furthermore, the tritium concentration <u>*measured*</u> by high temperature oxidation of the B3U11 pressure tube sample was ~ 7×10^6 Bq /cm^2, in excellent agreement with the calculated value of 6.7×10^6 Bq /cm^2.

Uranium and Transuranics in Irradiated Pressure Tube Material

The activities of isotopes of uranium and transuranic elements plutonium, americium and curium in pressure tube waste are another example of data reported by OPG/NWMO that are based solely on theoretical estimates rather than actual measurements. Thus, for the data presented in Table B.3 of the report: "*Reference Low and Intermediate Level Waste Inventory for the Deep Geological Repository*" OPG Report 00216-REP-03902-00003, issued in December 2010, it is explicitly stated that the values for transuranic isotopes have been estimated using "used fuel ratios". The data in question, in units of Bq per kg of irradiated pressure tube, and also converted to units of GBq per kg of initial uranium, are presented in Table 3 below. The latter unit was determined using the conversion factor 1 Bq U-238 = 80.35 μg uranium.

Table 3: OPG/NWMO Estimated Activities of Uranium and Transuranics in Pressure Tube Waste

Radionuclide	Activity (Bq/kg ZrNb)	Activity (GBq/kg initial U)
U-235	0.363	0.000154
U-238	29.4	0.01246
Pu-238	7910	3.360
Pu-239	14,200	6.020
Pu-240	19,400	8.259
Pu-242	21.4	0.009099
Am-241	23,400	9.939
Am-242m	39.5	0.01680
Cm-244	Not Reported	Not Reported

It is useful to compare the activities in column 3 of Table 3 – namely activities based on 1 kg of initial uranium – with data from calculations of the buildup of transuranic isotopes in CANDU fuel after various periods of irradiation. Such data comparisons form the basis of the "used fuel ratio" method. The report by L.J. Clegg and J.R. Coady: "*Radioactive Decay Properties of CANDU Fuel Volume 1:The Natural Uranium Fuel Cycle*", Atomic Energy of Canada Report No. AECL-4436/1, January 1977, provide the required data based on ORIGEN code calculations for irradiations up to 1150 GJ/kg initial U.

ORIGEN is an isotope production and depletion code developed by Oak Ridge National Laboratories for the calculation of the concentrations of radionuclides in irradiated nuclear fuel. The two most important parameters in ORIGEN calculations are the fuel burnup – a measure of the fuel irradiation period - and the decay time. CANDU fuel is typically irradiated to a minimum burnup of 7500 MWd/Mg initial U, (650 GJ/kg U), equivalent to an irradiation period of about 200 days. However, ORIGEN data in AECL's 4436/1 report extend to fuel burnups of 13,300, MWd/Mg initial U, equivalent to 350 days of irradiation.

In order to make predictions of the abundance of transuranic isotopes in irradiated pressure tubes, ORIGEN data for CANDU fuel irradiated up to 350 days and decayed 5 years have been compiled from AECL's 4436/1 Report and are shown in Table 4 below.

Table 4: ORIGEN Predictions for CANDU Fuel

Isotopic Species	Specific Activity for Specified Exposure Time (GBq/kg initial U)				
	40 days	150 days	200 days	240 days	350 days
Pu-238	0.081	1.42	2.63	4.29	9.11
Pu-239	2.74	5.39	5.92	6.16	6.34
Pu-240	0.89	5.90	8.18	10.33	14.17
Am-241	0.270	3.44	5.21	7.06	10.66
Cm-244	-	0.13	0.381	1.04	4.84

The most important transuranic isotopes (with half-lives greater than one year) are as follows:

Isotope	Half-Life (yr)
Pu-238	87.7
Pu-239	24,100
Pu-240	6,560
Pu-241	14.4
Am-241	433
Cm-244	18.1

For the purposes of comparisons between calculated and measured data it is preferable to look at data for long-lived isotopes such as Pu-239 or Pu-240. The process by which transuranic isotopes are produced in a CANDU reactor is neutron absorption by the natural uranium fuel which contains 99.27 % U-238. This leads, through β-decay of short-lived Np-239, to the formation of the important long-lived α-emitting isotope Pu-239:

$$\text{U-238 } (n,\gamma) \text{ U-239} \rightarrow \text{Np-239} \rightarrow \text{Pu-239}$$

Further irradiation of Pu-239 results in the slow build up of additional long-lived α-emitting isotopes such as Pu-240, Am-241, and Cm-244. The time-dependent variation in the concentration of Pu-239 is given by the equation:

$$dN_{239}/dt = N^{o}_{238}\, \sigma_{238}\, \varphi - N_{239}\, \sigma_{239}\, \varphi$$

Where:

N_{239} is the number of Pu-239 atoms per unit mass of fuel

N^{o}_{238} is the initial number of U-238 atoms per unit mass of fuel

σ_{238} is the total neutron capture cross section of U-238

σ_{239} is the total neutron capture cross section of Pu-239

φ is the thermal neutron flux

After a prolonged in-reactor exposure of uranium, the buildup of Pu-239 saturates and eventually reaches an equilibrium where $dN_{239}/dt = 0$. The equation above then reduces to:

$$N_{239} / N^{o}_{238} = \sigma_{238} / \sigma_{239} = 0.0027$$

Thus the equilibrium concentration of Pu-239 in CANDU fuel is 2.7 g per kg of initial U-238. This concentration may be converted to a Pu-239 saturation activity, A_{sat}(Pu-239) as follows:

$$A_{sat}(\text{Pu-239})/\text{kg U} = (2.7 \times 6.02 \times 10^{23} \times 0.693) / (239 \times 2.41 \times 3.156 \times 10^{11})$$

$$A_{sat}(\text{Pu-239})/\text{kg U} = 6.2 \times 10^{9} \text{ Bq/kg U}$$

This value for Pu-239 is very close to the OPG/NWMO value of 6.02×10^{9} Bq/kg U reported in Table 3 above. Converting this activity to a per kg of Zr basis, the OPG/NWMO values for U-238 and Pu-239 in pressure tube waste are consistent with an ORIGEN code calculation for a 350-day irradiation of a Zr-2.5%Nb pressure tube containing 2.4 mg/kg initial uranium. This concentration is well above the specification of 0.3 mg/kg for uranium impurity in Zr-2.5%Nb pressure tube material and suggests that in-reactor contamination of pressure tube surfaces by "tramp" uranium is responsible. But are there experimental data on the concentration of uranium and transuranic species in irradiated pressure tube samples to support this hypothesis? There certainly are suitable data but as demonstrated below, *measured values of uranium and transuranics in pressure tubes are consistently much higher than the OPG/NWMO estimates*.

Uranium and transuranics in pressure tubes are determined by techniques such as mass spectrometry and alpha spectrometry. Alpha spectra are acquired with an ion-implanted silicon detector typically having an energy resolution ~ 0.02 MeV (FWHM). In view of this practical limitation, it is not possible to resolve certain isotope pairs in an alpha spectrum – most notably Pu-239/Pu-240 and Cm-243/Cm-244. For this reason it is standard practice to report Pu-239 and Pu-240 as their combined activity. In the case of Cm-243 and Cm-244, ORIGEN code calculations show that the Cm-243 activity is typically less than 2 % of the corresponding Cm-244 activity which is therefore reported as Cm-244 alone without introducing significant error.

One of the most useful sets of data on the concentration of uranium and transuranic species in irradiated pressure tube samples is in the report by E. L. Cooper et al. "*Characterization of Radionuclides in Primary Heat Transport System Crud Samples and Pressure Tube Scrapes Samples from CANDU Reactors*". COG Technical Note TN-05-3053, April 2006. Data from this report are presented in Table 5.

Table 5: Uranium and Transuranic Radionuclides in Bruce Pressure Tube Samples

Sample ID	U-238 (mg/kg ZrNb)	Pu-238 (Bq/kg ZrNb)	Pu-239/240 (Bq/kg ZrNb)	Am-241 (Bq/kg ZrNb)	Cm-244 (Bq/kg ZrNb)
B5B16 (1.5 m)	25	280,000	190,000	470,000	73,000,000
B5B16 (4.0 m)	12	160,000	130,000	470,000	74,000,000
B7T02 (1.5 m)	20	250,000	170,000	190,000	22,000,000
B7T02 (4.0 m)	12	130,000	100,000	140,000	30,000,000

Data on uranium and transuranics on the surface of CANDU pressure tubes have also been obtained from SIMS (Secondary Ion Mass Spectrometry) analysis of a Bruce pressure tube inside surface oxide, (Data reported here are for a B3U11 pressure tube sample analyzed in 1999). The relative peak intensities in the SIMS spectra have been normalized to unity for U-238, converted to activities using the relation $A = N\lambda$, and multiplied by a factor of 2.35 μg for direct comparison with OPG/NWMO estimates. The results are collected in Table 6 below together with averaged values of the experimental data reported in Table 5.

Table 6: A Comparison of OPG/NWMO Data with SIMS and Alpha Spectrometric Measurements on Bruce Pressure Tubes

Radionuclide	Estimated Values	Measured Values	
	OPG/NWMO Activity (Bq/kg ZrNb)	Averaged Data from Table 5 (Bq/kg ZrNb)	SIMS Data for B3U11 (Bq/kg ZrNb)
U-235	0.363	-	0.701
U-238	29.4	214	29.4
Pu-238	7910	205,000	-
Pu-239	14,200	62,000	104,000
Pu-240	19,400	85,000	133,000
Am-241	23,400	318,000	146,000
Cm-244	Not Reported	50,000,000	14,900,000

A number of important conclusions may be drawn from the data presented in Table 6:

- The *measured* activities of alpha-emitting transuranic radionuclides in irradiated pressure tubes are considerably higher than the OPG/NWMO "used fuel ratio" estimates

- Cm-244, which is *not* included in the OPG/NWMO's estimates, is by far the highest alpha activity measured in irradiated pressure tube samples

- There is a high degree of variability, (by up to a factor of 3), between measurements from different pressure tube samples

These observations are further supported by data for Pickering pressure tube samples taken from the report by J.D. Chen et al. "*Measurement of C-14 and other Long-Lived Radionuclides in Irradiated Zr-2.5Nb Pressure Tubes from Pickering Units 3 and 4*" CANDU Owners Group Report No. COG-93-22, June 1993, as summarized in Table 7 for samples taken near the 3 meter axial location.

Table 7: Transuranic Radionuclides Measured in Pickering Pressure Tube Samples

Radionuclide	Sample Designation			
	P3J09 (Bq/kg ZrNb)	**P3F13 (Bq/kg ZrNb)**	**P4K10 (Bq/kg ZrNb)**	**P4N16 (Bq/kg ZrNb)**
Pu-238	47,000	32,000	44,000	77,000
Pu-239 + Pu-240	54,000	54,000	71,000	110,000
Am-241	< 10,000	200,000	200,000	200,000
Cm-244	18,000,000	2,400,000	13,000,000	5,500,000

A comparison of the pressure tube data in Tables 6 and 7 shows that the alpha-activities in Bruce samples are somewhat higher than the activities of the equivalent species in Pickering samples. Nevertheless, these measured values are consistently higher than the OPG/NWMO estimated values *by a factor of at least 3*. More importantly, however, the reported OPG/NWMO values imply that Cm-244 is entirely *absent* from irradiated pressure tubes when in fact this radionuclide accounts for more than 90% of the alpha activity in this type of waste. It is worth noting that Cm-244 is an important component of radioactive waste because it decays to another alpha-emitter, Pu-240, and is a significant neutron source through spontaneous fission and the associated (α,n) reactions with O-17 and O-18 in metal oxides in the waste matrix.

Finally there are additional reasons to reject the entire set of OPG/NWMO data for pressure tube waste as tabulated in "*Reference Low and Intermediate Level Waste Inventory for the Deep Geological Repository*", (OPG Report 00216-REP-03902-00003, issued in December 2010), because many of the measured fission product and activated corrosion product activities are orders of magnitude higher than estimated values. This is illustrated in Table 8 for a selection of published data on gamma-emitting radionuclides in removed pressure tubes.

Table 8: Comparison of Measured and OPG/NWMO Estimated Values of Gamma-Emitting Radionuclide Activities in Pressure Tubes

Type of Data	Sample ID	Radionuclide Activity (MBq/kg ZrNb)				
		Mn-54	Co-60	Cs-134	Cs-137	Sb-125
Estimated	*OPG/NWMO*	*4.94*	*2540*	*1.81*	*0.025*	*36.3*
Measured	**B5B16 (1.5 m)**	780	5300	190	170	-
Measured	**B5B16 (4.0 m)**	730	6800	200	160	-
Measured	**B7T02 (1.5 m)**	690	5800	100	62	-
Measured	**B7T02 (4.0 m)**	750	6800	90	70	-
Measured	**P3J09 (2.9 m)**	-	2800	-	50	-
Measured	**P3F13 (0.5 m)**	-	1500	-	35	61
Measured	**P3F13 (3.2 m)**	-	3100	-	340	190
Measured	**P3F13 (5.8 m)**	-	1700	-	19	110
Measured	**P4K10 (0.5 m)**	-	2800	-	12	-
Measured	**P4K10 (3.2 m)**	-	5000	-	130	-
Measured	**P4N16 (3.2 m)**	-	2500	-	110	-
Measured	**P4N16 (5.8 m)**	-	1300	-	20	-
Measured	**P4B17 (3.0 m)**	71	3500	-	47	-
Measured	**P4M11 (3.0 m)**	110	5600	15	50	200
Measured	**P4V13 (3.0 m)**	120	5200	23	43	88

The data in Table 8 clearly demonstrate that OPG/NWMO's gamma-emitting fission and activated corrosion product estimates for pressure tube waste are consistently less than the measured values, sometimes by a factor of more than 100.

The Overall Accuracy of OPG/NWMO`s Inventory Estimates

On April 18th, 2012 a meeting was held between the CNSC, OPG and the NWMO at which the CNSC raised its concern that the uncertainties and necessary conservatism in radionuclide inventory estimates for low and intermediate level waste have not been adequately addressed by OPG and the NWMO. These concerns are described in detail in two Environmental Impact Statement Information Requests - EIS-01-06 and EIS-01-20 – submitted by the Deep Geologic Repository Joint Review Panel of CEAA.

OPG/NWMO first addressed these questions in: "*Reference Low and Intermediate Level Waste Inventory for the Deep Geological Repository*" OPG Report 00216-REP-03902-00003, issued in December 2010, where we find the following statement:

> "*ORIGEN calculates radionuclides to within a factor of 3 in general (some exceptions), and Zr and Nb within 30% for a specific irradiation history. There is also some indication that the ORIGEN results are generally higher than actual inventories by a factor of 1 to 3*"

Unfortunately, no evidence is provided for the claim that neutron activation calculations using the ORIGEN code tend to give high numbers. Nevertheless, OPG/NWMO provide an overhead for the April 18th, 2012 meeting which is reproduced below as Table 9.

Table 9: **OPG Overhead**

"Data on ORIGEN Accuracy for Relevant Nuclides/Materials"

Nuclide	Accuracy (Calculated/Measured)	Source	Reference
Mn-54, Zr-95, Nb-95,Sn-113, Sb-125, Hf-181	Within factor of 1.5	Pickering Unit 2 Pressure Tube	Aydogdu et al. (1989)
Co-60 and Sb-125	Within factor of 3		
Ta-182	Within factor of 10		
Nb-94	2-3	Pickering Unit 3 & 4 Pressure Tubes	Chen et al (1993) Moir et al (1994)
Fission Products	~ 10 %	PWR/BWR fuel	SKB (2010)

There are some obvious concerns with these uncertainty estimates from OPG. For example:

- Data for Zircaloy-2, (used in pressure tubes for Pickering Units 1 & 2) are mixed with data for Zr-2.5%Nb. These alloys have quite different levels of trace elements such as Ni, Cr, Sn and Ta

- Data for PWR/BWR fuel, (which is enriched in U-235), are used instead of data for non-enriched CANDU fuel

However, there are other uncertainties associated with the application of neutron activation calculations to irradiated pressure tubes that need to be considered including:

- Uncertainties in the application of decay corrections to measured and calculated data

- Measured data are only available for tubes with irradiations up to about 15 years

- Variability in the concentration of surface contaminants such as uranium and transuranics

Nevertheless, even with all these uncertainties taken into account, neutron activation calculations should (in principle!), be capable of predicting radionuclide inventories in reactor waste to within a factor of about 10. Clearly, as shown in this letter, OPG/NWMO's estimated inventories do not meet this expectation, let alone the more ambitious claims of accuracies to within a factor of 3 for the radionuclides listed in Table 9. Remarkably, however, OPG's inability to reliably estimate radionuclide inventories is not due to any of the sources of uncertainty noted above, but rather to a failure to recognize how species in primary heat transport D_2O, such as Li, Be, Fe, Co and U, interact with and become attached to pressure tube surfaces.

Significantly, OPG do claim to address the issue of surface contamination of pressure tubes - See for example page 29 of their report: "*Reference Low and Intermediate Level Waste Inventory for the Deep Geological Repository*" OPG Report 00216-REP-03902-00003, issued in December 2010, where we read:

> "*The contribution from surface contamination is included for pressure tubes based on data from outlet feeder pipes*"

However, this is simply not a valid approach because feeder pipes are made of carbon steel and form a magnetite surface oxide layer as opposed to Zr-2.5% Nb pressure tubes which form a zirconium oxide layer on their inside surface during reactor operation, and there is no reason to expect these oxides to exhibit the same ion exchange properties for dissolved species in a PHTS. Furthermore, the pickup of Co-60 by pressure tubes has been measured directly as described by F. R. Greening in "*Post Irradiation Investigation of Corrosion and Deuterium Pickup by Zr-2.5% Nb Alloy Pressure Tubes: Isotope Tracers in Inside Surface Oxides*" CANDU Owners Group Report No. COG-96-618, Dec 1996. This report shows that Co-60 accumulates in irradiated pressure tubes by two mechanisms:

(i) Neutron activation of cobalt present as a trace impurity in the base Zr/Nb alloy.
(ii) Pickup of Co-60 by its incorporation into pressure tube inside surface oxides

The relative contributions to the Co-60 activities observed in irradiated pressure tubes have been evaluated by radiochemical analyses of Co-60 in tube sections cut to exclude the inside surface oxide. For pressure tube P3M11, a base metal Co-60 activity of 36 μCi/g was measured compared to 60 – 80 μCi/g for samples with the ID oxide still present. This shows that about 50 % of the Co-60 activity in a pressure tube is located in the surface oxide which, in the case of the P3M11 tube, is only 10 μm thick. This implies there is at least a 100-fold enrichment in the Co-60 concentration in the surface oxide compared to the base metal and explains why OPG's first-order neutron activation calculations of Co-60 activities in irradiated pressure tubes underestimate the true activity of this species.

A similar situation prevails for uranium fission products and transuranics in irradiated pressure tubes because production of these species by activation of uranium impurity in the base metal is much less than the production from uranium incorporated into a pressure tube's inside surface oxide *during reactor operation*. And the behavior of uranium on the surface of a pressure tube is quite different to its behavior on a feeder pipe surface, not only because the oxide substrates are chemically quite different (ZrO_2 vs.Fe_3O_4), but also because uranium undergoes continuous neutron irradiation in the former case, but not in the latter.

Conclusions

The specific activities published by OPG and the NWMO for radionuclide inventories associated with CANDU pressure tube refurbishment waste are seriously underestimated, sometimes by factors of more than 100. This discrepancy stems from undue reliance on calculations that do not properly account for neutron activation processes occurring in pressure tube material exposed to high neutron fluences in chemically aggressive environments such as high temperature lithiated D_2O. This problem could have been avoided by the authors of the calculations had they simply compared the results of their calculations with readily available data from direct measurements of pressure tube sections. Nevertheless, direct measurement of radionuclides in other types of CANDU waste, (e.g. steam generators), reveals there may also be problems with empirical data due to the variability seen in many directly measured radionuclide inventories. For example, even the relatively well-characterized radionuclide Co-60 shows a variability of a factor of 20 between different steam generator samples. It then becomes very problematic to use Co-60 data to develop scaling factors for other, difficult-to-measure radionuclides. I therefore urge you to address these issues and amend your radionuclide waste inventories accordingly.

Sincerely,
<original signed by>

Dr. F. R. Greening

c.c. Dr. M. Binder, Canadian Nuclear Safety Commission
Dr. S. Swanson, Canadian Environmental Assessment Agency