

CHARACTERIZATION OF PRESSURE TUBE WASTE FOR OPG'S L&ILW DGR

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Abstract

Detailed characterization information on pressure tube waste is required in support of safety assessment and design of Ontario Power Generation (OPG)'s proposed Deep Geologic Repository (DGR) for Low and Intermediate Level Waste (L&ILW). This paper presents an overview of the physical, chemical and radiological characteristics of CANDU pressure tube wastes based on a comprehensive review of the available literature and the results of OPG pressure tube waste characterization activities conducted at Kinectrics. The physical, chemical and radiochemical characteristics of the base metal, indigenous oxide layer and deposits formed on the pressure tube as a result of exposure to coolant during service were examined. Radiochemical data is presented for key long-lived radionuclides, including H-3, C-14, Cl-36, Co-60, Zr-93, Nb-94, Cs-137 and actinides. Data for selected radionuclides were compared with predictions based on 'first principles' models which consider neutron capture reactions, radioactive decay, fission and deposition from coolant, where appropriate. In general, agreement between measured data and model predictions for these radionuclides was reasonable.

1. Introduction

In a CANDU reactor core, each fuel channel consists of two concentric tubes with the annulus containing insulating CO₂ gas. The inner tube, called the pressure tube, houses a string of fuel bundles surrounded by flowing Primary Heat Transport System (PHTS) heavy water coolant. The outer tube, called the calandria tube, is surrounded by moderator heavy water contained in the calandria vessel.

Pressure tube waste, which is generated during refurbishment of OPG owned or operated reactors, will be disposed of in OPG's proposed DGR for L&ILW. Pressure tubes are a key waste stream in the DGR due to their concentration of long-lived radionuclides. In support of the safety assessment and design of the DGR, an extensive review of available literature on the physical, chemical and radiological characteristics of CANDU pressure tubes was recently conducted; a summary of the review is presented here. A theoretical assessment of the pressure tube activity characteristics is also presented. The derived relationships serve as a tool for data evaluation and as a means for assessing the dominant source of various radionuclides, such as activation of the base metal or contribution from time-dependent deposits.

2. Physical and Chemical Characteristics of Pressure Tubes

The un-irradiated pressure tubes at Pickering, Bruce and Darlington reactors are approximately 6 m long, 10 cm in diameter and have a wall thickness of 4 mm. Each pressure tube weighs about 61 kg. The physical and chemical characteristics of pressure tube base metal, oxide layer and deposits from the coolant are discussed next.

2.1 Base Metal Composition

Pressure tubes are generally fabricated from Zr-2.5 wt. % Nb although the original Pickering A Units 1 and 2 pressure tubes were fabricated from Zircaloy-2. Their nominal compositions are listed in Table 1; however, these alloys also contain various other elements and trace constituents, which together affect their material and radiological properties.

Table 1 Nominal Composition of Pressure Tube Alloys

Element	Composition (wt. %)*	
	Zircaloy 2	Zr-2.5Nb
Zr	98.2	97.5
Sn	1.5 (1.2-1.7)	-
Fe	0.12 (0.07-0.2)	0.06 (<0.15)
Cr	0.10 (0.05-0.15)	-
Ni	0.05 (0.03-0.08)	-
Nb	-	2.5

* Data in brackets represents the range in composition.

The base metal composition of pressure tubes is important for neutron induced activation. In particular, chlorine, cobalt, oxygen, nitrogen, and uranium are pre-cursors to key radionuclides for the DGR safety case.

2.1.1 Chlorine

Chlorine in pressure tubes, which is present as a result of the manufacturing process, leads to the formation of long-lived activation product Cl-36. The chlorine levels in the base metal are also relevant to the fracture toughness of irradiated pressure tubes. Prior to the late 1990s, the chemical specification for pressure tubes did not include a limit on chlorine content. Pressure tubes manufactured between 1975 and 1982 appear to have chlorine contents between 1 and 6 ppm. The new pressure tubes being installed in refurbished reactors are manufactured from quadruple melted ingots and appear to have chlorine levels below 1 ppm.

2.1.2 Cobalt

Stable cobalt-59 is readily activated to Co-60. Glow Discharge Mass Spectrometry (GDMS) measurements on approximately 36 un-irradiated offcut specimens (most from Pickering B pressure tubes) indicated an average cobalt level of about 0.5 ppm.

2.1.3 Oxygen and Nitrogen

Oxygen contributes to the total production of C-14 via the O-17 (n, α) C-14 reaction. Nitrogen leads to formation of C-14 primarily via the N-14 (n, p) reaction. Previous studies have shown that oxygen is present at levels of about 1000 ppm, and nitrogen typically ranges between 20 and 40 ppm, with recently fabricated pressure tubes having a lower nitrogen content than older tubes.

2.1.4 Uranium

Irradiation of uranium leads to the formation of various actinides and fission products. Unlike the uranium present in fuel bundles which is irradiated for about one year prior to removal from core, the uranium in pressure tubes undergoes prolonged irradiation. This leads to significant enrichment of higher mass actinides, principally Cm-244. Uranium is present at about 1 ppm based on GDMS or Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) measurements on un-irradiated offcut specimens and irradiated Point Lepreau and Bruce pressure tube samples.

2.2 Indigenous Pressure Tube Oxides

The average oxide thickness as a function of axial location is shown in Figure 1, based on data from several Pickering A Unit 3 pressure tubes. In general, the measured oxide thickness data exhibits 3 trends:

1. Oxide thickness increases along the length of the pressure tube, being the highest at the outlet end where the temperature is the highest.
2. Near the outlet, the oxide thickness at the top of the pressure tube is thinner than at the bottom of the tube. This is because of preferential coolant flow over the top of the fuel bundle which results in less heat removal from the bottom of the fuel bundle. Thus, the bottom of the pressure tubes is hotter and develops thicker oxide.
3. The average oxide thickness generally trends upwards with Equivalent Full Power Years (EFPY).

Overall, previous studies indicate that the oxide thickness on the internal and external surfaces of pressure tubes are 5-25 μm and 2-4 μm , respectively. These oxide thicknesses are small compared with the approximately 4 mm thickness of the pressure tube. However, they have different characteristics from those of the bulk metal as a result of its oxide form and the incorporation of various elements and radionuclides from the coolant or the annulus gas into its structure.

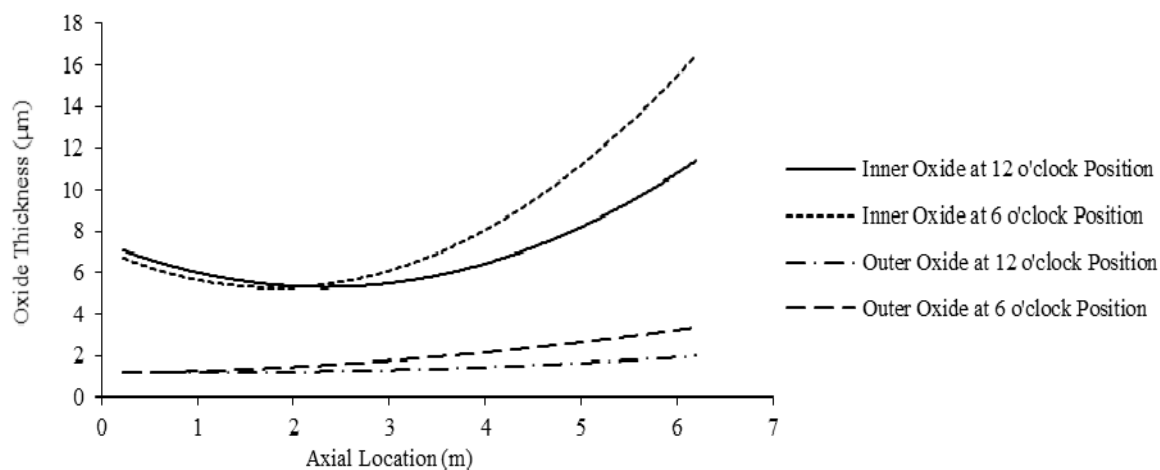


Figure 1 Variation in Oxide Thickness on the Inner and Outer Surfaces of a Pressure Tube

2.3 Deposits on Pressure Tubes

Deposits from the coolant may also form on the internal pressure tube surfaces. These deposits are largely magnetite originating principally from feeder pipe corrosion and also incorporate various minor elements from the coolant. In general, deposits at the inlet end of the pressure tube are elevated compared to the mid-point or outlet locations. This is consistent with the solubility behaviour of magnetite at reactor core temperatures. Specifically, the coolant entering the channels is relatively cool and over-saturated with iron and hence has a propensity for precipitating iron as magnetite at the inlet end of the pressure tube; as the temperature starts to increase along the length of the pressure tube, the extent of deposition becomes relatively small.

3. Radiological Characteristics of Irradiated Pressure Tube

Pressure tubes undergo bulk activation within the reactor core as a result of exposure to the prevailing neutron flux. In addition, deposits of activated corrosion products, fission products and actinides also form on the internal pressure tube surfaces due to exposure to the PHTS coolant. Fission products and actinides arise in the coolant as a result of releases from defective irradiated fuel and from small amounts of irradiated tramp uranium¹. The external pressure tube surfaces may also pick up contamination, notably C-14, from exposure to the annulus gas. Table 2 lists the key radionuclides.

Table 2 Key Longer-Lived Radionuclides Associated with Pressure Tubes

Component	Key Radionuclides	
	Bulk Activation	Deposited from Coolant
Zr-2.5%Nb Pressure Tube	H-3, C-14, Cl-36, Fe-55, Co-60, Ni-63, Zr-93, Nb-93m, Nb-94	H-3, Co-60, Ni-63, Sr-90, Cs-137, Pu-238 to Pu-241, Am-241, Cm-244

The following observations draw on measurements conducted by various authors at Whiteshell Laboratories, Chalk River Laboratories and Kinectrics Inc. over the last 30 years. The data is primarily collected from analysis of Pickering A and Bruce pressure tubes, with limited data available for Darlington. Data from Point Lepreau and overseas CANDU pressure tubes was also included in the review [1,2].

In general, specific activities of various radionuclides (alpha, beta, gamma emitters and x-ray emitter Fe-55) in pressure tubes vary axially along their length; for specific radionuclides, they may also vary radially across the pressure tube wall and azimuthally (i.e., at different "clock" locations) around their circumference. Specific activities also vary between pressure tubes in the same reactor and with duration in reactor. Of these various factors, it presently appears that the most important parameters are the relative contributions of the oxide and base metal, axial position along pressure tube, central (i.e., high power) channel versus peripheral (i.e., low power) channel, and in-reactor duration. The activity characteristics of gamma emitters, alpha emitters, and H-3 and C-14 are discussed separately in the following sections.

3.1 Gamma Activity Characteristics

In general, analysis of pressure tube samples located in higher power region or those irradiated longer showed higher gamma activities. Co-60, Nb-94 and Cs-137 were the major longer-lived gamma

¹ Tramp uranium refers to trace uranium impurities present in the coolant system.

emitters present in the samples. Circumferential variation of gamma activity in pressure tubes is relatively small.

The overall concentrations of activation radionuclides present in the oxide layer are lower than or comparable to the corresponding concentrations in the bulk alloy due to the volume increase which accompanies the conversion of the base metal into oxide. Based on the relatively small thickness of the oxide layer, the inventory of most radionuclides within the oxide layer is generally negligible compared to their base metal inventories. The notable exception is for radionuclides that are predominantly present on the inner oxide surfaces due to deposition from the coolant. Depth profiling showed that the activity of gamma emitters Co-60 and Nb-94 is uniform throughout the pressure tube material, whereas Cs-137 activity is enriched at the pressure tube surface.

The variation of gamma activity axially along the pressure tube was also reviewed. As an example, the activity profile of Co-60 and Cs-137 along the length of pressure tubes for Pickering A Units 3 and 4 is shown in Figure 2 [3,4]. For radionuclides which are produced mainly by bulk activation of the pressure tube material, such as Co-60, the specific activity profile would generally be expected to be parabolic consistent with the parabolic profile of the neutron flux. For radionuclides which are predominantly deposited from the coolant, such as Cs-137, the profile of the specific activity along the length of the pressure tube may be relatively flat. However, other factors will affect the actual profile. Figure 2, for example, suggests a parabolic profile for Cs-137 on Pickering A Unit 4 pressure tubes.

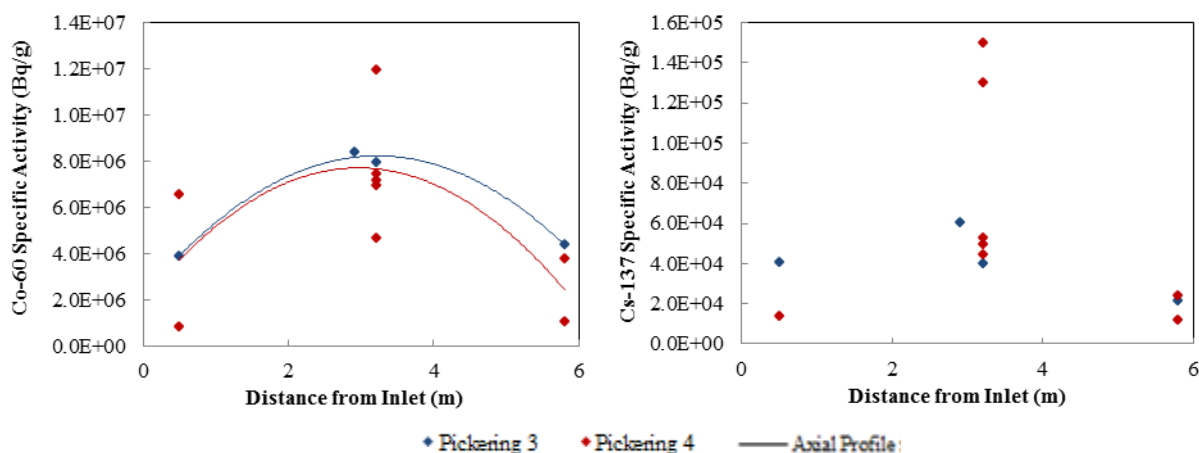


Figure 2 Co-60 and Cs-137 Profile along the Length of Pressure Tubes

3.2 Carbon-14 and Tritium Activity Characteristics

Similar to the gamma emitting radionuclides produced by bulk activation of the pressure tube material, the activity of C-14 and tritium was higher at the centre of the pressure tube compared to the inlet and outlet locations, and correlated with the expected neutron flux profile. Previous studies have shown that the C-14 activity is due to activation of the nitrogen impurity present in the pressure tube base metal [3,4].

Analysis of pressure tube samples with the oxide layer removed showed similar C-14 specific activity to samples with an intact oxide layer, thus indicating that C-14 is predominantly present in the bulk metal. Also, the tritium concentration on the inner oxide surface of the pressure tube (excluding the contribution of the base metal) was comparable to the average tritium concentration

for an intact sample including both the oxide and base metal layers, indicating that tritium is relatively constant across the pressure tube wall. However, the surface concentration of tritium on the outer pressure tube oxide surface was significantly lower than that on the inner surface, possibly because it is exposed to flowing annulus gas.

Presence of C-14 on the outer surface of the pressure tubes was investigated by Greening and Ramasubramanian [5]. Nitrogen was originally employed in the Annulus Gas System (AGS) at Pickering A Units 1-4; since their refurbishment in the mid-1980s, these units have been operating with carbon dioxide as the annulus gas. All other reactor units have employed a carbon dioxide AGS since their commissioning. For reactor units which employ a CO₂ AGS, the C-14 in the outer oxide layer is lower than the concentration in the bulk metal due to volume increase of the base metal upon oxidation. However, for reactor units which employ a nitrogen-filled AGS, the C-14 concentration on the outer surface of the oxide is sharply elevated compared to that in the base metal. Note, however, that because of the relatively thin oxide layer, the overall C-14 activity in Pickering A pressure tubes is still dominated by the bulk metal activity.

3.3 Alpha Activity Characteristics

For most pressure tube samples analysed, Cm-244 is the dominant alpha emitter. Although there is limited data available in the literature, the activity of actinides Pu-238, Pu-239, Pu-240, Pu-241, Am-241 and Cm-244 do not appear to display any trends with respect to the axial location on the pressure tube or the in-reactor location of the pressure tube.

Comparison of pressure tube samples with an intact oxide layer to those with the oxide layer removed have indicated that the total amount of alpha emitters in the bulk metal is as important or more important than that in the oxide layer. That is, the alpha emitters are not primarily in the oxide layers.

4. Theoretical Assessment of Pressure Tube Activity Characteristics

A simple ‘first principles’ model was used to estimate the activity of key longer-lived radionuclides associated with pressure tubes. The model considered neutron capture reactions, radioactive decay, fission and deposition from coolant, where appropriate.

A general equation which can be customized to each radionuclide is provided here. Consider the reaction scheme $A \rightarrow B \rightarrow C$ where radionuclide B is formed by activation of A and undergoes further activation to C. Another potential source of radionuclide B is deposition from the coolant (S_B). Radionuclide B also undergoes radioactive decay with a decay constant λ_B . A mass balance on the amount of radionuclide B per g of pressure tube is given by the following equation:

$$\frac{dN_B}{dt} = N_A \phi \sigma_A + S_B - N_B (\phi \sigma_B + \lambda_B) \quad \text{Equation (1)}$$

where:

N	atomic density (atoms/g),
t	irradiation time (s),
ϕ	neutron flux (n/m ² /s),
σ	neutron capture cross-section (m ²),
S	external source from fission or deposition from coolant (atoms/g/s), and
λ	decay constant (1/s).

Figures 3 and 4 show measured data for key longer-lived radionuclides of interest to the DGR safety assessment, decay corrected to the reactor shutdown date. All available pressure tube data are included in the plots, i.e., both low and high power channel data as well as data for all axial locations. These figures also show the calculated activity based on Equation 1. Activities are calculated for a location where the thermal flux is $1\text{E}+18 \text{ n/m}^2/\text{s}$.

General observations are summarized below:

- Nb-94 is a key radionuclides present in irradiated Zr-2.5Nb pressure tubes. It is formed by activation of natural Nb-93 and undergoes further activation to Nb-95. The results indicate that the Nb-94 activity levels off with increasing EFPY. The general agreement with the model indicates that bulk activation is the dominant source. (Data below the curve are likely for off-center channels or off-center axial locations.)
- Zr-93 is a significant radionuclide because it originates from zirconium, the principle pressure tube material. It is produced by neutron activation of natural Zr-92. Zr-93 production increases with EFPY, as the further reaction to Zr-94 is slow. The limited data are consistent with this bulk activation source.
- C-14 is a key radionuclide present in pressure tube waste. It is produced predominantly by the N-14 (n,p) C-14 reaction from the trace levels of nitrogen present. The data are consistent with this bulk activation source.
- The data shows appreciable H-3 levels in pressure tubes. There are several possible mechanisms. Tritium ingress from the coolant is possible, but the levels are higher than can be readily explained by this alone. Beryllium surface deposits would produce H-3 through Be-9 (n, α) Li-6 and Li-6 (n, α) H-3 reactions; however, this implies a higher level of beryllium than is supported by the limited data. Tritium in pressure tubes may also arise from deuterium ingress from the coolant. It is presently concluded that the theoretical basis for tritium levels in pressure tubes is uncertain, but may be linked to deuterium and tritium ingress from the coolant.
- Co-60 is formed directly by activation of stable Co-59 in pressure tube material; it undergoes further activation to Co-61. Co-60 may also be produced through stable Fe-58 (n, γ) Fe-59 activation followed by beta decay to Co-59. Calculated Co-60 activities are shown in Figure 3E for an initial cobalt content of 0.5 ppm plus a steady rate term which accounts for Co-60 production through Fe-58 activation. Based on the model calculations, and separately confirmed with measurements, it is concluded that Co-60 in pressure tubes arises primarily from activation of the bulk cobalt with a smaller but significant contribution from activation of iron.
- Cs-137 is formed by fission of U-235 and undergoes further activation to Cs-138. Calculated specific activities based on 1 ppm uranium in the bulk pressure tube material were not able to explain the high levels of Cs-137 in pressure tubes, indicating that bulk activation of uranium in the pressure tube is not a primary source for Cs-137. Another potential source of Cs-137 is tramp uranium and releases from defective fuel into the PHTS coolant. Accordingly, measured specific activity values can be explained by a steady Cs-137 source of 15,000 Bq/g/y (as shown in Figure 3F). Calculated results bound most of the data. A significant change in fuel defect events would affect the magnitude of this additional source term.

- Cl-36 is formed by activation of trace Cl-35 present in pressure tube material; it undergoes further (n, γ) and (n, p) reactions to form Cl-37 and S-36, respectively. Additional Cl-36 production can occur directly via K-39 (n, α) reaction and indirectly by neutron capture and beta decay of S-34. However, these reactions are not significant because potassium and sulfur are much less abundant than chlorine in pressure tubes. Cl-36 could also be present as a result of activation of chlorine in the coolant and subsequent deposition of Cl-36 on pressure tube oxide. Presently, the limited data are consistent with or bounded by an activation based estimate. Note that the model indicates that burnup of Cl-35 and Cl-36 are important factors.

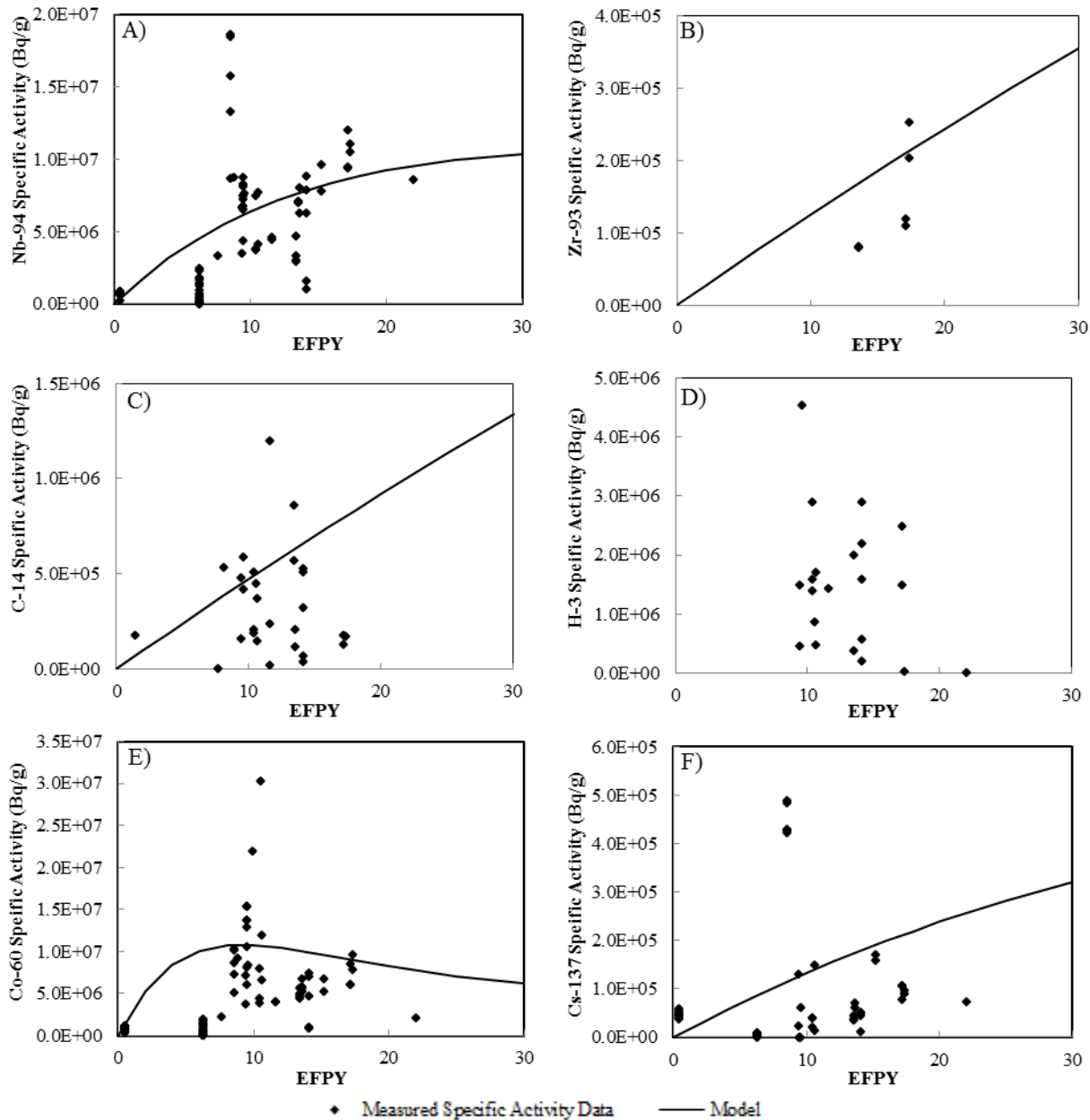


Figure 3 Variation in Pressure Tube Specific Activity with EFPY (Data for all Measured Locations Shown) A) Nb-94; B) Zr-93; C) C-14; D) H-3; E) Co-60; F) Cs-137

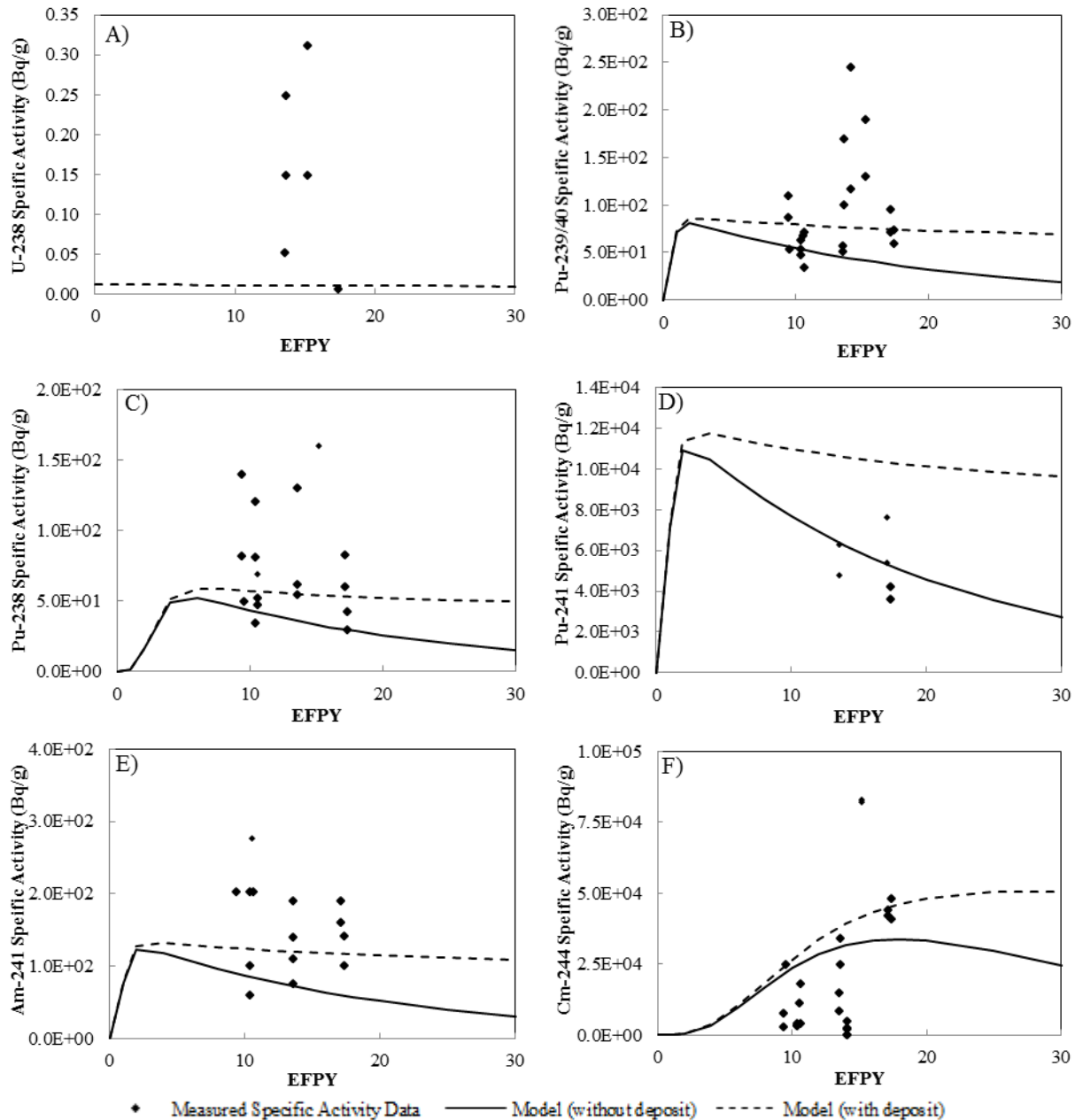


Figure 4 Variation in Pressure Tube Specific Activity with EFPY A) U-238; B) Pu-239+Pu-240; C) Pu-238; D) Pu-241; E) Am-241; F) Cm-244

- Actinides are produced from neutron activation of uranium. A simple model of the main actinide production routes is illustrated in Figure 5 showing a single path to each actinide (note that multiple pathways exist for some actinides). Actinide activities have been estimated based on an initial uranium level of 1 ppm as discussed in Section 2.1.4 (see solid line labeled Model without deposit in Figure 4), and a constant deposition rate of 1 mg/m²/y U-238 which corresponds to an in-core uranium deposition rate of about 1 g/y (see dotted line labeled Model with Deposit in Figure 4).

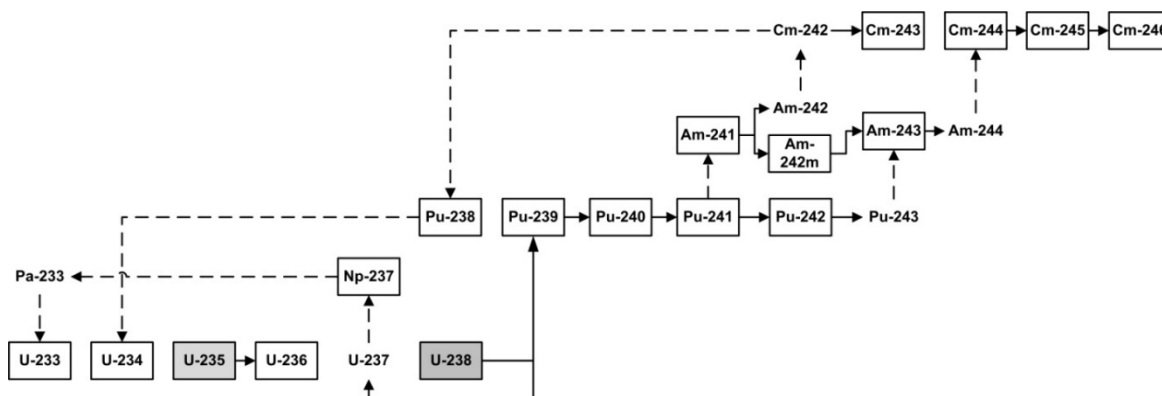


Figure 5 Main Production Pathways for Various Actinides

It can be seen that model predictions agree within an order-of-magnitude with the observed actinide levels despite the data being for a range of locations and EFPY values. The actual rate of U-238 deposition needed to explain the data is relatively modest since the initial 1 ppm uranium within the pressure tube is a significant source of the actinides (i.e., 1 ppm uranium is equivalent to a uranium deposition rate of 1 mg/m²/y over 27 years).

5. Conclusions

The physical and chemical characteristics of the base metal, indigenous oxide layer and deposits formed on the pressure tube as a result of exposure to coolant during service were examined. The elemental composition of the base metal including trace constituents was presented due to its importance to neutron induced activation.

Radiochemical data based on a detailed review of the available literature on CANDU pressure tubes was presented for key longer-lived radionuclides, including H-3, C-14, Cl-36, Co-60, Zr-93, Nb-94, Cs-137 and actinides. Measured pressure tube data was compared with predictions based on ‘first principles’ models in order to evaluate the data for various radionuclides and gain insight on their primary source and production mechanisms such as activation of the base metal or contribution from time-dependent deposits. In general, agreement between measured data and model predictions for these radionuclides was reasonable. Notable radionuclides of interest, with uncertainty in their theoretical underpinnings, are H-3 and Cl-36. Work is ongoing to improve the database and to develop similar understanding for other radionuclides of interest.

6. References

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