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CMD 22-M37.4

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Written submission from Frank Greening

Mémoire de Frank Greening

CNSC staff update on elevated hydrogen equivalent concentration discovery events in the pressure tubes of reactors in extended operation

Mise à jour du personnel de la CCSN sur les événements liés aux découvertes de concentrations élevées d’hydrogène équivalent dans les tubes de forces de réacteurs en exploitation prolongée

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Commission Meeting

Réunion de la Commission

November 3, 2022

Le 3 novembre 2022

Dear President Velshi,

Please accept this email as a written intervention to the November 2022 CNSC Public Hearing CMD 22-M37.1 which is to discuss issues related to the measurement of elevated hydrogen equivalent concentrations, [Heq], in pressure tubes for reactors in extended operation.

On July 5, 2021, Bruce Power reported that measurements obtained from a Unit 6 pressure tube after 271,729 hot hours of operation showed Hydrogen Equivalent Concentrations ([H_{eq}]) above the generic predictions and exceeding the Licence Condition 15.3 [H_{eq}] limit of 120 parts per million (ppm – by weight). Bruce Power reported that pressure tube B6S13 has a [H_{eq}] of 211 ppm at the burnish mark and 212 ppm at the burnish mark plus 10mm. Also, on July 8, 2021, Bruce Power reported that measurements obtained from a Unit 3 pressure tube showed [H_{eq}] above the generic predictions and above the Licence Condition 15.3 [H_{eq}] limit of 120 ppm. For the Unit 3 pressure tube B3F16, Bruce Power indicated a preliminary measurement of 131 ppm [H_{eq}].

At a Public Meeting held on September 3rd 2021, Bruce Power was asked by CNSC Commissioner Lacroix for its interpretation of the high [H_{eq}] observed in some of its operating pressure tubes, to which Bruce Power replied:

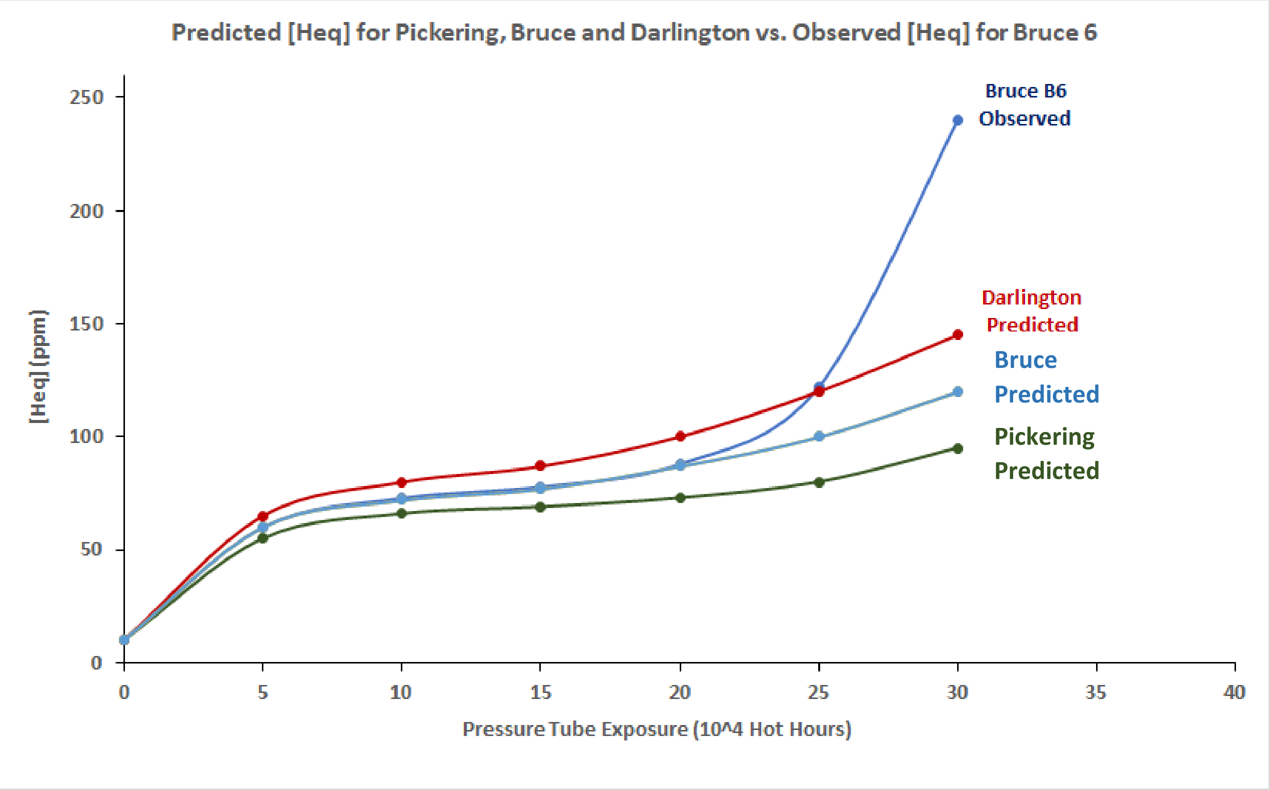
> "*We're not seeing a change in the rate of hydrogen uptake. What we're seeing is a redistribution (of the hydrogen) to the cooler region at the top of the pressure tube. So, it's not an acceleration but a redistribution*".

Similarly, in October 2021, the Pressure Tube External Advisory Committee expressed its support for Bruce Power's hydrogen redistribution hypothesis. Thus, at the present time, the consensus view held by the Canadian nuclear industry of the root cause of the high [Heq] observed near the outlet rolled joint of some Bruce pressure tubes is the fact that in this region the *average* temperature at the 6 o'clock circumferential position is about 10 °C *higher* than the temperature at the 12 o' clock position. This temperature difference causes deuterium entering a pressure tube to migrate to, and accumulate at, the coolest location around the tube's circumference which is at the 12 o'clock position.

Perhaps the most questionable aspect of Bruce Power's hydrogen redistribution hypothesis is the comment noted above that [Heq] "*is not showing a change in the rate of hydrogen uptake so that it's not an acceleration but a redistribution*". This is a very significant claim because the rate of change of Heq is a parameter that must satisfy the criteria set out in CSA Standard N285.4 for the maximum acceptable rate of change in H_{eq} – namely that the maximum allowable rate of increase in H_{eq} per 10,000 hot hours, or $\Delta H_{eq}/10^4$ HH, is limited to 3 ppm, 2 ppm and 1 ppm, for Units at Darlington, Bruce and Pickering respectively.

I have used Darlington, Bruce and Pickering H_{eq} data from the CNSC's *Appendix G*, (pages 271 - 272), of its 2019 *Regulatory Oversight Report*, (ROR) to determine values for $\Delta H_{eq}/10^4$ HH in pressure tube samples in order to investigate if the reported values do in fact satisfy Clause 12.3.5. 2 of CSA N285.4. In this way it was discovered that $\Delta H_{eq}/10^4$ HH increases significantly with increasing EFPHs for some Bruce pressure tubes. This is clearly in complete contradiction to the claim made by Bruce Power that [Heq] for pressure tube B6S13 "is *not showing a change in the rate of hydrogen uptake*".

The fact that the rate of change of [Heq] for pressure tube B6S13 shows *considerable acceleration* after about 200,000 Hot Hours of in-reactor exposure is well illustrated by plotting the predicted (deterministic) values of [Heq] as a function of pressure tube exposure using published data for outlet rolled joints in Units at Darlington, Pickering B and Bruce B, as shown below:



These curves show *predicted* [Heq] values for Pickering, Bruce and Darlington pressure tubes compared to the *measured* values for the B6S13 tube. As for [Heq} values measured for other operating Units, reported values of [Heq] for Pickering and Darlington outlet rolled joints may be found in OPG's September 3rd 2021 *Written Submission* to the CNSC, CMD 21-M37.2, where we read:

> *In Pickering Units 5-8, ORJ measurements were acquired during nineteen (19) in service scrape sampling campaigns and from four (4) removed tubes. The P5-8 measurements are substantially lower than B6S13 data. Among them, the highest [H]eq projected at EOL ranges from 85 ppm - 108 ppm corresponding to P6M14 removed tube data measured at outlet BM + 16 mm location.*
>
> *In Darlington Units 1-4, ORJ measurements were acquired during fifteen (15) in service scrape campaigns and from five (5) removed tubes. The D1-4 measurements are substantially lower than B6S13 data. Among them, the highest [H]eq projected at EOL ranges from 81 ppm - 97 ppm corresponding to D2M09 removed tube data measured at outlet BM + 16 mm location.*

Thus, we see that measured [Heq] values for Pickering and Darlington pressure tubes are well in line with the predicted values shown in the data plotted above, so that, to date, elevated values for [Heq] have only been observed in Bruce Units 3 and 6. But this raises questions about the validity of Bruce Power's hypothesis that the root cause of the high [Heq] observed in some Unit 3 and 6 pressure tubes is thermal diffusion of ingressed hydrogen in the temperature gradient between the 6 and 12 o'clock circumferential locations at the outlet of a pressure tube, which leads to a redistribution of hydrogen to the cooler 12 o' clock location of the tube. The obvious problem with this hypothesis is that *all* pressure tubes in mature CANDU reactors should exhibit some degree of hydrogen redistribution to the cooler 12 o' clock location of a tube.

Where data are available, they show that [Heq} is invariably higher at the 12 o'clock circumferential location than at the 6 o'clock location. A well-documented example of this behavior is provided by the P3 LSFCR tube L09 which had exceptionally high H/D pickup – in excess of 120 ppm – after 104500 EFPH of Unit operation. If we represent the concentration of H/D at a distance x from a pressure tube's inlet by $[D_6(x)]$ at the 6 o'clock circumferential location, and by $[D_{12}(x)]$ at the 12 o'clock circumferential location, the P3L09 data show that the ratio $[D_{12}(x)]/[D_6(x)]$ was 1.25 for x equal to 5.8 meters. From this value, a $\Delta T = (T_6 - T_{12})$ of about 22 °C at the pressure tube 5.8 axial location may be inferred.

The rate of increase of [Heq] near the outlet of the P3L09 pressure tube was about 10 ppm/10^4 HH. This should be compared to the current rate of increase of [Heq] for the B6S13 which is also about 10 ppm/10^4 HH. Nevertheless, the high [Heq] observed for the P3L09 pressure tube was never described as a phenomenon that was "*not an acceleration but a redistribution*", even though the data show clear evidence for H/D diffusion to the cooler 12 o'clock location near the L09 tube outlet.

However, the most important observation that demonstrates the invalidity of the H/D redistribution hypothesis is the fact that near the burnish mark, [Heq] averaged over the circumference of pressure tube B6S13, *exceeds the CSA N285.4 limit of 120 ppm*. Thus, using data from Table 2, found in OPG's September 3rd 2021 *Written Submission* to the CNSC, CMD 21-M37.2, we may calculate an average concentration of H/D at a distance x from a pressure tube's inlet as follows:

$$[D_{Av}(x)] = \{[D_6(x)] + [D_{12}(x)]\}/2$$

Then, for B6S13, the average H/D concentration near its outlet burnish mark, $[D_{Av}(BM)]$, is equal to (211 + 59)/2 or 135 ppm, *which is significantly above the CSA N285.4 limit of 120 ppm*. From this result we conclude that the postulated redistribution of H/D is unable to explain why the average circumferential [Heq] at the burnish mark of tube B6S13 is so high and in excess of the CSA N285.4 limit. Clearly, therefore, there is a need for an alternative explanation of this phenomenon and the following intervention is intended to provide such an alternative root cause.

However, before undertaking any discussion of H/D pickup measurements in CANDU pressure tubes, we must first make an assessment of the validity/reliability of the hydrogen/deuterium data used in this intervention. Such an assessment is necessary because of potential contamination issues related to the way pressure tube samples are collected and analyzed for their hydrogen and deuterium content.

For more than three decades, *two* methods have been used to collect pressure tube samples for H/D analysis:

(i) Through-wall punching at selected locations on a removed pressure tube in a controlled environment. Sample mass is typically ~ 0.3 grams

(ii) In-situ scraping of the ID surface of a pressure tube in a shutdown reactor where different, uncontrolled, environments are possible. Sample mass is typically ~ 50 mg

Station OPEX reveals that the collection of punched samples is relatively free from complications but, by comparison, the collection of scrape samples is fraught with difficulties because the scraping process exposes a fresh, oxide-free, surface of the alloy to the local in-reactor environment which may lead to additional H or D uptake by the sample.

Over the years, *three* scrape sampling regimes have been used:

(i) Scrapes are taken in a moist (D_2O vapor) environment – the original, (1980s), method

(ii) Scrapes are taken accompanied by the injection of a dry cover gas – the most commonly used method up to and beyond 2000

(iii) Scrapes are taken with liquid H_2O injection – first used for Bruce Unit 6 in 1995

The thinking behind method (iii) is that flooding the scraped area of a pressure tube with light water, (H_2O), will prevent any deuterium pickup by the sample during the scraping process. However, it is usually assumed that light hydrogen uptake by the sample *will* occur, so that the subsequent [H] measurement is expected to be higher than the true value.

In spite of this problem, Kinectrics' *Circumferential Wet Scrape Tool*, CWEST, which employs light water injection, has been widely used to collect scrape samples since its introduction in 2011. However, as illustrated by the data presented in OPG's Report CD# NK30-REP-31100-10395 R00, issued in March 2021, measured [H] data are ***not*** reported for such samples and only the *initial* hydrogen concentration, (measured in off-cuts from the original tube ingot), is used to calculate [Heq], resulting in its underestimation.

This issue is discussed in a recent letter, (dated September 17, 2021), from Kinectrics to L. Micuda at Bruce Power entitled: *Re: Hydrogen Equivalent Concentration Measurements Taken Near the Outlet Burnish Mark in the Bruce Unit 3 2021 Outage (A2131)*, which reads in part:

> *Dear Mr. Micuda,*
>
> *1.0 INTRODUCTION The purpose of this letter is to provide a summary of [H]eq data derived from measurements taken during the Bruce Unit 3 2021 outage (A2131).*
>
> *For comparison, measurements of punch samples from Bruce Unit 6 ex-service tubes B6N07 and B6S13 have been included where applicable. Note that the postulated*

> *bounding [H]eq level at MCR time for the risk-informed deterministic evaluation of fracture protection in the region of interest of Bruce Unit 3 has accounted for elevated observed [H] by assuming that measured [H] beyond the initial [H] is due solely to sample contamination. However, elevated [H] measurements have been observed in the region of interest (just inboard of the outlet rolled joint (RJ) at the top of the tube) which cannot be attributed entirely to contamination during scrape sampling and/or analysis, consistent with OPEX from removed tubes. Development of an approach for appropriately accounting for such elevated [H] measurements in RJ scrape samples is ongoing.*
>
> (My emphasis in red)

In other words: Although a scrape sample's exposure to light water may lead to some light hydrogen uptake, it appears that such light water contamination of scrape samples is insufficient to explain the occurrence of high light hydrogen concentrations observed in samples taken near the outlet of a pressure tube. Furthermore, the reason for such elevated levels of light hydrogen remains unknown and is the subject of ongoing investigations.

This issue has also been raised by the CNSC Regulatory Program Director, Dr. A, Viktorov, in a December 2019 letter to nuclear industry executives. In an attachment to his letter, we find a discussion of [H] measurements in scrapes, ("*Topic 5*"), and removed tubes, ("*Topic 7*"), respectively.

On Topic 5, Viktorov states that "*[H] values contributing to the total rolled joint [Heq] that are more representative should be included when trends in [H] are observed*". Similarly, on Topic 7, Viktorov states, in reference to [H] values observed for Bruce, Pickering and Darlington rolled joint samples, that the data implies "

> *There is a process by which protium is either re-distributed in areas of elevated deuterium or there is a source of additional protium which could affect [Heq] predictions both outboard and inboard of the pressure tube burnish mark.*
>
> (My emphasis in red)

These statements, coming as they do from recognized experts on the subject of H/D pickup by CANDU pressure tubes, show that light hydrogen concentrations near pressure tube rolled joints are often elevated to levels that cannot be blamed entirely on "light water contamination" of the sample during the scraping procedure – an issue that will be addressed in greater detail in this intervention.

1.0 Intervention

In this intervention I am focusing on annulus gas data because, as explained below, I suspect the high H/D pickup observed in a number of Bruce Unit 3 & 6 pressure tubes is coming from the annulus gas systems (AGS) of these Units. I say this because of some of the data that was provided in Bruce Power's overheads at the September 3rd CNSC meeting. The data I am referring to show values of both [H] and [D] in the outlet rolled joint regions of pressure tubes B6S13 and B3F16 from which H/D ratios may be calculated. The H/D *mass* ratios are as high as 13%. I believe this relatively high H/D ratio is definitive proof that the enhanced H/D pickup in these tubes is coming from the *outside*, not the inside of the pressure tube.

Reactor grade D_2O, as used in the primary heat transport system of a CANDU reactor, is specified to be > 99.3% deuterium. It follows that if the high $[H_{eq}]$ observed in the B6S13 and B3F16 pressure tubes was limited to ingress from *inside* surface corrosion, the H/D ratio should be < 0.7 %. However, the H/D mass ratio of ~ 10 % observed in the rolled joint region of these tubes obviously requires a source of light, as opposed to heavy hydrogen, and available data on the isotopic composition of hydrogen in the AGS of Canadian CANDU reactors consistently shows H/D ratios of at least 10 % which is in-line with the H/D ratios noted above for the B6S13 and B3F16 pressure tubes.

The concept of H/D entering a pressure tube from the annulus gas side, as opposed to the heat transport or so-called waterside, is not new, but, as described below, was proposed many years ago to explain a previous incident of elevated $[H_{eq}]$ in a removed Zr-2.5Nb pressure tube.

2.0 <u>The Annulus Gas Hypothesis</u>:

In July 1987, pressure tube L09 was removed from Pickering Unit 3 after 4350 effective full-power days of Unit operation. At that time, deuterium uptake by Zr-2.5Nb pressure tubes had been low and typically less than 3 mg/kg per year of exposure. However, the P3L09 tube was found to have a deuterium content at the outlet end that was about 5 times higher, (~ 135 mg/kg), than seen in any previously examined tube. In a paper written at that time, (See V. F. Urbanic et al: "*Oxidation and Deuterium Uptake of Zr 2.5Nb Pressure Tubes in CANDU-PHW Reactors*" ASTM STP 1023), the authors conclude that:

> "*The origin of the higher-than-expected deuterium concentration in the P3L09 tube is not completely understood, however, it is currently suspected that there may have been a considerable contribution from the annulus gas surrounding the tube where deuterium exists as an impurity.*"

A technical basis – including supporting experimental evidence – for the annulus gas hypothesis may be found in research carried out at the Hanford Laboratories by D. W. Shannon and published in his report: "*Role of the Oxidation Rate on the Hydriding of Zirconium Alloys in Gas Atmosphere Containing Hydrogen*", Report No. HW-76562, issued February 1963. This report includes a summary which reads in part:

> "*Mechanism studies have shown that the primary factor controlling the hydrogen absorption in zirconium alloys in gas atmospheres containing hydrogen is the rate at which oxidant (water) is transferred to the metal surface from the environment. When an oxidant is present, remarkable inhibition of gas phase hydriding at 400° C occurs even up to 1000 psi hydrogen pressure. However, at sufficiently low oxidant concentrations in the presence of an inert carrier gas, (He), the oxidation rate can be reduced, due to local depletion of the oxidant. Once the oxidation rate is diffusion limited, catastrophic hydriding can occur at low H_2 pressure and low temperature (150° C), in a few days, with pre-existing autoclaved oxide films offering only transitory protection.*"

A collaborative study by OPG and AECL in the early 1990s led to a so-called "*position paper*" entitled: "*Hydrogen Ingress in Zr-Nb Pressure Tubes*" issued as COG Report 91-277, in February 1992. In this report we read:

> "*The pressure tube (outside surface) oxide is stable at room temperature but can dissolve slowly into the underlying metal at reactor operating temperatures….. If sufficient oxidant (O_2, H_2O) is present, the rate of oxidation or growth of the oxide film will equal or exceed the dissolution rate and hence maintain the oxide in good repair. A few 10's of ppm of O_2 and/or H_2O continuously present in the annulus gas is sufficient for this.*
>
> *If insufficient oxidant is present (eg: vacuum or pure N_2), then the oxide protectiveness will gradually be degraded (e.g, formation of pores) by oxygen dissolution into the metal. This will result in H_2 ingress if H_2 or H-containing impurities are present in the annulus gas.*"

In order to prove that the elevated deuterium pickup by the P3L09 pressure tube involved a "considerable contribution" from the reactor's annulus gas system, one needs:

> (i) Evidence that there was an insufficiency of oxidizing agents in the L09 annular gap – chemically this would mean there was a dry, reducing, environment in the L09 channel.
>
> (ii) Evidence that there was very little, or <u>no</u> oxide growth on the outside of the L09 pressure tube, and more importantly, that there was some form of "*breakdown*" by the L09 outside oxide.

Clearly, we first need to define what constitutes "*an insufficiency of oxidizing agents in the L09 annular gap*". The authors of the COG position paper on the annulus gas hypothesis suggest that "*A few 10's of ppm of O_2 and/or H_2O, …, are enough to keep the oxide in good repair,*" To confirm this assertion requires a calculation of the amount of oxygen needed to form a protective oxide layer on the outside surface of a pressure tube; this may be carried out as follows:

Consider the formation of 1 µm of ZrO_2 on 1 cm^2 of the outside surface of a pressure tube. Assuming ZrO_2 has a density of 5.8 g/cm^3, we have an oxide mass of 5.8×10^{-4} grams per cm^2.

The fraction of this mass of ZrO_2 contributed by oxygen is 32/(91 + 32) or 0.26, so the mass of oxygen in 1 µm of pressure tube surface oxide is $0.26 \times 5.8 \times 10^{-4}$, or 1.508×10^{-4} g/cm^2.

The surface area of a pressure tube is equal to $\pi.d.l$, where d is the outside diameter (10.9 cm) and l is the length (600 cm) of a pressure tube. Hence, the outside surface area of a pressure tube is 20,546 cm^2.

A Pickering annulus gas system is configured with 196 *strings*, each consisting of *two* fuel channels connected in series. Thus, we need to consider the formation of oxide on 2 × 20,546 or 41,092 cm^2.

It follows that the oxygen requirement for the growth of 1 μm of oxide on two pressure tubes connected in series, is $41{,}092 \times 1.508 \times 10^{-4}$ grams or 6.32 grams of O_2.

Using the ideal gas equation, it may be calculated that 6.32 g of O_2 is equal to $6.32 \times 22.4/32$ liters or 4.42 liters of O_2 at STP.

Or, if we assume that D_2O is the primary oxidizing agent in an annulus gas, we may calculate that it would require 0.395 moles of D_2O, which occupies 8.85 liters of D_2O vapor at STP.

Now that we have determined the amount of oxidant required to grow 1 μm of oxide on the outside surface of a pressure tube, we are in a position to calculate the availability of oxidizing agents in an annulus gas string using four parameters as follows:

(i) The concentration of each oxidant present in an annulus gas system, C_{Ox}, (by volume),

(ii) The annulus gas string flow rate, F_{AGS}, (in liters/minute).

(iii) The percentage of the maximum available AGS flow, P_B, in a particular fuel channel.

(iv) The exposure time, t_{Ox} (in minutes) for an oxide to form/degrade on a pressure tube.

Before installation, a pressure tube is autoclaved for 24 hours in 400° C steam which results in the formation of a protective oxide film about 1 μm thick. It is this oxide layer that must be maintained in an oxidizing environment to prevent the type of breakdown reported in Shannon's 1963 study. Table VIII from Shannon's paper shows that in the temperature range 200 – 300 °C, a ZrO_2 protective oxide can be completely degraded if starved for oxidizing agents such as O_2 or H_2O for 15 days.

In addition, at the time of the discovery of the high deuterium pickup in the L09 channel of Pickering Unit 3, it was suspected that there was some degree of flow restriction in some annulus gas strings. For this reason. a flow blockage term P_B must be included in the calculation of the availability of oxidizing species (O_2 and/or D_2O) in an annulus gas system. If we represent the volume (in liters) of an oxidizing species in an annulus gas system that is available for oxide maintenance by V_{Ox}, we may write:

$$V_{Ox} = (1 - P_B/100).\ F_{AGS,}.C_{Ox}.t_{Exp}$$

<u>The Selection of Parameter Values for the Calculation of V_{Ox}</u>:

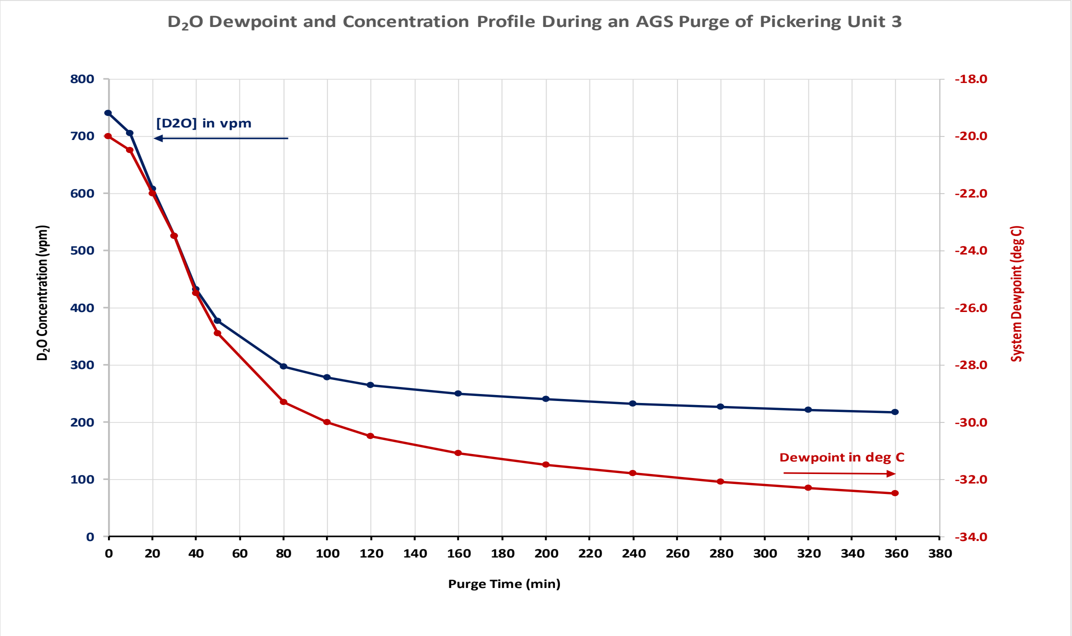
(i) The oxidant concentrations, C_{Ox}

The nitrogen used in the Pickering Unit 3 annulus gas system was specified to be "high purity" which means it was 99.99% (v/v) N_2. Nevertheless, during over 10 years of reactor operation, there were *two* significant oxidizing species in the Pickering Unit 3 annulus gas − O_2 and D_2O. The O_2 concentration was generally relatively constant and typically in the range 100 – 1000 vpm.

However, to be conservative for our calculation, we have used the lower limit of this range, namely, $C_{Ox}(O_2) = 100$ vpm.

Water in a N_2 annulus gas supply is specified by its dewpoint, which is typically stated to be – 60 °C, equivalent to 10 vpm. However, during reactor operation, water, as D_2O, always leaks into an annulus gas system and has to be purged periodically to maintain a viable leak detection capability. In practice, an annulus gas purge is maintained until the dewpoint has dropped to about – 32 °C which corresponds to 250 vpm D_2O. A typical D_2O concentration profile during a system purge is shown in Figure 1, below. However, to be conservative for our calculation, we have used a minimum value for $C_{Ox}(D_2O)$ of 225 vpm.

Figure 1:



(ii) The annulus gas string flow rate, F_{AGS}, (in liters/minute).

The Pickering Unit 3 annulus gas system employed a total N_2 flow rate of 351 liters/min which was shared by 195 strings. We have assumed that each string operated with the same average flow rate, and therefore have use a value of 1.8 liters/minute for F_{AGS}.

(iii) The percentage of the maximum available AGS flow, P_B, in a particular fuel channel.

For an initial scoping calculation of V_{Ox} we assume 100% flow was present in each string, i.e. P_B is equal to zero. The effect of increasing the amount of flow blockage is investigated in subsequent calculations discussed below.

(iv) The exposure time, t_{Ox} (in minutes) for an oxide to form/degrade on a pressure tube.
As previously noted, a ZrO_2 protective oxide can be completely degraded if starved for oxidizing agents such as O_2 or H_2O for 15 days. Therefore, we consider 15 days, (equal to 21600 minutes), to be the time interval of interest in the present calculations.

It follows that:

$$V_{Ox} = (1 - P_B/100).\ F_{AGS,}.C_{Ox}.t_{Exp} = 1.8 \times 21600 \times C_{Ox} = 38{,}880 \times C_{Ox}$$

The results of our calculation of the required minimum concentrations of O_2 and D_2O vs. the available concentrations are presented below in Table 1.

Table 1: Oxidant Requirements and Availability in the Pickering 3 Annulus Gas System

Oxidant	Required Minimum Concentration (vpm)	Calculated Available Concentration (vpm)
O_2	103	100
D_2O	228	225

The data in Table 1 show that the concentrations of oxidizing agents available in the P3 annulus gas system were very close to the minimum concentrations required to maintain a protective oxide layer on the outside surfaces of the pressure tubes. However, it should be noted that:

(i) The *total amount of oxidant* in an AGS string is the limiting factor in maintaining a protective oxide on a pressure tube.

And,

(ii) Each of the required oxidant concentrations in Table 3 was calculated assuming it was the only oxidizing species present.

Thus, we conclude that, as long as there was 100 % of the theoretical gas flow, (~ 1.8 liters/min in each string), there was a sufficiently oxidizing environment present in the P3 annulus to maintain a protective oxide on the outside surface of every pressure tube. From this result we see why it was necessary to invoke flow blockages in the P3 AGS to account for the high D ingress observed in the P3L09 pressure tube.

3.0 Annulus Gas Contributions to H/D Pickup by Bruce Pressure Tubes:

As previously noted, the presence of 13 % light hydrogen, compared to a balance of 87 % heavy hydrogen, (deuterium), in Bruce pressure tubes B3F16 and B6S13, is explicable only if we assume that the AGS in these Units is a significant source of the high $[H_{eq}]$ observed in these tubes. However, we still need to determine the root cause of the high hydrogen pickup in these tubes.

As discussed above, the best-known example of a significant AGS contribution to D ingress by an operating CANDU pressure tube is the P3L09 tube analyzed in the late 1980s. However, this example was for an AGS filled with N_2 and, since about 1990, all OPG and Bruce Power AGS have been filled with CO_2. Before considering the different chemistries associated with these different fill gases, we note that the basic operation of an AGS is the same, regardless of the fill gas. Thus, all AGS are first flushed with the fill gas – an operational mode known as an AGS purge – which typically takes up to 6 hours. Next, the make-up gas is “valved-out” of the system and the AGS is placed in what is called recirculation mode.

An AGS purge is required to bring the system dewpoint to as low as possible to improve pressure tube leak detection. This low dewpoint is typically ~ − 35 °C, equivalent to about 200 vpm D_2O. However, once switched to recirculating mode, the system dewpoint slowly rises because water ($H_2O + D_2O$), invariably enters the system through pathways such as leaky rolled joints. Water ingress into the AGS is allowed to continue until the system dewpoint reaches about − 10 °C, equivalent to 1500 vpm D_2O, which typically takes between three to ten days depending on the “leakiness” of the system. At this point the AGS is returned to purge mode and the cycle repeated.

To continue this discussion, it is important to first note that there are *two* major differences in the chemistry of an AGS operating with N_2 vs. CO_2 as the fill gas:

(i) It is often assumed that N_2 is essentially an inert carrier gas, however, the P3L09 oxide was observed to include a ZrN phase and the main effect of the incorporation of nitrogen in a pressure tube outside oxide is the creation of porosity in the mixed oxide-nitride layer due to their molar volume mismatch. In addition, the ZrN is readily re-oxidized in the presence of oxygen, and this re-oxidation of ZrN to ZrO_2 results in a significant volume expansion and severe degradation of the mixed oxide-nitride layer thereby allowing facile entry of H/D into the pressure tube.

(ii) By comparison, CO_2 does not contribute directly to the formation of a pressure tube oxide, but is involved in the system chemistry through the so-called reverse water-gas shift reaction:

$$CO_2 + H_2/D_2 \leftrightarrow CO + H_2O/D_2O$$

The related (forward) water gas shift reaction:

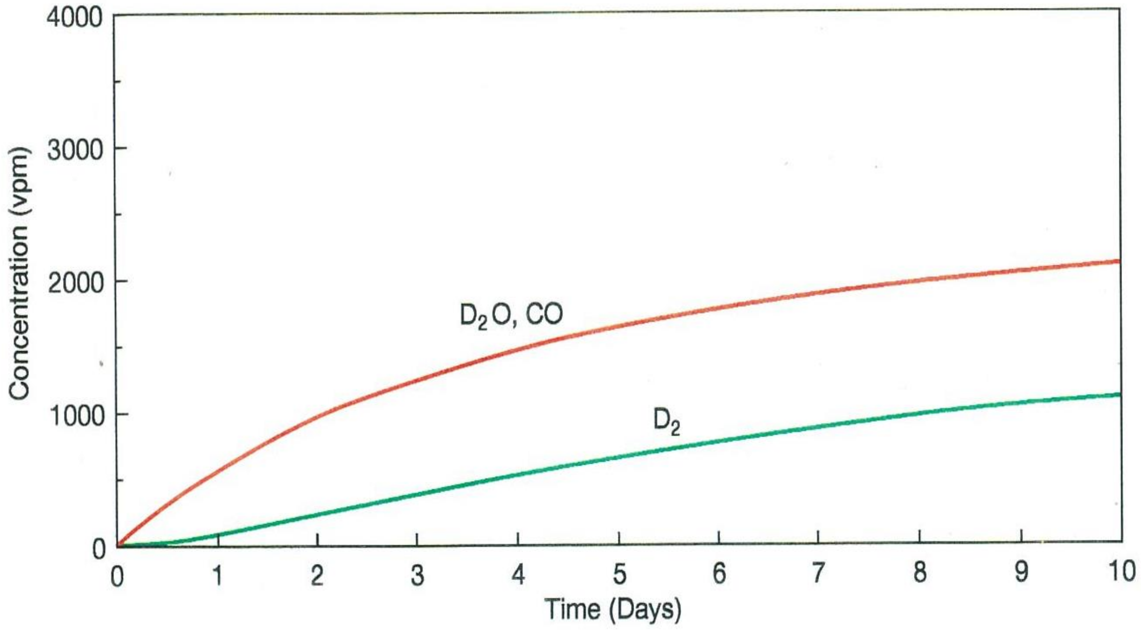
$$CO + H_2O \rightarrow CO_2 + H_2$$

is well-known in the petrochemical industry through its role in the steam hydrogenation of CO for the production of hydrogen in so-called synthesis gas.

For both the forward and reverse reactions, the equilibrium constant is a function of the system temperature, with the forward reaction being favored at low temperatures. However, in the case of the reverse water gas shift reaction in a nuclear reactor environment, the equilibrium constant deviates from its purely thermal value because of CO_2 radiolysis which leads to the direct formation of CO.

This deviation in the equilibrium constant of the reverse water gas shift reaction under radiolysis was included in a model developed at Ontario Hydro Research that has been used to predict the behavior of $[D_2]$, [CO], and $[D_2O]$ in an AGS between purges. To obtain good agreement with measured data, (See Figure 2, below), it was found necessary to include a CO_2 make-up term which compensates for the slow out-leakage of the fill gas over time., (See the Discussion Section of this email for more details on this).

Figure 2: AGS Major Impurity Concentrations Calculated for Bruce B which show good agreement with measured data for Unit 6



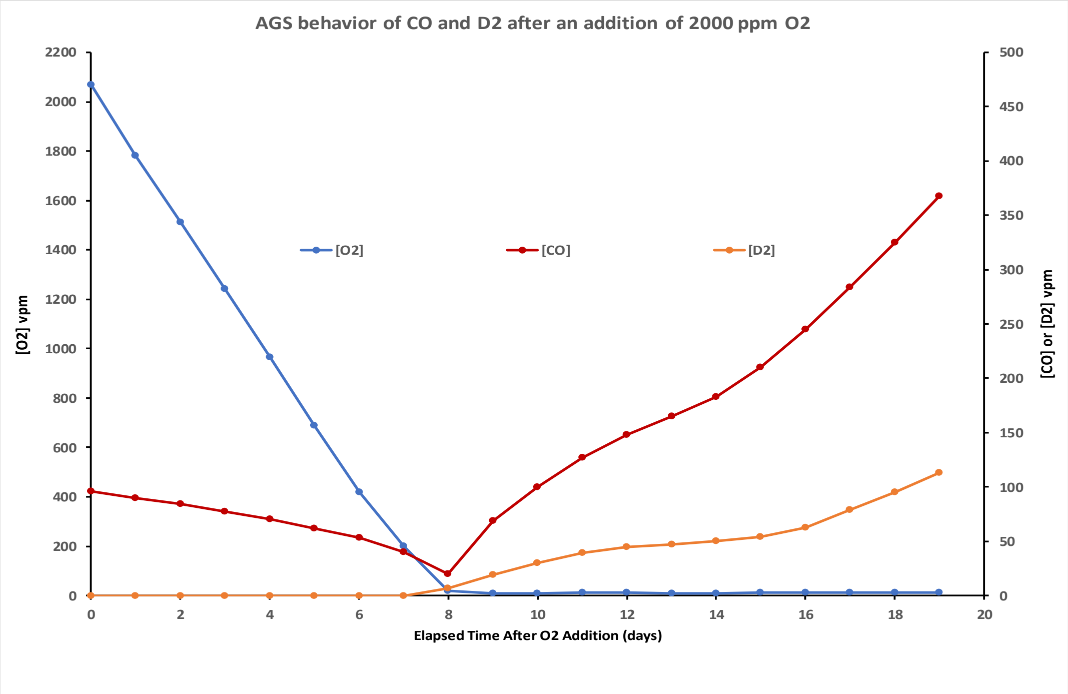
The presence of significant amounts of carbon monoxide, CO, in an AGS has a number of deleterious consequences for the optimum performance of the system – a fact that was first recognized in the late 1980s:

> (i) CO is the major precursor for the formation of a viscous yellow-colored deposit that tends to form in out-of-core sections of an AGS
>
> (ii) CO is reactive towards some of the alloys used in the construction of an AGS. This leads to the formation and transport throughout an AGS of volatile carbonyl compounds such as $Ni(CO)_4$ and $Fe(CO)_5$.

Item (i) first became an issue in the period 1985 to 1990 due to the blockage of a number of flow rotameters controlling the supply of CO_2 to the AGS of Bruce Units 3 and 4. Significantly, samples of yellow deposit collected from these Units showed the presence of Ni and Fe – each at concentrations ~ 5 mg/g. This observation is consistent with the expected formation of metal carbonyls, as noted in item (ii) above. Nevertheless, it begs the question of *where* in an AGS the iron and nickel observed in these deposits originated – an issue that is addressed below.
First however, it is important to note that by 1992 all Canadian CANDU stations were adding oxygen to the annulus gas CO_2 in an effort to prevent the buildup of CO and D_2 in the system. Both batch and continuous O_2 additions were investigated and the concentrations of CO, D_2, and D_2O monitored by on-line GC and dewpoint measurements.

Figure 3, below, shows the results of such a batch addition of O_2 to an operating AGS. Approximately 20 liters of O_2 were added to an AGS with a system volume of ~ 10,000 liters, bringing the initial [O_2] to ~ 2000 vpm. Following this oxygen addition, the system was placed in recirculating mode and the concentrations of O_2, CO and D_2 followed for a period of 19 days. As Figure 3 below shows, the system D_2 was immediately undetectable, while the concentration of CO slowly decayed from approximately 100 vpm to about 20 vpm over a period of 8 days, at which point the O_2 concentration had fallen below 20 vpm.

Figure 3: Effect of a Batch Addition of O_2 to an Operating CO_2 AGS



It is useful to consider in some detail the data presented in Figure 3, as well as related information on the O_2 batch addition, as described in the COG Report COG 94-370. More specifically, we shall endeavor to account for the observed depletion of O_2 by considering the major contributing processes involved, as follows:

(i) Radiolytic oxidation of CO to form CO_2

The oxidation of CO to form CO_2 is a radiation-induced reaction:

$$CO + \frac{1}{2} O_2 \overset{\gamma\text{-rays}}{\longleftrightarrow} CO_2$$

It is important to note that this reaction is reversible so that some oxidized CO is effectively regenerated by the radiolysis of CO_2 thereby slowing the removal of CO. This fact explains the behavior of CO seen in Figure 3: In the presence of excess O_2, the concentration of CO decreases slowly at a rate of about 12.5 vpm/day. However, once O_2 is totally depleted, the CO concentration increases rapidly at an initial rate of about 100 vpm/day.

The amount of CO formed in 1 day in an AGS having a total volume of 10,000 liters is then equal to $100 \times 10^{-6} \times 10{,}000$ liters/day or 1 liter/day. For the 8-day interval following the O_2 addition shown in Figure 3, this amounts to a total production of 8 liters of CO which requires 4 liters of O_2 to be oxidized to CO_2.

(ii) Radiolytic oxidation of D_2 to form D_2O

The oxidation of D_2 to D_2O is a radiation-induced reaction:

$$D_2 + \tfrac{1}{2} O_2 \xrightarrow{\gamma\text{-rays}} D_2O$$

As seen in Figure 3, in the presence of excess O_2, the concentration of D_2 is consistently below the GC detection limit of about 5 ppm. Hence, we conclude that the oxidation of D_2 to D_2O is a rapid, essentially non-reversible reaction. If we assume that the initial production of D_2 is 50 vpm/day, we have a D_2 accumulation rate in a 10,000-liter AGS of 0.5 liters/day. It follows that for an O_2 addition period of 8 days we have a total buildup of 4 liters of D_2 which would require about 2 liters of O_2 to fully oxidize.

(iii) O_2 required to maintain a passive oxide film on AGS fuel channel surfaces

This oxygen removal process was previously discussed in this email where is was shown that for a Pickering Unit over a 15-day period, about 4.5 liters of O_2 is required to maintain a passive oxide film on the inside surface of two pressure tubes connected in series in an AGS string. In the case of a Bruce Unit, the AGS string configurations involve a minimum of four pressure tubes so that a minimum of 9 liters of O_2 is required to maintain a protective oxide.

(iv) Loss of O_2 due to AGS leakage

The leakiness of CANDU annulus gas systems varies considerably from Unit to Unit and tends to increase over time. However, for this study, I have used a system leak rate from COG Report COG 94-370 which was 12 liters of CO_2 per hour. Combining this leak rate with the data in Figure 3 for the addition of 20 liters of O_2 to an operating AGS, a loss of 4.6 liters of O_2 in 8 days, (or a *fractional release* of 0.0288/day), may be determined. AGS leak rates observed for specific Pickering and Bruce Units are considered separately in the Discussion Section of this email.

Table 2, below, provides a summary of the four major contributions to the consumption of O_2, approximately 8 days after a 20-liter batch addition of O_2 to an operating AGS. The calculated values show that the oxidation of CO and D_2 accounts for only 30% of the O_2 consumption, while surface oxide passivation and system leakage account for 70%.

Table 2: Contributions to the consumption of 20 liters of O_2 after addition to an AGS

Process Number	Process Description	Oxygen Consumed (Liters)	Percent of Total
1	Oxidation of CO	4	20
2	Oxidation of D_2	2	10
3	Surface Oxide Passivation	9	45
4	Leakage of O_2 from the AGS	5	25
Total	All Processes	20	100

4.0 Annulus Gas Chemistry of a Shutdown Reactor:

Under normal operating conditions, 93 % of a CANDU reactor's power output is due fast neutrons and prompt γ-rays, while 7 % comes from the heating effects of the uranium fuel's fission product decay. Following a reactor shutdown, these fission products continue to function as a thermal power source, although radioactive decay of short-lived radionuclides will rapidly decrease the magnitude of this source to about 1% of the reactor's full power level. Nevertheless, this residual power output still amounts to about 25 MW_t for several hours after a reactor is shutdown.

Furthermore, and of great significance for the chemistry of an AGS in a shutdown reactor, the gamma-ray dose rate at the center of a fuel channel is estimated to be as high as 600,000 Rem/hr several days after shutdown, at which time the temperature of the AGS is typically about 60 °C. As shown below, these two factors – high intensity radiation fields and relatively low temperatures – combine to create an environment favorable to the formation of volatile transition metal carbonyls. However, we must first consider an additional factor, namely the presence or absence of O_2 in the AGS of a shutdown reactor because O_2 is known to inhibit carbonyl formation.

When a CANDU reactor is shut down for maintenance, the AGS is placed in a so-called "stagnant pressurized" state in which the recirculating pumps are turned off and the system is held at its normal operating pressure, (~ 1 atmosphere). While in this operational mode the AGS is continuously monitored to maintain system pressure above a pre-selected value. For operating Bruce Units, CO_2 is used to fill the AGS together with O_2 additions up to 5 vol %. This means that for an AGS having a total volume of ~ 10,000 liters, each shutdown period begins with approximately 9,500 liters of CO_2 and 500 liters of O_2 in the system.

As previously shown, even under reactor shutdown conditions, gamma-radiolysis of the CO_2 in an AGS continues at a very high dose rate and leads to the rapid depletion of O_2 accompanied by a buildup of CO and D_2. Available data show that significant O_2 depletion in a shutdown AGS can occur in less than 1 week. During the transitional period from oxygen-rich, to oxygen-poor, there are two additional changes in the AGS chemistry to consider:

(i) The lowering of the AGS temperature, from its normal operating value of ~ 160° C to its shutdown value of ~ 60° C, has a profound impact on the behavior of the vapor-phase concentration of D_2O in an AGS. For example, the cooling of the pipework in an AGS in shutdown mode inevitably causes water to be adsorbed on metal surfaces throughout an AGS as discussed in these reports:

1. *Water Absorption in the Pickering Unit 3 Annulus Gas System.* OHRD Report 92-2-K, (April 1992).
2. *The Measurement of the Isotopic Composition of Water Vapor in CANDU Annulus Gas Systems.* OHT Report A-NFC-96-114-P, (July 1996).

CANDU reactors operate with an AGS containing varying amounts of ingressed water, (100 – 2000 vpm), in a CO_2/O_2 atmosphere. The presence of water and oxygen at temperatures up to 250 °C creates a relatively corrosive environment for the $> 10^7$ cm^2 of metal surfaces in an AGS. These surfaces include zirconium alloys (pressure and calandria tubes), stainless steel (lattice tubes and end fittings), hardened tool steel (bearing and journal rings), carbon steel (shielding sleeves) and Inconel (bellows). Of these materials, carbon steel is the most susceptible to corrosion, which leads to the formation of hydrated ferric oxide or “rust”. Thus, reddish-brown colored deposits, exhibiting very high specific activities of Fe-55, (600 mCi/g), have been observed on many AGS surfaces in Pickering and Bruce Units during their refurbishments.

In the temperature range relevant to an AGS, namely 60 to 250 °C, rust deposits are subject to two reversible transformations involving the adsorption or desorption of water:

$$\underset{\text{Hydrated Ferric Oxide}}{Fe_2O_3.H_2O} \leftrightarrow \underset{\text{Hematite}}{Fe_2O_3} + H_2O \leftrightarrow \underset{\text{Goethite}}{2\ FeOOH}$$

It is readily calculated that oxidation of a 100 µm layer of the carbon steel components in an AGS would create sufficient goethite to absorb/desorb about 500 g of water; this would be more than enough to explain the sluggish response of Pickering Unit 3 during its AGS moisture injection tests in 1991.

(ii) The formation of nickel and iron carbonyls:

As previously noted, during the production of synthesis gas, not only carbon monoxide and hydrogen are formed but also small amounts of volatile carbonyl compounds of nickel and iron. Iron pentacarbonyl is typically formed by the reaction of carbon monoxide with steel materials in the process equipment. Metal carbonyls can also be formed when synthesis gas is transported or stored in metal containers. Nickel tetracarbonyl and iron pentacarbonyl can cause serious problems during the treatment or use of synthesis gas, mainly due to their thermal decomposition and/or chemical reaction rates at relatively low temperatures, typically below 250 °C.

Metal carbonyls have also been reported in the circuits of graphite moderated and CO_2-cooled reactors that were used in nuclear power stations in the UK in the period 1960 to 2015. As a result, a considerable amount of research into CO and CO_2 radiolysis – including the influence of metal carbonyls on deposit formation – has been carried out at nuclear facilities in the UK. These investigations showed that several percent of nickel and/or iron were found in CO radiolysis products when only trace amounts of these carbonyls were present in the initial CO or CO_2.

5.0 Elevated Deuterium Pickup in Bruce Units 3 & 6 Pressure Tubes:

The original annulus gas hypothesis was formulated in the late 1980s to explain the occurrence of very high [H_{eq}] levels – up to 135 mg/kg – in a pressure tube removed from channel L09 in Pickering Unit 3. The hypothesis was that the entry of H/D into the wall of an operating pressure tube was brought about by a breakdown in the passivity of the oxide film on the *outside* of the tube. This breakdown of passivity was itself caused by two factors:

(i) Flow blockages in the AGS string that was feeding the L09 channel so that the atmosphere above the pressure tube was starved for oxidizing species

(ii) In the absence of sufficient oxidant, nitrogen was able to form a mixed zirconium oxide-nitride layer which induced porosity

Now once again, in July 2021, we are faced with the discovery of more examples of unexpectedly high H/D pickup by pressure tubes. This time, *two* Bruce Units near their channel outlets are involved – B6S13 and B3F16 – as shown in Table 3, below:

Table 3: H/D Pickup at the 12 o'clock Location of Pressure Tubes B6S13 and B3F16

B6S13 Axial Location (mm)	[H] (mg/kg)	[D] (mg/kg)	[H_{eq}] (mg/kg)
8	55	520	315
13	55	530	320
28	57	520	317
44	51	450	276
59	44	360	224
69	46	330	211
79	42	340	212
145	17	109	71.5
B3F16 Axial Location (mm)	[H] (mg/kg)	[D] (mg/kg)	[H_{eq}] (mg/kg)
9	111	1340	781
40	79	880	519
54	67	670	402
113	31	240	151
127	29	190	124

In contrast to the P3L09 example of high H/D pickup that was observed in the body of the pressure tube, the high H/D pickup in Bruce tubes B6S13 and B3F16 involve H/D ingress near the outlet rolled joints of these fuel channels. Furthermore, we note that elevated H/D pickup in the vicinity of a pressure tube rolled joint is, in fact, a well-known phenomenon, with [H_{eq}] levels up to about 150 mg/kg being commonplace in removed tubes after many years of in-reactor exposure. However, as shown in Table 3 above, the B6 and B3 examples exhibit H/D pickups that are two to three times *higher* than any previously reported levels.

V. Urbanic, in studies carried out in the 1980s at AECL Chalk River, has shown that the intimate coupling of 403 stainless steel and Zr-2.5Nb at a pressure tube rolled joint, especially under the high temperature reactor coolant conditions at a fuel channel outlet, increases the hydrogen uptake relative to the hydrogen uptake of an uncoupled sample. In out-reactor tests, the increase in hydrogen uptake is by a factor of ~ 2 for a coupled sample, while in-reactor, the increase is by a factor of ~ 5. These increases are ascribed to a galvanic effect, with the cathodically produced hydrogen being absorbed by the 403 stainless steel. Furthermore, because of the intimate contact between the steel end fitting and the zirconium alloy pressure tube, the hydrogen subsequently diffuses into, and is absorbed by, the zirconium.

V. Urbanic has also investigated the kinetics of hydrogen isotope pickup by pressure tubes near their rolled joints and reported that reactor data, collected over about 15-years of Unit operation, show good agreement with a model based on a declining deuterium ingress rate that exhibits parabolic kinetics. Urbanic's data, presented at a 2002 CNSC Meeting, predict an average deuterium pickup by a mature CANDU reactor at a pressure tube outlet rolled joint of about 180 mg; however, the subsequent diffusion of this deuterium away from its point of entry into the pressure tube determines the final distribution and concentration of deuterium, as discussed below.

Available data on deuterium concentrations near pressure tube outlet rolled joints consistently show high deuterium levels, (up to 120 mg/kg), that drop off rapidly within a few cm of the outlet end of the pressure tube. This is clear evidence that deuterium is diffusing away from its point of entry at the rolled joint. For pressure tubes after at least 10 EFPY of reactor service, the diffusion-lengths, x_d, (which may be derived from published deuterium profiles), are typically ~ 15 cm for the outlet ends of the tubes. Using this type of data, it is possible to convert estimates of the total amount of deuterium picked up at a rolled joint to an approximate value for the average deuterium *concentration* in the vicinity of an outlet rolled joint as follows:

Let the volume of pressure tube material retaining the ingressed deuterium be denoted by V_D, then we have:

$$V_D = \pi \times d \times t \times l$$

Where,

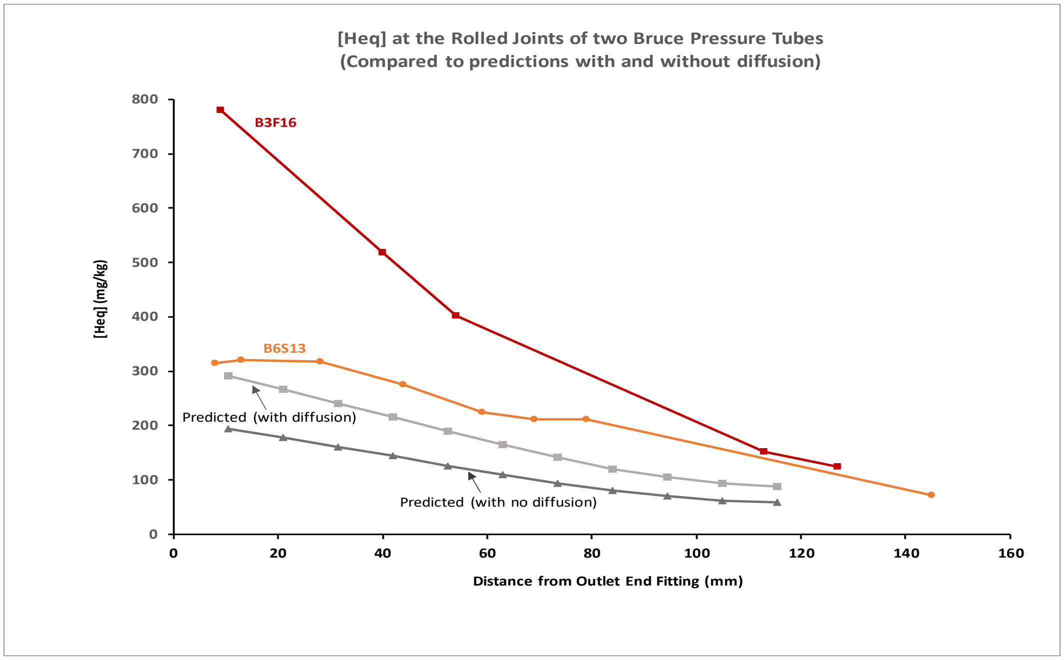
d is the pressure tube diameter = 10.3 cm
t is the pressure tube wall thickness = 0.4 cm
l is the diffusion length = 15 cm

From this relationship, V_D is calculated to be 194 cm^3. Then, taking the density of Zr2.5Nb to be 6.5 g/cm^3 we determine the *mass* of pressure tube containing the ingressed deuterium to be 1261 g. Finally, using Urbanic's 2002 data noted above showing the average deuterium pickup at a pressure tube outlet rolled joint is about 180 mg, we determine that the *average deuterium concentration* in a tube's outlet rolled joint region is 180/1.261, or 143 mg/kg. However, it should be noted that the H/D pickup values reported in Table 5, above, were measured at the 12 o'clock locations of the B6S13 and B3F16 pressure tubes.

Additional data collected by Bruce Power for these tubes, (not included in Table 5), show that the [H_{eq}] values at other circumferential locations are much *lower* that the values at the 12 o' clock location. This behavior is due to the fact that the fuel bundles contained in the 6-meter length of a pressure tube, sit at the bottom of the tube and are therefore slightly off the center-axis of the tube. In addition, this asymmetry *increases* as a Unit ages because neutron-induced creep causes pressure tube circumferential expansion by up to 6% of the original, as-installed diameter.

Published data on the rate of neutron-induced diametral expansion of CANDU pressure tubes shows that the expansion is greatest near the outlet of a tube where the tube's diameter increases at a rate of up to 0.2 % per EFPY. Furthermore, such data show that with 3% diametral creep, (which is reached after about 15 EFPY of Unit operation), the *average* temperature at the 6 o'clock circumferential position is about 10 °C *higher* than the temperature at the 12 o' clock position. This temperature difference causes deuterium entering a pressure tube at its outlet end to migrate to, and accumulate at the coolest location around the tube's circumference, which is at the 12 o'clock position; this redistribution of deuterium has been quantified as shown in Figure 4, below:

Figure 4: [H_{eq}] Profiles (at 12 o'clock): Measured vs. Predicted Data



The profile labelled "*with diffusion*" in Figure 4 was derived by applying a correction factor to the "*with no diffusion*" profile, which itself is based on V. Urbanic's data, (noted above), extrapolated to 30 EFPY of Unit operation. A correction factor of 1.5 was selected based on the average ratio {[H_{eq}] at 12 o'clock}/{[H_{eq}] at 6 o'clock} observed for CANDU pressure tubes.

The profiles presented in Figure 4 show that the redistribution of deuterium induced by the temperature gradient between the top and bottom of the outlet end of a pressure tube *is insufficient* to account for the elevated [H_{eq}] levels observed at the B6S13, and especially at the B3F16 outlet rolled joints. Thus, it is evident that an additional source of deuterium must be invoked to account for the observed [H_{eq}] levels in these pressure tubes. This conclusion is clearly *not in agreement* with the comments made by Bruce Power, in a letter to the CNSC dated September 9th, 2021, (File No: BP-CORR-00531-02004), which stated:

> *The apparent cause evaluation completed by Bruce Power, identified through two independent sources, determined the observed redistribution of [H]eq is due to the temperature gradient, with the top of the pressure tube cooler than the bottom. Bruce Power is working with industry to finalize the root cause of the elevated [H]eq.*

Before concluding this Section, it is worth considering an additional, and very fundamental reason to reject the proposal that the high [Heq] observed near outlet rolled joints of a number of Bruce pressure tubes is solely due to the redistribution of ingressed H/D caused by thermal diffusion from hotter to colder regions of the tube. Thermal diffusion is certainly a factor in the distribution of ingressed H/D in a pressure tube. However, the final distribution of hydrogen isotopes in a pressure tube is not only controlled by *thermal gradients*, but also by *concentration gradients*, especially at the outlet end of the tube. Thermal gradients generally control the *circumferential* distribution of ingressed H/D, but as we have already shown, these distributions differ quantitatively by less than a factor of two between the hot and cold regions at the bottom (hot) and cold (top) of a tube. By comparison, *concentration gradients* determine *axial* H/D distributions in the region between the outlet end of a pressure tube and up to about 100 cm inboard of this location, and it is these distributions that need to be evaluated.

By way of a useful example, consider the [Heq] at the outlet end of pressure tube B3 F16. Data reported by Bruce Power for this tube, (See BP-CORR-00531-01863, issued July 16th, 2021), show a [Heq] value of 680 mg/kg at a location 1 cm from the outlet end of the tube, that drops to about 100 mg/kg at a distance of approximately 13 cm inboard of the outlet – See Figure 5, below. At the time of these measurements pressure tube B3F16 had been exposed in-reactor for 271,330 hot hours, equal to about 27 EFPY.

Figure 5: Measured [Heq] Data for the Outlet End of Pressure Tube B3F16

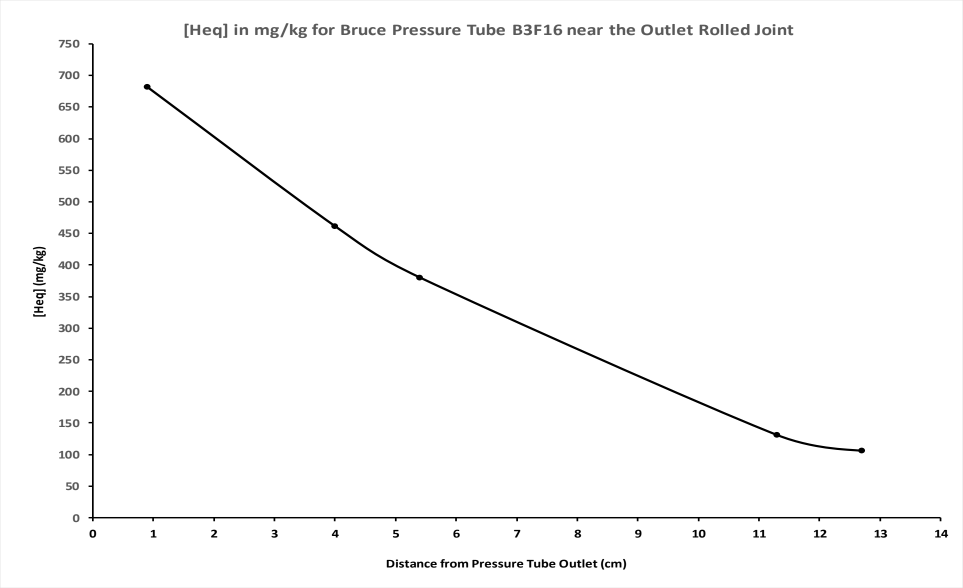
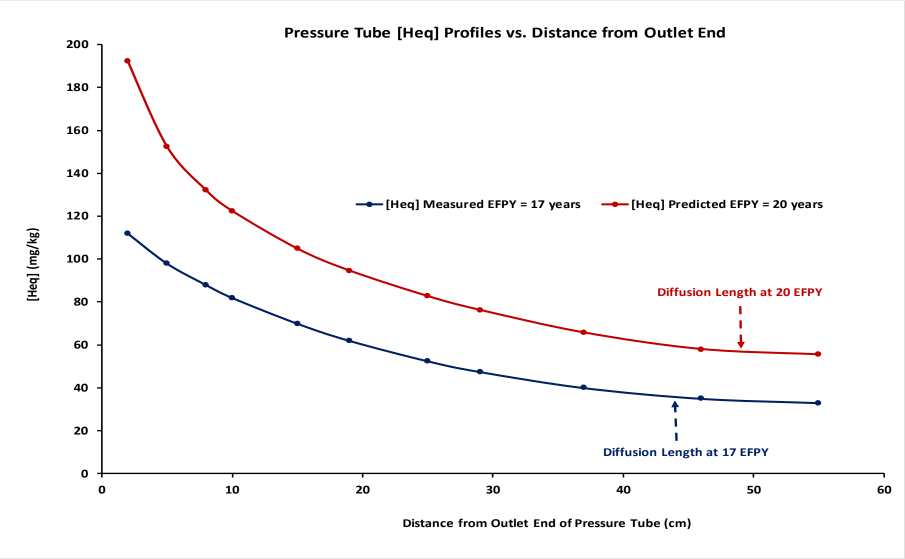


Figure 5 shows the variation of [Heq] for pressure tube B3F16 up to a distance of 13 cm inboard of the outlet end of the pressure tube. This graph provides a measure of the *diffusion length*, L_D, of the H/D, defined as the distance from the end of a pressure tube to a point at which the hydrogen isotope concentration has dropped significantly, say by a factor of at least 3. It is useful to compare this value for the B3F16 diffusion length, (i.e. $L_D = 13$ cm), to values measured or predicted in other pressure tubes. Thus, we have selected two such examples as illustrated in Figure 6 below:

(i) A measured [Heq] profile, see D. Rogers, 2016, for a pressure tube after 17 years of service.
(ii) A calculated [Heq] profile, see D. Metzger, 2019, for a pressure tube after 20 years of service.

Figure 6: [Heq] Profiles near the Rolled Joints for two Exposures



A convenient way to estimate a diffusion length L_D is to consider Brownian motion and the random walk of atoms in a lattice. This approach leads to a diffusion distance of atoms in a 2D space according to the relation:

$$L_D = \sqrt{4Dt}$$

Where,

D is the diffusion coefficient in cm^2/s, and t is the exposure time in seconds

For the case of the diffusion of deuterium at the outlet rolled joint of a pressure tube, where the temperature is ~ 300 °C, D is equal to 9.02×10^{-7} cm^2/s and if we measure the exposure time in years instead of seconds, we may write:

$$L_D = \sqrt{4 \times 9.02 \times 3.156 \times t_{EFPY}}$$

Where,

t_{EFPY} is the number of effective full power years of in-reactor exposure

Using this relationship, we determine the L_D for a 17-year exposure to be 44 cm, and for a 20-year exposure to be 48 cm. As noted above, the typical diffusion length of H/D in pressure tubes corresponds to a concentration of ~ 30 % relative to the concentration at the pressure tube outlet rolled joint. On this basis, the calculated values of L_D for the two examples under consideration are in excellent agreement with the values shown by the [Heq] profiles in Figure 6.

However, if we now try to apply the above relationship to determine L_D for the B3F16 example shown in Figure 5, we run into problems because this sample was subject to a 27-year exposure but exhibits an L_D of only 13 cm. Such a small L_D implies an in-reactor exposure of less than 2 years. It appears the only way to explain this apparent anomaly is to assume that for the B3F16 pressure tube, H/D ingress has not been slow and uniform, but was subject to a recent event – say within the last 3 years – that led to the rapid entry of H/D at or near its outlet rolled joint. This conclusion is clearly at odds with the suggestion that the high [H_{eq}]'s observed in Bruce Units 3 & 6 are solely due to the redistribution of ingressed H/D by thermal diffusion from hotter to colder regions of a pressure tube.

In Section 6 of this report, I review the available evidence that *the annulus gas systems* of Bruce Units 3 and 6 are the most likely source of the elevated [H_{eq}] levels observed in the B3F16 and B6S13 outlet rolled joints.

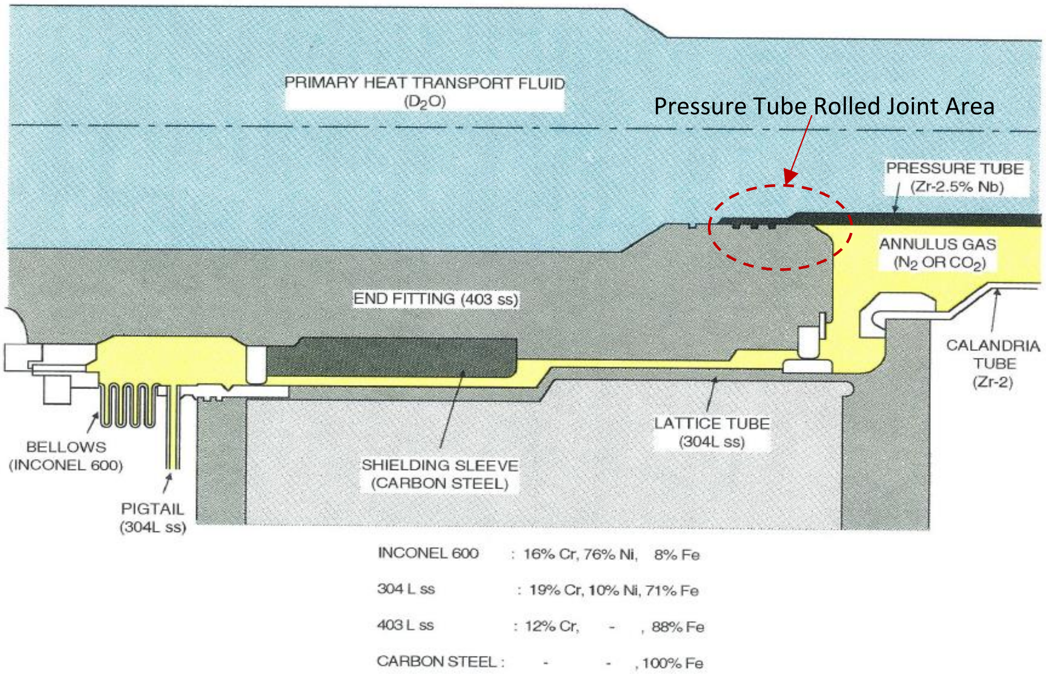
6.0 A New Annulus Gas Hypothesis for Bruce Units 3 and 6

As previously discussed, the entry of H/D into a pressure tube at its outlet rolled joint is usually attributed to "galvanic corrosion' induced by the close coupling of a zirconium pressure tube with a steel end fitting. The electrochemical series predicts that iron in the steel will corrode more rapidly than zirconium. In addition, most of the protons that are discharged by the oxidation reaction are absorbed by the steel. Nevertheless, because of its affinity for hydrogen, some of the hydrogen released by this galvanic corrosion reaction is also absorbed by the zirconium.

The results of a comparative study of the uptake of hydrogen by zirconium alloy/transition metal couples in 300 °C water has been presented in a 1993 IAEA report – IAEA-TECDOC-684. The study showed that *the presence of nickel* in the transition metal alloy used to form the couple to a Zr-2.5Nb specimen, *promoted hydrogen pickup by the zirconium*. Pure nickel couples to Zr-2.5Nb led to pickups as high as 3780 mg/kg [H_{eq}] after only 10 days of in-reactor exposure. This hydrogen pickup is 3 to 10 times *higher* than the pickups measured for stainless steel couples, such as the 403 or 304 varieties used for end fitting components in a CANDU reactor.

Figure 6, below, presents a schematic of the design and construction materials used in a CANDU AGS. While the Zr-2.5Nb pressure tubes only make direct contact with 403 stainless steel at the end fittings, (which contain no nickel), the remaining components in proximity to the pressure tubes are fabricated from nickel-rich alloys such as Inconel 600 and 304 stainless steel. However, the question remains: Is there a plausible mechanism by which nickel is transported within an AGS, to a pressure tube rolled joint? – specifically, the area highlighted in red in Figure 7.

Figure 7: Schematic of an End Fitting/Pressure Tube Assembly showing the Annulus Gas System



A considerable amount of research into CANDU annulus gas chemistry was carried out at Ontario Hydro Research Division in the period 1985 to 1995. This research included the analysis of samples from the annulus gas systems of Units 2, 3, 4, and 8 at Bruce NGS. A consistent, and remarkable feature of these analyses was the detection of *iron and nickel* at concentrations as high as 5 mg/g in viscous/oily deposits collected at locations tens of meters from the Unit's reactor core – a region of an AGS where the temperatures is as low as 60 °C. This observation is consistent with the presence of Fe and Ni carbonyls in the AGS of these Units. Additional evidence for the formation of transition metal carbonyls in these AGS is seen in the detection of the gamma-active species listed in Table 4.

Table 4: Radioactive Species Detected in a Bruce Unit 3 Annulus Gas Deposit Sample

Radionuclide	Source	Activity (Bq/gram)
Mn-54	Fe-54(n,γ)Mn-54	57
Fe-59	Fe-58(n,γ)Fe-59	33
Co-58	Ni-58(n,p)Co-58	195
Co-60	Co-59(n,γ)Co-60	171
Mo-99	Mo-98(n,γ)Mo-99 and U-235(n,f) Mo-99	149,370
Tc-99m	Mo-98(n,γ)Mo-99 → Tc-99m	183,150
Ru-103	U-235(n,f) Ru-103	137,160
Ru-106	U-235(n,f) Ru-106	32,150
Os-191	Os-190(n,γ)Os-191	34,350
Ir-194	Os-192(n,γ)Os-193 → Ir-193(n,γ)Ir-194	2,920

The source terms in Table 4 involve transition metals that are known to form volatile carbonyls at relatively low temperatures – typically less than 120 °C – by direct action of CO gas on the exposed metal. These metals include: iron, cobalt, nickel, molybdenum, ruthenium, osmium and iridium.

Of all the radionuclides listed in Table 6, Co-58 is of particular interest because it is produced by neutron activation of nickel through the Ni-58(n,p)Co-58 nuclear reaction. This means that the nickel observed in a deposit collected *well outside* of a Unit's reactor core, *must have passed through the core* in order to be activated to Co-58, implying the nickel was subject to vapor-phase transport in the Bruce Unit 3 AGS. However, it is also significant that the level of activation of the nickel in the sample is quite low, ($\sim 4 \times 10^4$ Bq/gram), indicating the nickel was subject to only a short, (< 10 day), period of irradiation.

These observations are consistent with the history of this particular Bruce sample which reads as follows: In the period April 12th to 17th, 1990, Bruce Unit 3 was shut down for routine maintenance. After startup on the 17th, very low CO_2 gas flow rates were measured in several flow rotameters and an oily yellow substance was observed to accumulate on the sight glass of the main AGS flow transmitter tube FT2. Finally, on April 23rd, the FT2 assembly was removed and a sample of the yellow deposit was collected and reserved for subsequent analysis.

This sequence of events coincides with a period when the Bruce Unit 3 AGS was exposed to the following atypical operating conditions:

(i) The AGS was stagnant and/or subject to only low CO_2 flow
(ii) Because Bruce Unit 3 was recently shut down, the AGS was still subject to intense gamma-radiolysis
(iii) The AGS was deprived of oxidizing agents and there was no O_2 addition requirement at the time
(iv) The AGS was held at a relatively low temperature, (~ 60 °C), for several days and then returned to its normal operating temperature, (~ 150 °C)

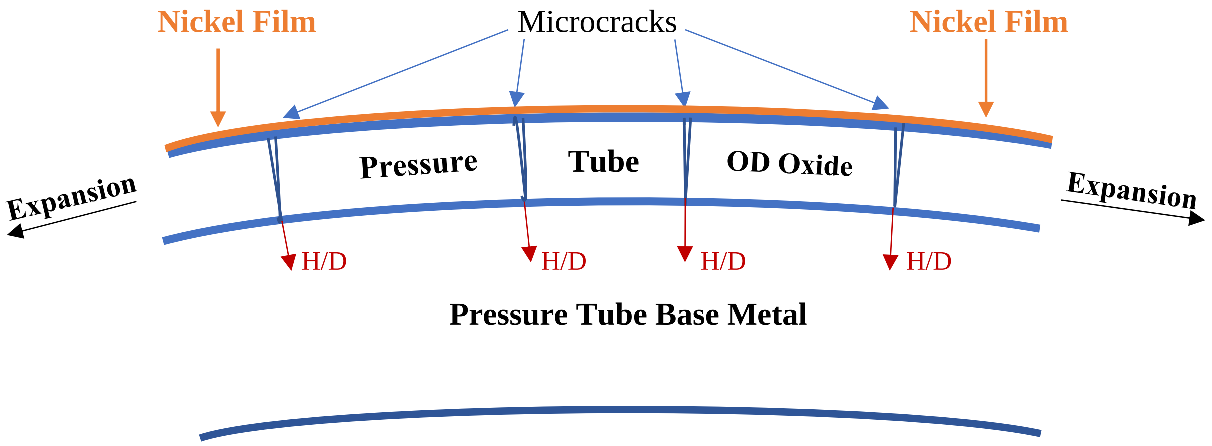
All of these conditions favor the accumulation of carbon monoxide in the AGS, and because of the low temperatures, the production of nickel and other transition metal carbonyls was also promoted.

T. Baird at Glasgow University was among the first to investigate the radiolysis of mixtures of CO and CO_2, and reported that iron and nickel carbonyls exerted a pronounced influence on radiolytic deposit formation. Baird's investigations showed that iron and nickel impurities in the CO were concentrated from a few ppm in the initial gas phase, to sevcra1 per cent in the deposited solids. From this observational evidence, I propose the following mechanism for the mobilization and transport of nickel in an AGS:

- Gamma-radiolysis of CO_2 leads to the continuous production of CO
- CO reacts selectively with Ni alloys in an AGS, forming volatile $Ni(CO)_4$, b.p. 43 °C
- As a Unit is returned to full power, $Ni(CO)_4$ decomposes at $T > 150$ °C to Ni and CO
- The decomposition of $Ni(CO)_4$ is accompanied by Ni deposition on hot AGS surfaces

An important feature of this proposed mechanism of nickel transport is that Ni deposition during reactor startup occurs mainly on the *hottest sections* of an AGS which are located at a pressure tube's outlet rolled joint where the surface temperature at full power reaches 300 °C. This deposition process eventually leads to the formation of a thin film of nickel which, as we shall see, has consequences for subsequent ingress of H/D into this region of a Unit's pressure tubes.The outside diameter (OD) of a pressure tube is normally well-protected from direct H/D ingress from the AGS by a thin, (2 – 4 µm), passive oxide film. However, after many years of Unit operation this film is increasingly stressed by the slow, but inexorable circumferential expansion caused by neutron-induced creep of the irradiated Zr-2.5Nb pressure tube. This leads to the formation of microcracks in the pressure tube OD oxide, as shown in Figure 8, below.

Figure 8: Schematic of the Formation of Microcracks in the OD Oxide at the Outlet End of a Pressure Tube with a Nickel Deposited Film



Under normal operating conditions, with a plentiful supply of oxidizing species in the AGS, these microcracks would be self-repairing and of no concern to a pressure tube's fitness for service. However, the presence of a nickel film on the OD surface of the pressure tube oxide, prevents entry of oxidizing species such as D_2O and O_2 while providing a "window" for the facile entry of H/D into the wall of the pressure tube. Available data show that under such conditions, H/D pickups > 100 mg/kg over very short, (< 1 month), time intervals are possible.

However, there is an additional factor that must be considered in assessing H/D entry from an AGS in the region of a pressure tube rolled joint. The annulus gas flow rate through a single channel of a CANDU reactor is as low as 0.054 l/s at the end of a channel. At this location the annulus has an effective cross-sectional area of only ~2.5 cm^2 due to the tight-fitting bearing journals and sleeves at the end of each channel. In addition, after exiting a channel, the annulus gas passes through a second narrow bearing before entering a metal bellows assembly. Gas exits these bellows through a 0.2-inch ID stainless steel tube (known as a pigtail), which provides the approximately 1-meter-long interconnecting tubing to the next AGS channel, (See Figures 7, 9a and 9b).

The question then arises: how will this tight-fitting arrangement of concentric tubing behave in a mature reactor subject to iron and nickel deposition? And how will the annulus gas flows vary as the temperature of a Unit changes from ~ 60 °C under shutdown conditions to ~ 300 °C at full power? Measurements of Darlington end fitting bearing discharges under simulated pressure tube leak conditions have shown that, at reactor operating temperatures (~300 °C), the discharge through a channel bearing assembly is reduced by a factor of about two compared to the cold (room temperature) rate.

Furthermore, the complex AGS geometry in the region of a pressure tube rolled joint, and the fact that a pressure tube rests on bearing journals and sleeves *at the bottom of each channel*, will *decrease* the gas flow in this region while *increasing* the gas flow at the top of the pressure tube-end fitting assembly. This will have a major impact on the deposition of iron and nickel in this region leading to enhanced coverage at the top of the tube, with little or no coverage at the bottom. Thus, the net effect of this difference is that we would expect greater H/D ingress at the top of the tube, compared to the bottom, *with no need to invoke any H/D diffusion effects on* [H_{eq}].

Figure 9a: Schematic of a Pressure Tube-End Fitting Assembly Showing the Location of a Pressure Tube Bearing Journal

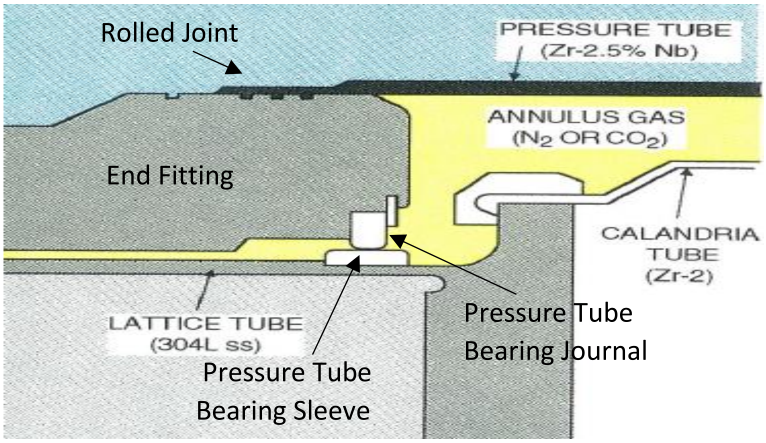
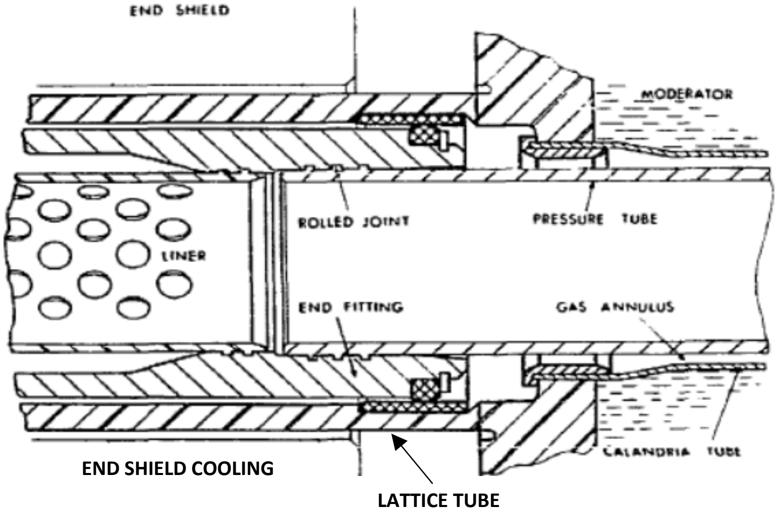


Figure 9b: Engineering Drawing (To Scale) of a Pressure Tube-End Fitting Assembly



Figures 9a and 9b show how convoluted an annulus gas system is in the region of a pressure tube-to-end fitting rolled joint. However, these Figures also reveal another important feature of this location in a CANDU reactor, namely, the close proximity, (~ 5 cm), of a pressure tube's bearing journal, (and sleeve), to the lattice tube/end shield cooling assemblies. This is significant because of the extreme temperature difference between these two locations.

Thus, a pressure tube outlet rolled joint temperature is typically about 300 °C during full-power reactor operation, while a lattice tube is typically below 100 °C by virtue of its close contact with the reactor's two, (east and west), end shield cooling, (ESC), systems. An ESC removes about 3 MW of thermal energy from the hot end fittings of an operating reactor.

This 200 °C temperature difference implies a thermal gradient of about 40 °C/cm between an outlet end fitting and a lattice tube, resulting in a thermal gradient that is much greater than the postulated thermal gradient of less than 2 °C/cm between the bottom, (6 o'clock), and the top, (12 o'clock), location at the outlet of a pressure tube.

Unfortunately, it is beyond the scope of this intervention to enter into great detail of the complexities of a CANDU end shield cooling system. However, suffice it to say that the various ΔT's in an ECS need to be determined in order to accurately predict the associated distributions of ingressed H/D in the vicinity of a pressure tube's outlet rolled joints. (See Addendum 2 and 3, below, for further discussion of this issue).

7.0 <u>Discussion</u>:

In July 2021, very high $[H_{eq}]$ levels were measured in pressure tube samples removed from Bruce Units 3 and 6. At a CNSC Public Meeting held on September 3rd, 2021, to discuss this finding, Bruce Power was asked by Commissioner Lacroix for its interpretation of this observation, to which Bruce Power Chief Engineer, Gary Newman, replied:

> "*We're not seeing a change in the rate of hydrogen uptake. What we're seeing is a redistribution (of the hydrogen) to the cooler region at the top of the pressure tube. So, it's not an acceleration but a redistribution*".

Here we see Bruce Power proposing that the very high $[H_{eq}]$ levels measured in a number of pressure tubes from Bruce Units 3 and 6 are simply due to a *redistribution* of ingressed H/D and that this ingress does not represent *acceleration* in the H/D pickup rate. However, in order to validate the assertion that there is no accelerated H/D ingress occurring in Bruce pressure tubes, we need to look for evidence of this in the available data. With this in mind, I have collected recent data reported for Bruce Unit 3 pressure tubes near the 12 o'clock location as shown in Table 5, below. The Table includes values for the initial hydrogen in the pressure tube ingot, $[H_{Init}]$, which is needed to make a small correction to the hydrogen pickup data used in calculating the ratio $\{[H]_{Cor} / 0.5[D]\}$, where:

$$[H]_{Cor} = [H] - [H_{Init}]$$

Table 5: Hydrogen and Deuterium Concentrations Near the Outlet Rolled Joints in Selected Pressure Tubes from Bruce Unit 3

Bruce Unit 3 Pressure Tube ID (~10 mm from ORJ $^{\text{Ref 1}}$)	[D] (mg/kg)	[H] (mg/kg)	$[H_{Init}]$ (mg/kg)	Ratio $\{[H]_{Cor}/0.5[D]\}$
F16	1340	111	12.6	0.147
L11	790	60	9.3	0.128
G15	853	103	11.3	0.181
K10	1016	74	7.4	0.156
Q16	853	96	10.9	0.233
H06	730	66	15.0	0.329
X09	475	73	14.9	0.245
O20	921	96	12.3	0.182
Q12	850	99	10.2	0.209
N04	337	58	14.7	0.257
O15	303	56	8.7	0.312
O17	122	28	9.0	0.311
O13	443	72	12.5	0.269
P14	191	34	9.0	0.262
Q13	582	87	11.7	0.259
L12	156	27	6.7	0.260
F05	75	25	11.7	0.355
L22	42	24	9.3	−
R10	199	26	5.5	0.206
S13	314	38	6.0	0.204

Ref 1: ORJ = Outlet Rolled Joint

Inspection of the data in Table 5 shows that there is a great deal of variability in the deuterium concentrations in these samples: from a high of 1340 mg/kg for sample F16, to a low of 42 mg/kg in sample L22. In a few cases, such as sample X09, the pressure tube outlet temperatures are known to be somewhat lower, (~ 290 °C), than the temperatures for samples from high power channels such as L12, (~ 297 °C); however, the D pickups for these samples are *the reverse* of what might be expected based in these temperatures alone; thus, the D-pickup is 475 mg/kg for X09, but only 156 mg/kg for L12.

As noted above, Table 5 includes values of the $[H]_{Cor}/\{0.5\times[D]\}$ ratio, where $[H]_{Cor}$ represents the *corrected* hydrogen concentration, derived by subtracting $[H_{Init}]$ from the measured [H], and the factor of 0.5 in the denominator is needed to convert the ratios to *atom ratios*. What is noteworthy about these values is that the atom ratios are relatively constant, averaging 0.24 ± 0.08, even though the tube-to-tube values of $[H_{eq}]$ vary by a factor of more than 20.

The most important question concerning the data in Table 5 relates to the notion of "redistribution" of ingressed H/D. This phenomenon has been proposed by Bruce Power to explain the high H/D levels observed in some B3 and B6 tubes analyzed in July 2021. However, the suggestion that ingressed H/D could *redistribute* within the wall of a pressure tube is not new. Thus, in a COG

Report issued in 1998, we read in an Appendix C entitled: “*Influence of Temperature & Concentration Gradients on the Redistribution of Hydrogen Isotopes*”:

> *Based on a thermal hydraulic simulation, temperature differences between the 6 and 12 o’clock locations in a tube with 2% diametral creep have been calculated to be 20 °C. Modeling results, assuming a 20 °C temperature difference, show that the deuterium concentration may be up to ~ 17% higher at the top compared to the bottom of the pressure tube.*

The modeling calculation referred to in this COG Report is for a pressure tube after about 12 EFPY of operation which was the longest exposure of pressure tubes in Canadian reactors at that time (1998). If we extrapolate this calculation to currently operating Units, we would expect the diametral creep to have increased from ~ 2% to ~ 6%. The resulting diffusional redistribution of H/D may then be estimated using the following formalism:

Assuming that the diffusion of hydrogen isotopes in zirconium alloys is a thermally activated process, an Arrhenius-type temperature dependence is expected which may be modelled by the following equation:

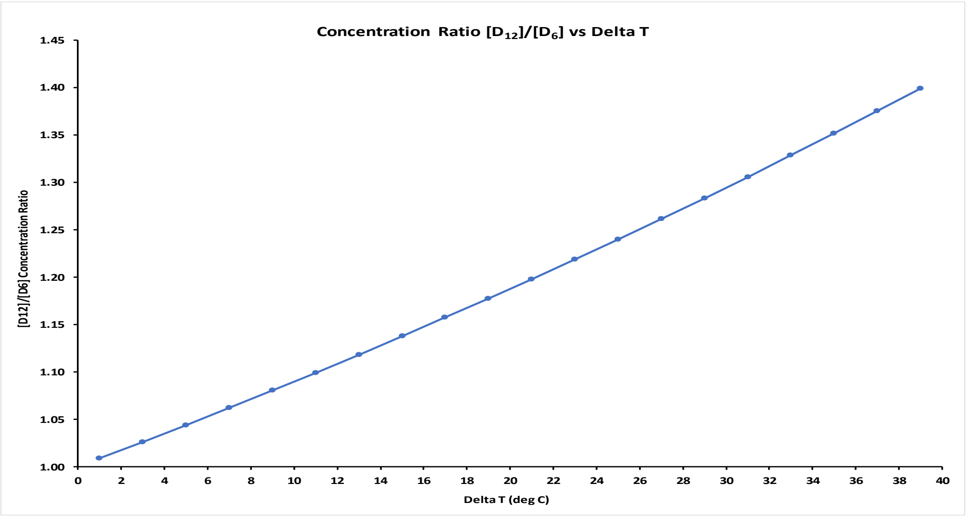
$$\ln\{[D_{12}]/[D_6]\} = (Q/R) \times \Delta T/(T_6 \times T_{12})$$

where,

$[D_{12}]$ is the deuterium concentration near the pressure tube outlet at 12 o’clock
$[D_6]$ is the deuterium concentration near the pressure tube outlet at 6 o’clock
Q is the activation energy for deuterium diffusion in Zr-2.5Nb = 22.7 kJ $\text{mol}^{-1}\text{K}^{-1}$
R is the gas constant = 8.314 J $\text{mol}^{-1}\text{K}^{-1}$
T_6 is the temperature at the bottom, 6 o’clock, position at the outlet of the pressure tube
T_{12} is the temperature at the top, 12 o’clock, position at the outlet of the pressure tube
ΔT is the temperature difference between the 6 o’clock and 12 o’clock locations

Figure10, below, is a graphical representation of this equation plotted for ΔT values up to 40 °C, which may be considered as the highest value of ΔT achievable in mature pressure tubes.

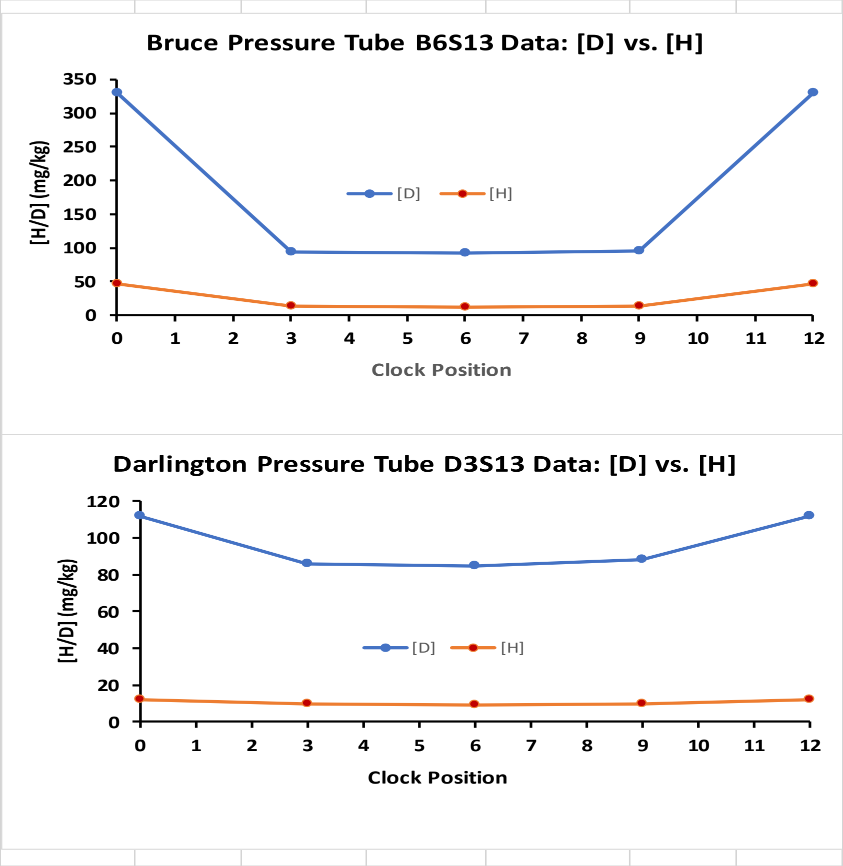
Figure 10: Deuterium Concentration Ratio $[D_{12}]/[D_6]$ vs. $\Delta T = (T_6 - T_{12})$



This formalism was previously used to analyze [H] and [D] concentration data in the P3LSFCR sample set at different clock positions and locations approximately 150 mm from the pressure tube outlets – see for example, OHRD 1994 Report A-NFC-94-115-K. For this particular case the observed $[D_{12}]/[D_6]$ ratios were in the range 1.18 ± 0.06 corresponding to a ΔT of 20 °C which is in good agreement with predictions of ΔT for a CANDU reactor after 12 EFPY of Unit operation. Similar H/D data for a Darlington pressure tube, (D3S13), after 25 EFPY was recently reported by OPG – See the July 2021 OPG Memo: NK38-CORR-31100-0934854. For this pressure tube, data are reported at distances between 8- and 120-mm inboard of the outlet rolled joint and at several different circumferential (clock) positions. The observed $[D_{12}]/[D_6]$ ratios for these samples are in the range 1.25 ± 0.05 corresponding to a ΔT of about 25 °C. Once again, these values are in good agreement with predictions of ΔT for a CANDU reactor after 25 EFPY of Unit operation.

Turning now to [H/D] data for a Bruce pressure tube, namely B6S13, (See OPG Memo: NK38-CORR-31100-0934854), we find the observed $[D_{12}]/[D_6]$ ratio is about 3 which gives a physically unrealistically high value > 60 °C for the corresponding ΔT. This indicates that an additional, (non-thermally activated), process is involved in the H/D ingress into the B6S13 pressure tube. This conclusion is supported by the behavior of H (light hydrogen) in the B6S13 sample which is quite different to the behavior of H in the D3S13 sample, as shown in Figure 11, below. This, once again, is a good indication of an additional source of H/D for the B6S13 sample.

Figure 11: [D] and [H] for Pressure Tubes at Different Clock Positions: Data for Bruce and Darlington near the Outlet Rolled Joints



The data in Figure 11 are taken from measurements using hot vacuum extraction spectrometry reported in March 2021 by B. Payne at the Canadian Nuclear Laboratories – See Report # COG-19-1034. These results are also discussed in a CNL memo, (ID No: RCC-21-018), dated September 17th 2021, entitled: *Concentrating Hydrogen Isotopes at the Top of Tube at the Outlet rolled Joint Region,* where we read:

> *Hydrogen isotopes in the rolled joint region of the pressure tube originate from three sources: hydrogen initially present in the tube from fabrication, deuterium (including minor amounts of hydrogen) entering the tube during operation from corrosion reactions between the tube and coolant, and deuterium (including minor amounts of hydrogen) entering the tube from the stainless-steel end fitting during operation from corrosion reactions between the end fitting and coolant. The operational sources are evaluated during surveillance examinations and ingress through the end fitting has been observed to be the greater contributor to hydrogen isotope concentrations in this region. For the case of B6S13, the ingress through the inside surface of the pressure tube is in line with other surveillance tubes and scrape campaigns, while the ingress through the rolled joint is marginally greater but well within prior experience projected forward. There is no need, or obvious evidence, for an additional and unknown source of hydrogen to account for the current observations.*

There are two statements that I would question in this CNL assessment of the root cause of the high [H_{eq}] observed in pressure tube B6S13:

(i) The statement that there are only *three* sources of the hydrogen observed in the vicinity of the outlet rolled joint region of a pressure tube
(ii) The statement that "*there is no need, or obvious evidence, for an additional and unknown source of hydrogen*"

Both of these statements ignore the existence of H/D entry into a pressure tube from the *annulus gas system*. Certainly, the three operational sources of H/D identified in this CNL memo are generally considered to be the *major* sources of H/D in CANDU pressure tubes; however, H/D entry from the AGS cannot be ruled out *a priori*. Indeed, there are *two* recent examples of pressure tube failures from high H/D pickup – namely, KAPS-2 on July 1, 2015 and KAPS-1 on March 11, 2016 – that were attributed to H/D entry from the AGS of these Units. Specifically, for item (i) above, it is important to consider potential H/D pickup contributions of *light hydrogen,* H – as opposed to heavy hydrogen, D – to the total hydrogen pickups observed in Bruce pressure tubes. The CNL memo identifies two such sources:

- Hydrogen initially present in the tube from fabrication
- Hydrogen present in the primary heat transport water

Table 5 of this report includes values for the initial hydrogen, H_{Init}, for twenty Bruce Unit 3 pressure tubes, from which an average value for [H_{Init}] of 10 ± 5 mg/kg may be calculated. If we conservatively take an upper limit of 15 mg/kg for [H_{init}], this represents the *minimum* value for [H] after in-reactor exposure of these tubes. It follows that any [H] value *greater* than 15 mg/kg is due to entry from external sources of hydrogen such as the heat transport water. However, as previously noted, heat transport D_2O is specified to have an isotopic purity of at least 99.3 % deuterium, so that the light hydrogen content is only 0.7%.

Using these data, it is possible to estimate a *theoretical hydrogen pickup,* [H_{calc}] for each of the twenty measured deuterium pickups referred to above. Thus, starting with the initial hydrogen contents, [H_{Init}], noted in Table 5, we add a contribution from hydrogen that is assumed to have entered the pressure tube as a fixed, (small), percentage of the measured ingressed deuterium. To allow for kinetic isotope effects in the corrosion reactions leading to such hydrogen ingress, (which depends on the square root of the ratio of the atomic mass of deuterium to the atomic mass of hydrogen), this percentage hydrogen ingress is assumed to be equal to $\sqrt{2} \times 0.7\%$, or 1.0% of [D]. Table 6, below, shows the observed [D] and [H] data for twenty Bruce 3 pressure tubes, as well as the calculated hydrogen concentrations, [H_{calc}], expressed as a percentage of the observed [H].

Table 6: Hydrogen and Deuterium Concentrations Near Bruce Unit 3 Outlet Rolled Joints: Comparison of Data at Three Locations Including [H] Predictions as a % of Observations

Bruce Unit 3 Pressure Tube ID	Data for Samples taken at 10 mm			Data for Samples taken at 55 mm			Data for Samples taken at 112 mm		
	[D] (mg/kg)	[H] (mg/kg)	$[H]_{calc}$ as % of Obs	[D] (mg/kg)	[H] (mg/kg)	$[H]_{calc}$ as % of Obs	[D] (mg/kg)	[H] (mg/kg)	$[H]_{calc}$ as % of Obs
F16	1340	111	23.4	670	67	28.8	241	31	48.4
L11	790	60	28.7	350	29	44.1	99	12	85.8
G15	1016	103	20.8	531	63	26.4	178	30	43.6
K10	853	74	21.5	330	35	30.6	120	26	33.1
Q16	730	96	19.0	314	51	27.5	130	32	38.1
H06	310	66	27.4	171	42	39.8	104	41	39.1
X09	475	73	26.9	186	40	41.9	107	24	66.5
O20	921	96	22.4	451	53	31.7	218	35	41.4
Q12	850	99	18.9	400	52	27.3	142	29	40.1
N04	337	58	31.2	87	22	70.8	100	28	56.1
O15	303	56	20.9	151	31	32.9	94	24	40.2
O17	122	28	36.5	103	26	38.6	89	20	49.5
O13	443	72	23.5	216	50	29.3	108	26	52.2
P14	191	34	32.1	125	24	42.7	86	22	44.8
Q13	582	87	20.1	341	61	24.8	139	29	45.1
L12	156	27	30.6	99	23	33.4	83	19	39.6
F05	75	25	49.8	82	23	54.4	69	27	45.9
L22	42	24	40.5	42	21	46.3	43	18	54.1
R10	199	26	28.2	122	20	33.6	93	16	40.2
S13	314	38	24.1	133	19	38.6	98	17	41.1
Averages	–	–	27.4	–	–	37.2	–	–	47.2

Table 6 shows that for these B3 pressure tubes, the observed light hydrogen concentrations are significantly *higher* than the predicted concentrations. In particular, and taking *average* values, the measured light hydrogen concentrations, [H], are 3.7, 2.7 and 2.2 times higher than the calculated values at the 10 mm, 55 mm and 112 mm locations, respectively.

First, however, it is important to note that the theoretical [H] values in Table 8 are calculated based on the following assumptions:

(i) The heat transport D_2O is the sole source of both hydrogen and deuterium pickup.

(ii) The heat transport D_2O in Bruce Unit 3 contains ~ 1% H_2O

(iii) The calculated [H] values are corrected for contributions from the initial hydrogen in the Zr-2.5Nb ingot used to fabricate the pressure tube.

The fact that the observed concentrations are up to three times *higher* than the calculated concentrations is clear evidence that B3 pressure tube hydrogen isotope pickups near their outlet rolled joints do not conform with the proposal that H/D entry into these pressure tubes comes solely from heat transport D_2O. Furthermore, this excess light hydrogen needs to be explained because it contradicts the claim, made in the CNL memo, (ID No: RCC-21-018), dated September 17th 2021, that "*there is no need, or obvious evidence, for an additional and unknown source of hydrogen*."

However, it is acknowledged that there are examples of pressure tubes in other CANDU reactors that *are* consistent with H/D entry solely from the heat transport system. Thus, consider the H/D data reported in the July 2021 OPG Memo: NK38-CORR-31100-0934853 for the Darlington pressure tube D3S13, as shown in Table 7, below. The calculated [H] values in the Table are derived assuming an average [H_{Init}] of 10.5 mg/kg for the three samples of interest.

Table 7: H and D Concentration Data Near a Darlington Unit 3 Outlet Rolled Joint: Comparison of Data at Three Locations Including [H] Predictions as a % of Observations

Darlington Unit 3 Pressure Tube ID	Data for Samples taken at 8 mm			Data for Samples taken at 64 mm			Data for Samples taken at 79 mm		
	[D] (mg/kg)	[H] (mg/kg)	$[H]_{calc}$ as % of Obs	[D] (mg/kg)	[H] (mg/kg)	$[H]_{calc}$ as % of Obs	[D] (mg/kg)	[H] (mg/kg)	$[H]_{calc}$ as % of Obs
D3S13	109	12	96.6	112	12	96.8	122	12	97.7

In contrast to the corresponding data for Bruce Unit 3, (See Table 6, above), these Darlington Unit 3 samples show calculated [H] values that are within a few percent of the observed [H] values.

Thus, in the case of the D3S13 pressure tube at least, the observed H/D entry at the outlet rolled joint is consistent with the heat transport D_2O being the sole source of ingressed hydrogen.
As previously noted, a number of Canadian nuclear industry experts have suggested that the root cause of the high $[H_{eq}]$ observed near the outlets of some Bruce Unit 3 & 6 pressure tubes is the *redistribution* of ingressed $[H_{eq}]$ induced by diffusion of H/D in the temperature gradient at this location; with the top of the pressure tube being *cooler* than the bottom by about 25 °C, so that ingressed hydrogen migrates to, and accumulates at the cooler top of the tube.

However, if this is in fact true, evidence for H/D thermal diffusion in a circumferential temperature gradient should be observed at the outlets of *all* mature CANDU pressure tubes, which is certainly *not* the case for the D3S13 example noted above. Furthermore, proponents of the diffusional redistribution of H/D as the sole cause of the high $[H_{eq}]$ observed at the 12 o'clock position near a pressure tube outlet, should explain how at least *five* Bruce Unit 3 pressure tubes could pick up close to 100 mg/kg of *light* hydrogen at this location.

The corresponding heavy hydrogen pickups were approximately 1000 mg/kg, (See Table 5). This implies a H/D *atom ratio* of about 0.2. And one has to ask: What is the *source* of this light hydrogen? Surely the answer must be: the light hydrogen is coming from the AGS of these Units. So, we need to consider evidence for the presence of light hydrogen in operating AGS.

Unfortunately, there are only a few published data on light hydrogen concentrations, (H_2 or H_2O), in CANDU AGS; however, as shown below, what little data there is, shows three significant trends:

(i) Measured H/D atom ratios are typically in the range 0.1 to 0.25

(ii) H/D ratios are highest immediately after an AGS purge and decrease over time

(iii) H/D ratios tend to be higher in the AGS of older Units

Available evidence suggests that the largest contributor to light water in an AGS is the CO_2 gas supply itself. This is because, at its specified dewpoint of – 45 °C, CO_2 that is deemed to be "dry", nevertheless contains about 70 vpm H_2O.

Studies caried out by myself in the period 1990 to 1998 have shown that light hydrogen, in the form of absorbed water, (H_2O), is always present on the pipework of an AGS and is only *partially desorbed* after system exposures of over 3 hours to dry CO_2, as in a typical AGS purge. (See OHRD Report A-NFC-96-114-P and COG Report COG-96-308).

Such incomplete purges leave significant amounts of light water, H_2O, in the system; and this becomes the initial condition of an AGS at the start of its inter-purge period which usually lasts between 5 and 15 days depending on the Unit. During this time period, water – now mostly as D_2O – builds up in the system via the reverse water gas shift reaction, ($D_2 + CO_2 \rightarrow D_2O + CO$), which is in line with trend (ii) noted above.

There are a few especially useful sets of data derived from previous measurements of H/D ratios in operating AGS; e.g., data for Units at Darlington, Bruce and Point Lepreau, as presented below:

a. **Darlington Unit 1** – See OHRD Report A-NFC-96-114-P

FTIR data recorded in 1996 for Darlington Unit 1 show that the AGS water vapor isotopic composition is quite variable over a purge cycle. Thus, while it is generally above 90%, tests show that the H/D isotopic always increases to a value of about 96% D as the high dewpoint limit (~ − 10° C) of the AGS is approached. However, during a system purge, (which typically lasts 2 to 3 hours), the isotopic purity of the annulus gas water vapor rapidly degrades to about 60%. This change is brought about by the addition of CO_2 makeup gas which contains trace amounts, (50 – 100 vpm), of light water, (H_2O), impurity.

b. **Bruce Unit 3** – See OHRD Report A-NFC-95-19-P

FTIR analysis of the vacuum pyrolysis products of a sample of viscous yellow deposit removed from flow Bruce Unit 3 rotameter FG2 in 1995 revealed the presence of $NH_3/NH_2D/NHD_2$, in addition to the expected $H_2O/HDO/D_2O$. The formation of deuterated ammonia species in an AGS filled with CO_2 is surprising, but is undoubtedly due to the relatively high impurity specification of ~ 800 vpm N_2 permitted in the “bone-dry” CO_2 used in all Bruce AGS. This nitrogen undergoes radiolytic combination reactions with H/D-containing impurities in an AGS to produce gaseous $NH_3/NH_2D/NHD_2$ species which react further to form solid deposits containing complex C/N/O/H/D compounds. These compounds release water, ammonia, CO and CO_2 under vacuum pyrolysis – species that are readily detected and quantified by gas-phase FTIR analysis. The H/D ratios determined for hydrogen containing gases released by pyrolysis of the Bruce 3 AGS deposit sample were 0.80 for ammonia and 0.75 for water. However, it is likely that these ratios are elevated above their original, in-reactor values, by the adsorption of light water from exposure of the sample to room air prior to analysis.

c. **Point Lepreau** – See New Brunswick RPC Report PET/96/415

On-line GC measurements were carried out on the AGS at Point Lepreau in the period 1994 to 1995. Maximum simultaneous D_2, HD, and H_2 concentrations of 611 vpm, 196 vpm, and 26 vpm, respectively were measured prior to system purge. This composition corresponds to a H/D ratio of 0.15. This observation is consistent with previously discussed modes of ingress of H_2O via the CO_2 supply. However, the CO_2 makeup rate at Point Lepreau can only partially account for the observed rate of rise in the AGS HD concentration, indicating that additional source(s) of light water, such as the End Shield Cooling System, (ECS), must also contribute to the observed hydrogen concentration in the Point Lepreau AGS. A similar example of in-leakage of light water into an operating AGS from a leaking ECS has been reported for Pickering Unit 6.

From these data it may be concluded that, although H/D ratios in AGS in CANDU reactors operating at Canadian nuclear stations may vary somewhat over a purge cycle, these ratios are on average in the range 0.15 ± 0.05. This shows that a typical CANDU AGS contains sufficient hydrogen, most probably in the form of light water, H_2O, to account for the elevated levels of H pickup observed near the outlet ends of some Bruce pressure tubes.

8.0 Additional AGS Chemistry Data for Units at Bruce and Pickering NGS:

In the week of November 5th, 2021, I received a large amount of AGS chemistry data from Bruce Power and OPG. Of particular interest in this newly available data are oxygen concentrations measured on a regular basis over at least 5 years for a number of currently operating or recently shutdown CANDU Units, namely: Bruce Units 3 and 6; Pickering Units 1, 4, 5, 6, 7, and 8. As discussed below, these data show a great deal of variability between these eight Units, but are nonetheless useful in estimating leak rates for these AGS.

In an earlier section of this email it was determined that, in the absence of any significant AGS leakage, a minimum oxygen concentration, [O_2], of about 1000 vpm is more than sufficient to oxidize ingressed D_2 and CO and to maintain a passive oxide film on the outside surface of a Unit's pressure tubes. Furthermore, oxygen additions that bring the system [O_2] to levels *above* 1000 vpm may be expected to be simply lost through system leaks and therefore to have no detrimental effects on the preferred AGS chemistry.

Inspection of the oxygen addition data for the eight Units noted above shows that the average oxygen addition brings the system [O_2] to ~ 1.0 vol% for Bruce Units and to ~ 2.0 vol% for Pickering Units, or 10,000 vpm and 20,000 vpm, respectively, i.e. concentrations well in excess of the minimum requirement. Thus, we may safely assume that any subsequent depletion of [O_2] in an AGS, especially over the first few days immediately after an oxygen addition, must be attributed to system leakage – at least until the [O_2] falls below about 1500 vpm. In addition, since AGS leakage is dealt with by adding pure CO_2 make-up gas to the system, [O_2] depletion is an indirect measure of the AGS leak rate.

To demonstrate this behavior, consider the oxygen concentration data for two Units, one exhibiting rapid [O_2] depletion, (Pickering Unit 4), and the other showing slow [O_2] depletion, (Pickering Unit 5). Because individual oxygen additions vary somewhat from one addition to another, and from Unit to Unit, it is convenient to consider a *fractional depletion* defined as follows:

Let the initial, *maximum* oxygen concentration in an AGS be given by C(0), and the oxygen concentration at a time t days after the oxygen addition be represented by C(t), then we may write the equation:

$$C(t)/C(0) = 1 - f_{dep} \times t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where,

f_{dep} is the *fractional* oxygen depletion in the AGS per day

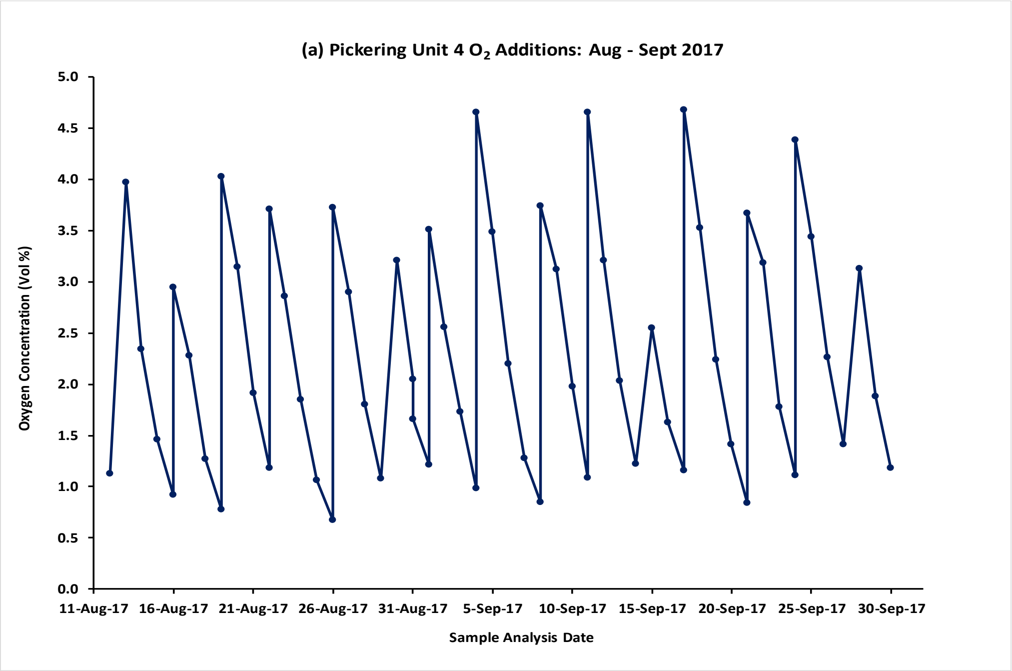
Thus, for example, if 25% of the initial O_2 is lost in 1 day, f_{dep} is equal to 0.25, and C(t)/C(0) is equal to 0.75. Then, for a steady state leak, station data for an operating AGS should show a relatively constant value for f_{dep}. Applying the above equation to data for Pickering Units 4 and 5 we find:

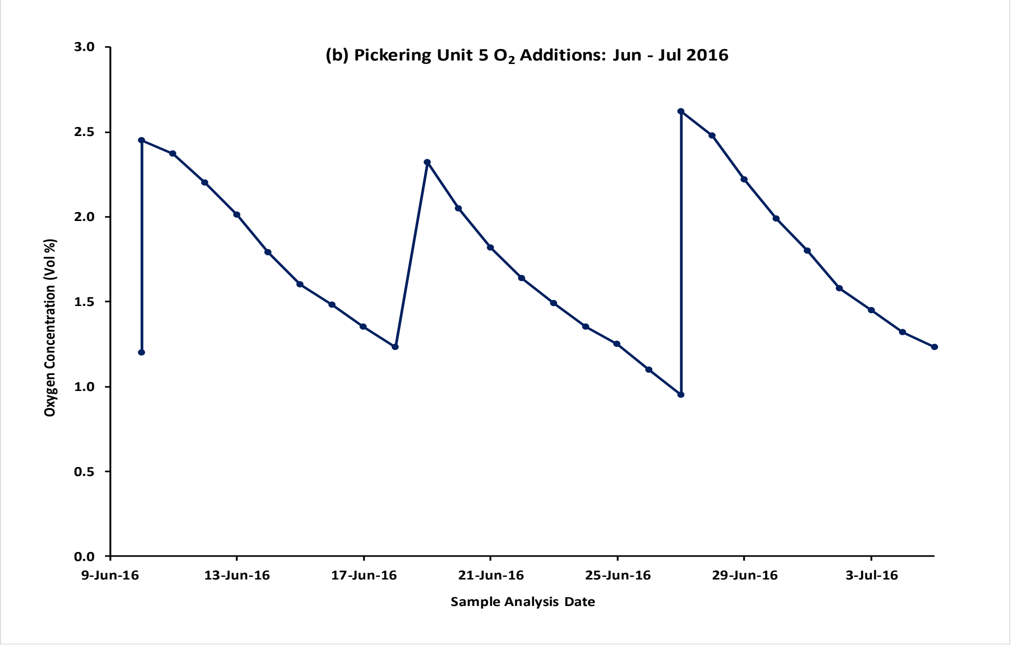
P4 (August 2017): $C(t)/C(0) = 0.992 - 0.242 \times t$, with a goodness of fit $R^2 = 0.997$

P5 (June 2017): $C(t)/C(0) = 0.984 - 0.069 \times t$, with a goodness of fit $R^2 = 0.990$

The data used to derive these equations are presented in Figure 12, below. A selection of up to four time intervals, spanning one oxygen addition to the next, were evaluated and the resulting data normalized by dividing each oxygen concentration C(t) by C(0), the initial oxygen concentration, to obtain an average value for f_{dep}, the fractional oxygen depletion per day. The excellent fit of these data points to a linear function demonstrates the AGS leak rates for these Units are constant over time, as predicted for a steady-state leak rate.

Figure 12: [O_2] Profiles for the AGS of two Pickering Units: (a) Unit 4 and (b) Unit 5





An additional parameter, t_{dep}, which we define as the time for a particular Unit to reach complete oxygen depletion, may be derived from these oxygen concentration profiles. Thus, by setting C(t) to zero in equation (1), above, we may write:

$$C(t)/C(0) = 0, \text{ so that } f_{dep} \times t_{dep} = 1$$

Or,

$$t_{dep} = 1/f_{dep}$$

where,

t_{dep} is the time (in days) for $[O_2]$ to fall to zero

The resulting t_{dep} values for Units of interest are presented in Table 8, below.

Table 8: $[O_2]$ Fractional Depletions, f_{dep}, and Depletion Times, t_{dep}, for Selected CANDU Units

CANDU Unit	Fractional $[O_2]$ Depletion, f_{dep} (days^{-1})	Time to $[O_2]$ Depletion, t_{dep} (days)
Bruce 3	0.248	4.0
Bruce 6	0.120	8.3
Pickering 1	0.215	4.7
Pickering 4	0.214	4.2
Pickering 5	0.072	13.9
Pickering 6	0.0302	33.1
Pickering 7	0.0467	21.4
Pickering 8	0.0566	17.7

In reviewing the data in Table 8, it is important to note that although the AGS $[O_2]$ is a parameter that indicates when an oxygen addition is required, it is *not* generally used for that purpose. Instead, an AGS *purge* is implemented when the *system dewpoint* exceeds a specified limit, usually around – 10 °C, equivalent to 1600 vpm of D_2O. Nevertheless, station operating procedures do require that oxygen additions should take place if the system $[O_2]$ falls below its specified minimum concentration, typically ~ 0.2 vol %. Such additions are typically made immediately *after* a purge is completed and the AGS has been returned to recirculating mode; this behavior is illustrated by the data shown in Figure 13, below, for Pickering Unit 5.

Figure 13: An example of the changes in an AGS [D_2O] and [O_2] over several purge cycles

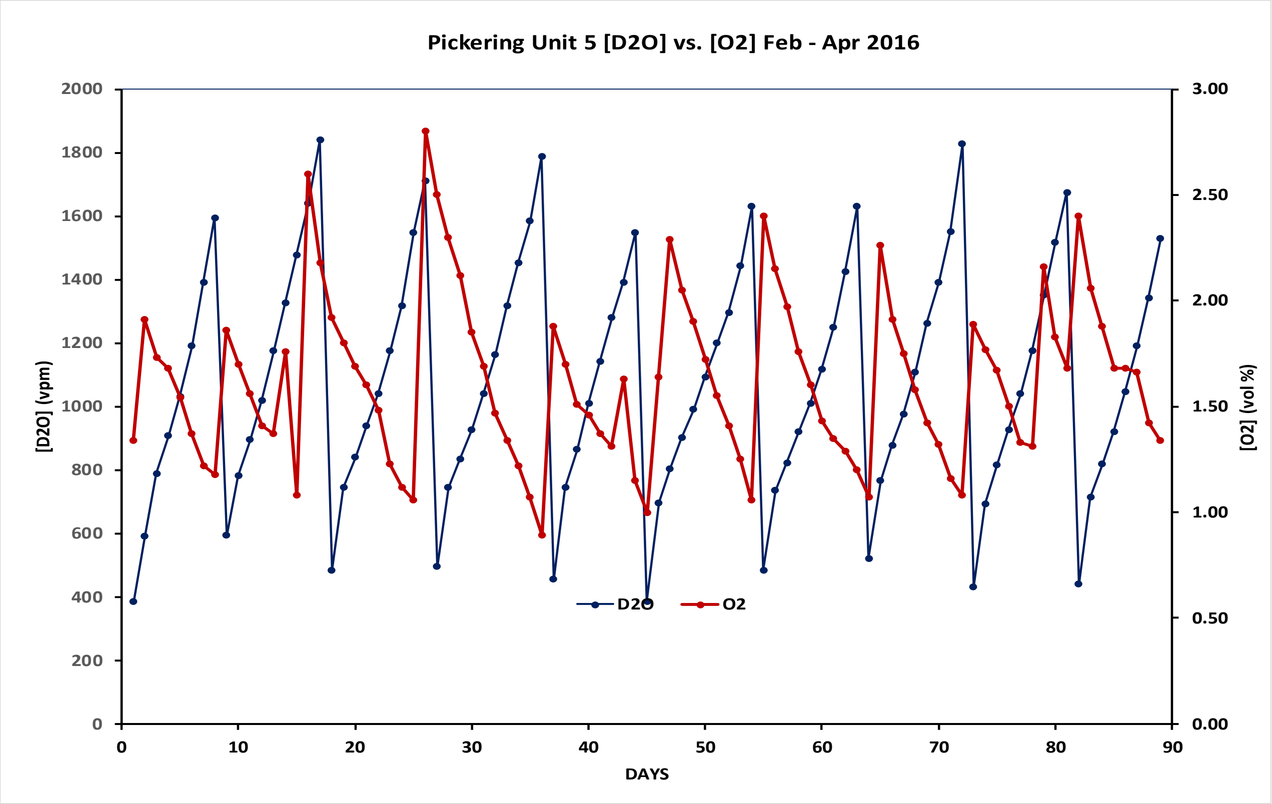


Figure 13 shows that after an AGS purge is completed the [D_2O], (as measured by the system dewpoint), rises steadily until the [D_2O] is above about 1500 vpm when the next purge is implemented. At the same time, when the purge is complete, oxygen is added to attain a system concentration ~ 2.5 vol % and subsequently falls off at a constant rate until the next system purge.

However, because of the priority given to maintaining a system's moisture content *below* a specified dewpoint limit, rather than maintaining [O_2] *above* a pre-set limit, there are instances of an operating Unit's AGS [O_2] falling to values ≤ 0.1 vol %. For example, in 2018 Bruce Unit 3 recorded ten cases of the AGS [O_2] being below 0.1 vol %. Similarly, in 2016, Bruce Unit 6 recorded eight cases of the AGS [O_2] below 0.1 vol %. However, in all of these cases, the AGS [O_2] was returned to a concentration above 0.1 vol % within 24 hrs.

Nevertheless, the low concentration of oxygen in an AGS, especially when it has been under shutdown conditions for an extended period of time, *is potentially detrimental to maintaining an oxidizing environment throughout the system*. Furthermore, as previously noted, oxygen additions to an AGS are *not* mandated if the Unit is shutdown, and it appears likely that no oxygen additions are made to a stagnant AGS, which is the normal state of an AGS while the Unit is shut down.

Table 9, below, provides some recent examples of the outage schedules for two Bruce Units. In those cases where the annual Unit outage total exceeds 30 days, a *single* outage of at least 30 days is always involved. For such prolonged outages, with no oxygen additions, it is postulated that *complete oxygen depletion* occurs after a Unit's t_{dep} is passed.

Table 9: Annual Outage Days for Bruce Units 3 & 6: 2015 - 2019

Unit	Total Annual Outage Days				
	2015	2016	2017	2018	2019
Bruce 3	36	91	59	28	133
Bruce 6	86	8	67	2	23

More recent data on the maintenance outages for Bruce Units show that all four Bruce A Units were shut down on May 9th, 2022, to install a new filtration system in the vacuum building – an operation that was expected to require 60 days to complete. As previously described, with an AGS starved for oxygen for many days, carbon monoxide builds up from CO_2 radiolysis and reacts with susceptible metals, such as iron and nickel, forming volatile carbonyl species. After Unit restart these species decompose and subsequently deposit active metal films on AGS surfaces that provide a "window" for H/D entry into pressure tubes.

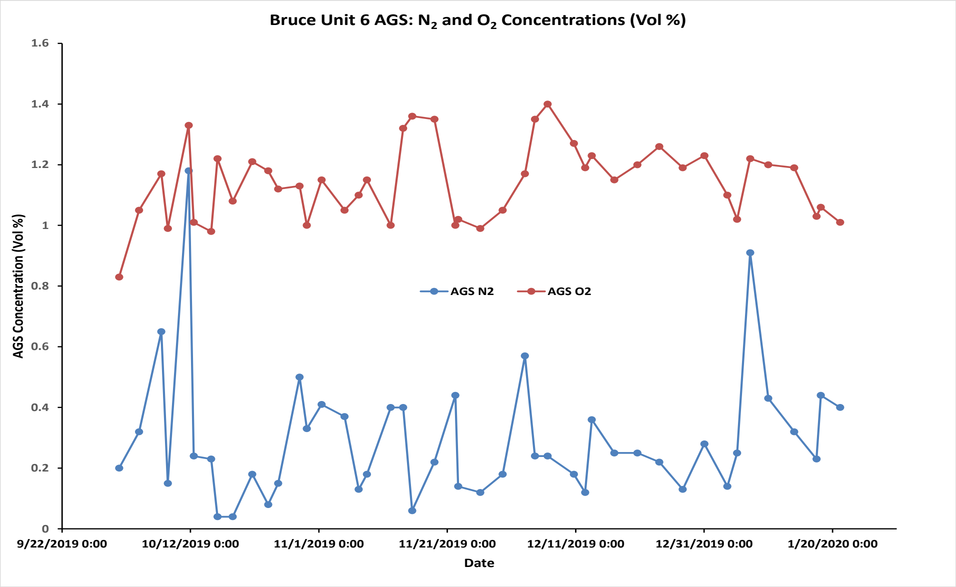
9.0 Adverse Effects of N_2 Entry into a CO_2-filled AGS Undergoing O_2 Addition

As briefly noted in Section 7.0 of this intervention, a relatively high impurity specification of ~ 800 vpm N_2 is permitted in the "bone-dry" CO_2 used as the fill-gas in all Bruce AGS. In the absence of deliberate O_2 additions, nitrogen undergoes radiolytic recombination reactions with H/D-containing impurities in an AGS to produce gaseous NH_3/NH_2D/NHD_2 species which react further to form solid deposits containing complex C/N/O/H/D compounds. However, for an AGS operated under an O_2 addition scenario, the chemistry of N_2 is radically different, and may in fact be quite deleterious to the integrity of an AGS.

First, it is important to note that, although the N_2 impurity concentration of the AGS CO_2 fill gas is specified to be < 800 vpm, N_2 concentrations *well above this limit* are observed due to air in-leakage into the AGS – an event that sometimes occurs during gas-cylinder change-outs, and/or immediately following an AGS bellows compressor failure, (e.g., bellows rupture, reed valve failure or motor failure).

A survey of available data on the chemical composition of AGS for operating CANDU reactors in Canada shows that short-term spikes, up to 1 vol % N_2, are quite common – a concentration that is more than ten times the 800 vpm N_2 specification noted above. This behavior is well illustrated by some recent data for Bruce Unit 6, as shown in Figure 14, below. Included in this figure are the corresponding data points for O_2. Interestingly, the O_2 data points do *not* correlate well with the N_2 data points, showing that deliberately added O_2 is *not* the source of the nitrogen spikes. Certainly, air in-leakage into an AGS will involve a contribution from O_2, but this will only be ~ 1/5th of the in-leaking N_2 concentration. Figure 14 shows that the *average* concentration of N_2 in the Bruce Unit 6 AGS over the time period studied – about 3 months – is ~ 0.3 vol %, or approximately three times the 800 vpm N_2 specification in the make-up CO_2.

Figure 14: Trends in $[N_2]$ and $[O_2]$ in the Bruce Unit 6 AGS: 2019 - 2020



In a 1995 study, (See OPG Report No: A-NFC-95-19), it was noted that, in an AGS undergoing O_2 additions, attention must be paid to the level of N_2 impurity in the system to limit the radiolytic production of NO_2, nitrogen dioxide, and other potentially problematic oxides of nitrogen such as N_2O, nitrous oxide, and NO, nitric oxide. In a dry AGS NO_2 is only mildly corrosive, but in the presence of water vapor, nitrous and nitric acids are formed by the reaction:

2

$$NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$

Under such circumstances, an equilibrium is established in which H_2O, NO_2 and HNO_2 are present in the gas phase, but HNO_3 becomes strongly adsorbed on annulus gas system surfaces where it can initiate corrosive attack. In Canadian CANDUs, in the 1990s, there were two cases where high concentrations of NO_2 were observed in the Bruce Unit 4 AGS, (See Memorandum File No: 833.74, from F. Greening (OPT) to J. Mistry (NTS, OPG), dated February 17th, 1994). Table 10, below, presents the concentrations of species measured in the Bruce Unit 4 AGS in January 1994.

Table 10: Annulus Gas Composition Measured in Bruce Unit 4, January 1994

Analyte	Concentration (vpm)
D_2/H_2	65
O_2	12300
N_2	1290
CO	5120
NO_2	500
N_2O	12
H_2O/D_2O	270

The presence of nitric acid, HNO_3, in the Bruce Unit 4 AGS at the time these measurements were made, (January 2004), was confirmed by the detection of nitrate, as a strong infrared absorption peak at 1389 cm^{-1}, in evaporated methanol wash solutions of metal surfaces exposed to the Bruce Unit 4 annulus gas. Nitrate concentrations ~ 4.5 $\mu g/cm^2$ of exposed metal surfaces were inferred from the data.

These observations, made almost 30 years ago, have recently found support in a study carried out by scientists at the Bhabha Atomic Research Center in Trombay India – See the paper by Sai Karthik Nouduru et al. in the Journal of Nuclear Materials Vol. 545, 152640, (2021). In this study zirconium base alloys were exposed to gaseous mixtures of CO_2 and O_2, with and without the presence of various contaminant. The results of these experiments, *with nitric acid as the contaminant*, are described by the authors as follows:

> *During normal operation of a PHWR, there is no possibility of air ingress into the AGS, as the gas-mixture flows at a pressure, higher than ambient pressure. However, during shut-down, if and only if gas-mixture is not flown/kept pressurized in an AGS, there is a possibility of air ingress into the AGS. During this stage, nitrogen present in air can undergo radiolysis in the presence of radiation and result in the formation of nitric acid. Therefore, it was felt necessary to establish the effect of the presence of nitric acid as an impurity in the AGS on the corrosion of the pressure tube. As opposed to the common understanding that zirconium alloys are immune to nitric acid, it was observed in this study that nitric acid, when present in small amounts in the "gas mixture" does lead to localized oxidation. The pressure tube cylindrical specimen in the full-scale test setup developed numerous nodules after exposure to nitric acid. The exact mechanism by which nitric acid is able to locally dissolve the protective zirconia layer can be described as follows. Nitric acid first transforms the zirconia into its salt zirconyl oxynitrate ($ZrO(NO_3)_2$) as per the Equation below:*
>
> $$ZrO_2\,(s) + HNO_3\,(g) \rightarrow ZrO(NO_3)_2\,(s) + H_2O\,(g)$$
>
> *The salt then gets dissolved into nitric acid at the temperature of the experiment/operation of the reactor. Once the protective zirconia layer is locally dissolved, the bare metal surface would come in contact with the oxygen in the "gas mixture" and again lead to nodule formation. However, the kinetics of the dissolution in this case are sluggish and therefore it would take longer time for the acid to cause localized oxide dissolution and nodule formation.*

These observations are in full accord with the detection of gas-phase NO_2 and surface absorbed nitrate in the Bruce Unit 4 AGS in 1994 and are consistent with the suggestion that air ingress was indeed the source of the Bruce Unit 4 NO_2/NO_3^-. However, and more importantly, the Bhabha researcher's study describes how these NO_x species may lead to the rapid degradation of a pressure tube OD oxide – with the potential for premature pressure tube failure – thereby emphasizing the need to keep $[N_2]$ as low as possible in an AGS at all times, (i.e., under both operating and shutdown conditions).

10.0 Summary, Conclusions and Recommendations:

On July 5, 2021, Bruce Power reported that measurements obtained from a Unit 6 pressure tube showed a Hydrogen Equivalent Concentration ([H_{eq}]) above the generic predictions and exceeding the Licence Condition 15.3 [H_{eq}] limit of 120 parts per million (ppm – by weight). Bruce Power reported that pressure tube B6S13 has a [H_{eq}] measurement of 211 ppm at the burnish mark and 212 ppm at the burnish mark plus 10mm; whereas [H_{eq}] measurements varied from 59 to 98 ppm at the burnish mark plus 20 mm (depending on the circumferential position). Also, on July 8, 2021, Bruce Power reported that measurements obtained from a Unit 3 pressure tube showed [H_{eq}] above the generic predictions and above the Licence Condition 15.3 [H_{eq}] limit of 120 ppm. For the Unit 3 pressure tube, B3F16, Bruce Power indicated a preliminary measurement of 131 ppm [H_{eq}].

In the months following this Bruce Event Report there have been a number of CNSC Meetings/Hearings to discuss these findings. At the Public Meeting held on September 3rd 2021, Bruce Power was asked by CNSC Commissioner Lacroix for its interpretation of the high [H_{eq}] observed in some of its operating pressure tubes, to which Bruce Power replied:

> "*We're not seeing a change in the rate of hydrogen uptake. What we're seeing is a redistribution (of the hydrogen) to the cooler region at the top of the pressure tube. So, it's not an acceleration but a redistribution*".

Similarly, on October 8th 2021, the Pressure Tube External Advisory Committee stated its belief that Bruce Power should:

> *"... revise the modeling to predict the circumferential migration of [H_{eq}] in the outlet end rolled joint region and the region of interest. Attention should be given to the prediction of [H_{eq}] migration in the axial inboard direction from the burnish mark due to smaller axial temperature gradients associated with flow bypass resulting from PT circumferential creep. This will improve confidence in the modeling of [H_{eq}] distribution in regions of interest".*

Evidently, these statements are suggesting that the occurrence of high [H_{eq}] near the outlet rolled joint region of some Bruce pressure tubes is caused by the diffusion of H/D in the thermal gradient between the bottom (hotter) and top (cooler) regions of the tube. Unfortunately, such a conclusion mistakes an *effect* for a *cause*. The diffusion of H/D is *not* the cause of the high [H_{eq}], but an effect resulting from *the temperature gradient between the top and the bottom of a pressure tube*.

Thus, Bruce Power is proposing that this postulated temperature gradient is the cause of the high hydrogen at the top of the tube, and the diffusion of hydrogen is the resulting effect. However, it is important to point out that this temperature gradient is known to be present in *all* CANDU pressure tubes and to increase with the age of the Unit – a fact that was first recognized many years ago, (See for example: OPG Report No; OH A-FC-97-113-P by D. Metzger et el: *Influence of Temperature and Concentration Gradients on the Redistribution of Hydrogen Isotopes*).

An additional point of concern with Bruce Power's position on this issue is its assertion that the high [H_{eq}] observed near some of its Unit's outlet rolled joints "*is not an acceleration but a redistribution*". This claim is at odds with the views expressed in the OPG Report noted above, where it's pointed out that an inferred H/D uptake rate, (in the event of a significant temperature difference between the top and bottom of a pressure tube), may also include a contribution from an accelerated uptake *from an undefined source at this location*.

This intervention was written with two interrelated goals in mind:

(i) To confirm or deny the possibility that the high $[H_{eq}]$'s of concern in Bruce Units 3 & 6 are solely due to the redistribution of ingressed H/D by its thermal diffusion from hotter to colder regions of a pressure tube

(ii) To confirm or deny the possibility that the high $[H_{eq}]$'s of concern in Bruce Units 3 & 6 may be accounted for by H/D entry from a Unit's AGS

Item (i) is addressed mainly in Section 5.0 of this email, while item (ii) is addressed in Sections 3.0 and 6.0. The main conclusions arising from the discussions in these Sections are as follows:

Item (i):

(a) Simple, scoping calculations of hydrogen isotope diffusion show that the redistribution of deuterium, induced by the temperature gradient between the top and bottom of the outlet end of a pressure tube, *is insufficient* to account for the elevated $[H_{eq}]$ levels observed at the B6S13 and B3F16 outlet rolled joints.

(b) The observed levels of *light* hydrogen picked up by the B6S13 and B3F16 pressure tubes are inconsistent with the primary heat transport system, (PHTS), D_2O being the sole source of ingressed hydrogen. Therefore, there must be an additional source of H/D, external to a Unit's PHTS, that is sufficient to account for the excess light hydrogen. A Bruce Unit's AGS is the most plausible source of light hydrogen.

Item (ii):

(a) The entry of H/D, from a Unit's AGS, into a pressure tube through its outside surface oxide occurs only when this oxide is degraded in some way. It is proposed that such a degradation occurred in Bruce Units 3 & 6 due to the inadvertent establishment of a reducing environment in these Unit's AGS by the following mechanism: (i) CO_2 radiolysis to form CO, (ii) Mobilization of iron and nickel in the AGS by the formation of volatile carbonyl species, and (iii) An accompanying lack of O_2 which occurs especially when a Unit is shut down for prolonged periods of time, (> 1 week).

(b) Consideration of the AGS geometry in the region of a pressure tube bearing journal and the associated flow restrictions, suggests that H/D ingress at the top, 12 o'clock location, is likely to be higher than at the bottom, 6 o'clock location.

> (c) A survey of oxygen addition data for selected Units at Bruce and Pickering NGS shows that, because it has the highest leak rate of the Units studied, the Bruce Unit 3 AGS is depleted in oxygen in less than a week and is therefore the most likely of these Units to exhibit anomalously high H/D uptake near the outlets of its pressure tubes.

Although an annulus gas contribution to the high [H_{eq}] observed in a number of pressure tubes from Bruce Units 3 & 6, remains an unproven hypothesis, it nevertheless offers a far better fit to the data for these Units than the thermal diffusion theory proposed by Bruce Power. In addition, the likelihood that the high [H_{eq}] stems from H/D ingress from the AGS, highlights the need to make oxygen additions to an AGS, *regardless of the operational status of the Unit*. For this reason, and as a precautionary measure, it is recommended that batch oxygen additions to an AGS should be maintained, not only during normal Unit operation, but also when the Unit is shut down. In addition, it is also recommended that the CO_2 "bone-dry" grade, containing up to 800 vpm N_2, currently used as the fill-gas in all Bruce Units, should be replaced with higher purity CO_2 such as "instrument grade", to maintain [N_2] below 100 vpm.

Addendum 1:

In July 2021, the CNSC offered Bruce Power a choice:

Either, (a) Get more analytical data to confirm the existing [Heq] measurements, and also analyze more samples to see how widespread this phenomenon is, (a so-called *extent of condition* investigation). Or, (b) Prove that the very high [Heq]s measured in a number of Bruce tubes do not negatively impact the fitness-for-service of these pressure tubes.

Option (a) is clearly required in order to complete a root cause analysis of this problem. However, option (b) provides an escape clause for Bruce Power because, if successfully implemented, it obviates the need to comply with option (a).

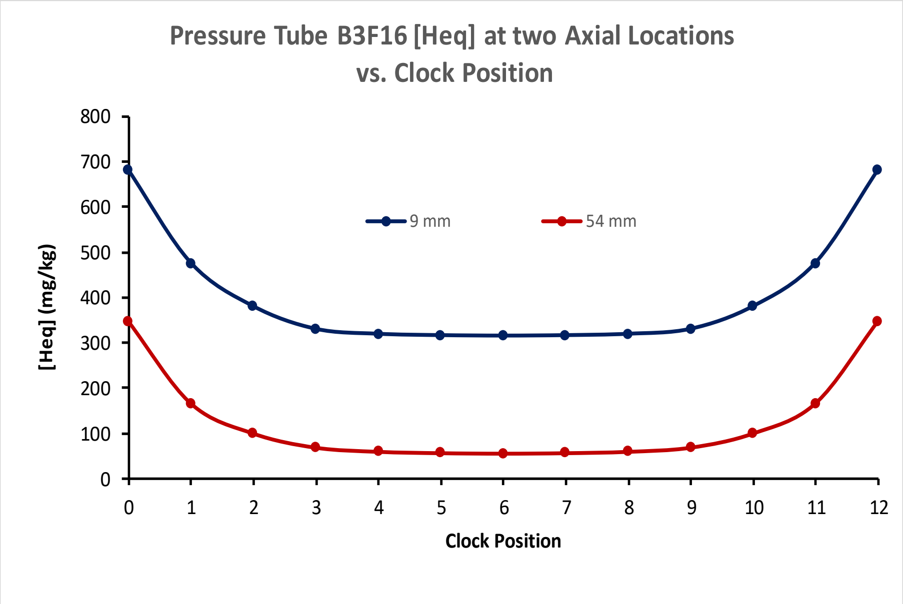
In Bruce Power's Event Report B-2021-93819-DR issued July 8th, 2021, we read:

Measurements obtained from the A2131 outage Circumferential Wet Scrape Tool (CWEST) scrape campaign showed elevated Hydrogen equivalent concentration (Heq) measurements found near the top of the pressure tube in the outlet Rolled Joint (RJ) region for three channels with front end outlet (FEO) orientation (B3C11, B3F16 and B3L11), which may be above the generic predictions for the locations outboard of the burnish mark. Based on additional scrape scope in A2131, B3F16 has a measured scrape sample inboard of the rolled joint burnish mark that is >120 ppm.

Also, under the heading **Causes** we read:

Potential cause: Circumferential variability in Heq from top of the tube to bottom of the tube.

The figure below provides data showing the circumferential variation of [Heq] with clock position for measurements made at 9 mm and 54 mm from the outlet of pressure tube B3F16.



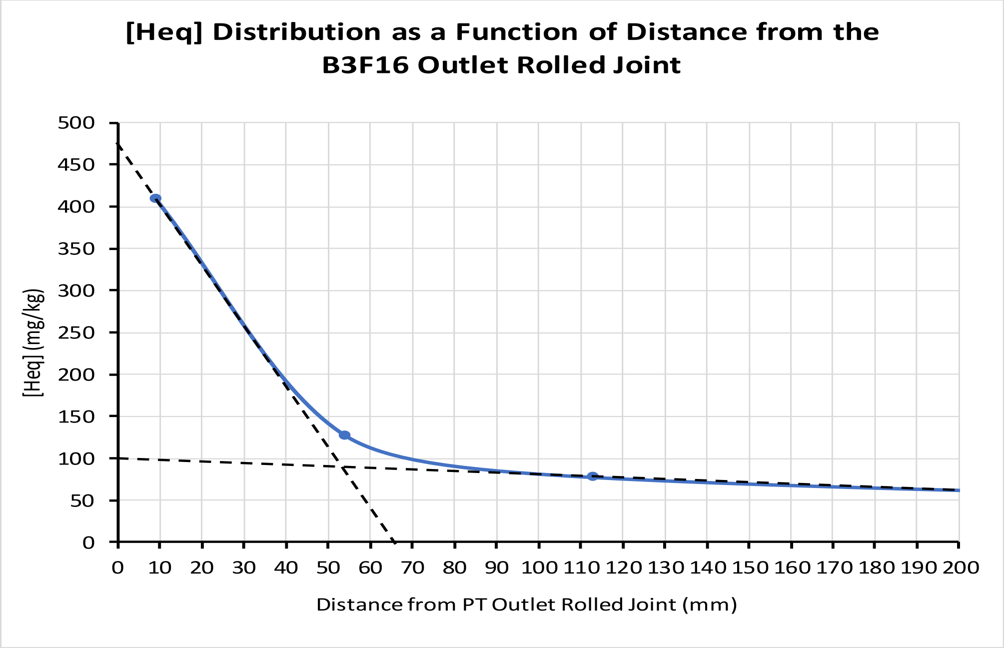
These plots show that there is an enrichment of hydrogen near the top (12 o'clock position) of tube B3F16 compared to the bottom (6 o'clock position) by a factor of about two at the 9 mm axial location, and by a factor of about six at the 54 mm location. However, the claim that this enrichment does <u>not</u> represent accelerated hydrogen pickup is incorrect as the data for [Heq] at the 9 mm location amply demonstrate. Thus, the *average value* of [Heq] at the 9 mm location is calculated to be 409 mg/kg which is almost *four times higher* than Bruce Power's Licence Condition 15.3 which sets a [H_{eq}] limit of 120 mg/kg, as per CSA N285.8.

Mass balance requires that the amount of deuterium entering a pressure tube rolled-joint over a given time period, (by whatever mechanism), *<u>must be conserved</u>*, regardless of how it may redistribute *after* entry. Thus, we can conceptually consider the ingress of hydrogen into a pressure tube at an outlet rolled joint to be a two-step process:

(i) Entry by absorption into the metal;
(ii) Diffusion away from the point of entry.

Under these circumstances, the *rate* of entry of hydrogen into the underlying metal is independent of any subsequent diffusion; however, the *concentration* of hydrogen at a given location *is* influenced by diffusion. Now, if we accept the proposal that ingressed deuterium diffuses away from hot regions at the bottom of a pressure tube, towards colder regions at the top of the tube, the hydrogen concentration at the top will *increase*, but only at the expense of hydrogen at the bottom of the tube where its concentration will *decrease*.

Using the *<u>average</u>* [Heq] measured around the circumference of a pressure tube outlet rolled joint, the effects of thermal diffusion may be corrected for which allows a precise analysis of the *axial* migration of H/D to be made. The figure below shows such a corrected axial variation of [Heq] at the outlet end of the B3F16 pressure tube.



The resulting plot shows *two* types of axial behavior of [Heq] for the B3F16 tube:

(i) At short distances from the end of the tube, (< 100 cm), [Heq] drops off rapidly with distance

(ii) At long distances from the end of the tube, (> 100 cm), [Heq] drops off slowly with distance

The plot also provides a measure of the ***diffusion length***, L_D, of the ingressed H/D, defined as the distance from the end of a pressure tube to a point at which the hydrogen isotope concentration has dropped significantly, say by a factor of at least 3. A convenient way to estimate a diffusion length L_D is to consider the Brownian motion and the resulting random walk of atoms in a lattice. This approach leads to a diffusion distance of atoms in a 2-D lattice according to the relation:

$$L_D = \sqrt{4Dt}$$

Where,

D is the diffusion coefficient in cm^2/s,
t is the exposure time in seconds

For the case of the diffusion of deuterium at the outlet rolled joint of a pressure tube, where the temperature is ~ 300 °C, D is equal to 7.0×10^{-7} cm^2/s, and if we measure the exposure time in years instead of seconds, we may write:

$$L_D = \sqrt{4 \times 7.0 \times 3.156 \times t_{EFPY}} = 9.4\sqrt{t_{EFPY}}$$

Where,

t_{EFPY} is the number of effective full power years of in-reactor exposure

If this formalism is applied to the B3F16 data plotted in the figure above, *two* diffusion lengths may be defined, (i) A near surface L_D value of about 6.5 cm and (ii) A much higher L_D, ~ 50 cm, obtained by linear extrapolation of the data to a point where the [Heq] value drops to ~ 20 mg/kg corresponding to the “background” concentration of H/D. The rate of entry of hydrogen isotopes into a pressure tube may be determined from the data in the above figure using the following relationship, based on the known parabolic kinetics of H/D ingress at a rolled joint, as first reported by V. Urbanic in 2002:

$$d[\mathrm{Heq}]/dt \; = \; d[\mathrm{Heq}]/dx \times \sqrt{\{D/t\}}$$

Where,

d[Heq]/dt is the change in the concentration of hydrogen isotopes with time

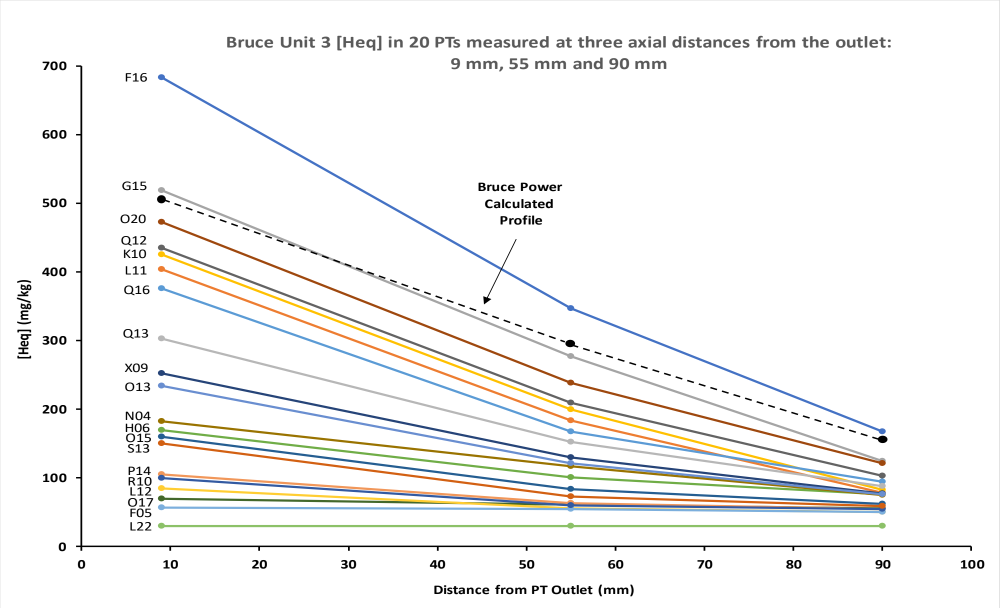
d[Heq]/dx is the change in the concentration of hydrogen with distance from the outlet end of a pressure tube

For the B3F16 pressure tube, the quantity d[Heq]/dx is simply the slope of the [Heq] vs. distance plot presented above, and as previously noted, the diffusion coefficient, D, is equal to 7.0×10^{-7} cm^2/s at ~ 300 °C. Hence, converting from time units of seconds to years we may write:

$$d[\mathrm{Heq}]/dt\ (\mathrm{mg/kg/year}) \; = \; d[\mathrm{Heq}]/dx\ (\mathrm{mg/kg/cm}) \times 4.7\ (\mathrm{cm/year})$$

I have selected [Heq] data measured in July 2021 for 20 Bruce Unit 3 pressure tubes at three axial distances – approximately 9 mm, 55 mm and 90 mm – from the outlet ends of these tubes, and plotted the values in Figure 1a, below. Also included in Figure 1 are the predicted values at the same axial locations for a generic “Bruce” pressure tube calculated using the methodology discussed above.

Figure 1a: Bruce Unit 3 [Heq] Measured in 2021 in 20 Pressure Tubes

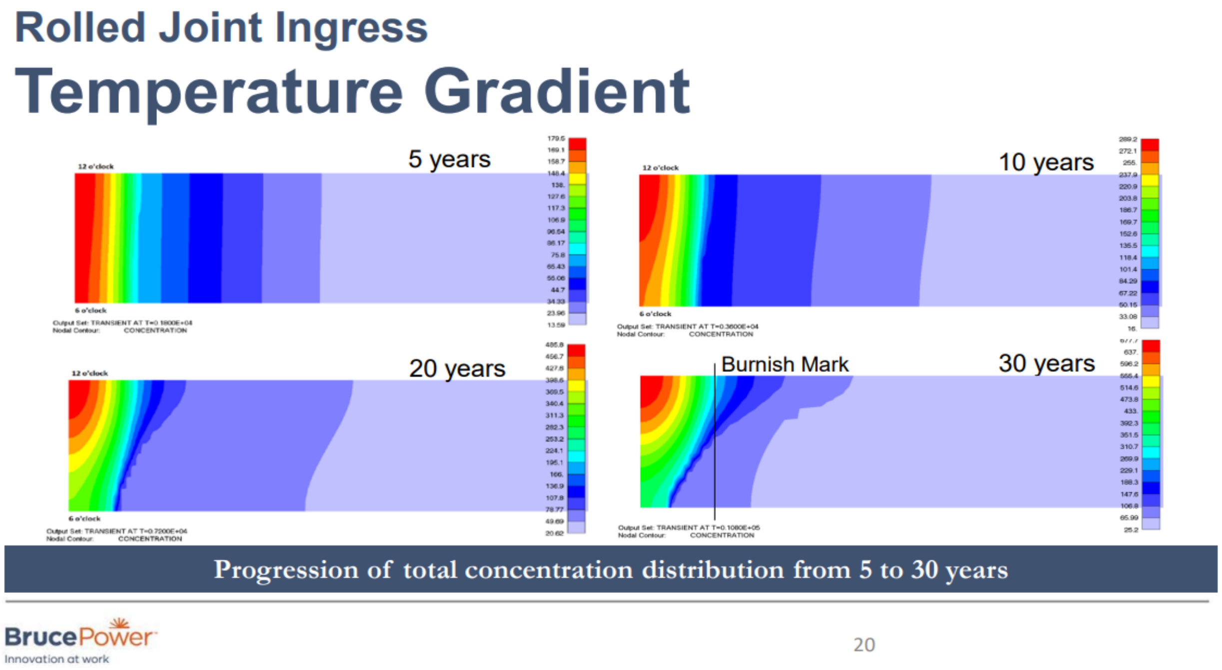


The most striking feature of the data in Figure 1a is the great variability – spanning a range of more than a factor of ten – in the [Heq] values among 20 randomly selected pressure tubes. Also included in Figure 1a are the values predicted by Bruce Power for the calculated [Heq] at the 9-, 55- and 90-mm locations inboard of the outlet end of a typical Bruce pressure tube. These theoretical vs. experimental plots clearly demonstrate the unpredictability of [Heq] in pressure tubes removed from Bruce Units.

More importantly, however, it is evident that Bruce Power's simple model, involving deuterium redistribution induced by thermal diffusion, is unable to explain this variability. By comparison, the annulus gas H/D entry model presented in this intervention – incorporating, as it does, the random failure of protective pressure tube OD oxide layers through the formation of micro-cracks – is consistent with the observed variability in [Heq].

Additional Questions:

1. For my first question I wish to address some of the material presented by Bruce Power on September 10th, 2021, at CNSC Public Hearing CMD 21-H11.2A. Specifically, I am especially interested in Slide No. 20 from this Hearing – as shown below:



Rolled Joint Ingress

Temperature Gradient

Progression of total concentration distribution from 5 to 30 years

BrucePower
Innovation at work

20

Slide No. 20 is entitled: "*Temperature Gradient*" – suggesting it could provide some insight into the alleged hydrogen redistribution phenomenon; but most remarkably, *no temperature gradient data whatsoever are provided by Slide 20*. Instead, we are presented with hydrogen concentration profiles calculated for a generic pressure tube outlet rolled joint after 5, 10, 20 and 30-years of Unit operation, *with no indication as to how these concentration profiles were determined*. Worse yet, *the magnitude of the alleged temperature gradient is not even mentioned in Slide 20*, and neither is any information provided as to the values of the diffusion coefficients and H/D ingress rates that must have been used to calculate these concentration profiles.

However, regardless of the paucity of useful information provided by Slide 20, we know that Bruce Power's so-called "predictive model" for [Heq] in operating pressure tubes has been *seriously in error* for many years. By way of acknowledging this problem, Bruce Power agreed back in July 2021 to undertake the "*development of a predictive model accounting for elevated [Heq] and circumferential variation of [Heq] observed in the outlet rolled joint region.* – See Bruce Power's letter to the CNSC File No. BP-CORR-00531-01884.

Now, I assume that Slide 20 represents [Heq] values derived from Bruce Power's promised new and improved "predictive model" for [Heq] in its operating pressure tubes. But, for such a model to be scientifically valid, and not merely a curve fitting exercise, it should clearly identify its starting assumptions, input parameters and computational methodology – which is something that has never been provided by Bruce Power. From this observation I beleive that Bruce Power's current attempt to predict H/D pickup at pressure tube rolled joints – as exemplified by Slide 20 – is totally unacceptable because it is entirely lacking in scientific rigor, and adds nothing to our understanding of this high H/D pickup phenomenon. But I have to ask if the CNSC would agree with this assessment, or please show me where I am in error.

2. My second question concerns statements made by CNSC staff member Blaire Carroll at the CNSC Public Meeting held on September 3rd, 2021, (See, CMD 21-M39/21-M37/21-M37.A), as follows, (with my emphasis in red):

MR. CARROLL:

> *For the record, my name is Blaire Carroll. I'm a technical specialist with the Operational Engineering Assessment Division at the CNSC. Dr. Viktorov has provided overall a very good answer from the CNSC staff perspective. We do understand--or we don't understand the root cause at this point. And with regards to some of the modelling that Bruce Power has provided in its presentation, that has not been formally submitted to CNSC staff yet, so we have not completed a technical review of that. In theory, it would be the thermal gradients that would move the hydrogen to the top of the pressure tube because that's where the tube is coldest, and the hydrogen tends to migrate to the colder temperature locations in the tube. That would explain why the concentration is highest at the top. But it doesn't explain the magnitude of the concentration that's been seen, and that's an area where CNSC staff is expecting licensees to do more work to try to determine the cause of the elevated values.*

This statement by CNSC Staff Member Carroll suggests that the CNSC is not satisfied with Bruce Power's hydrogen diffusion explanation of the high [Heq] observed in some of its pressure tubes. I therefore have to ask, one year on from this statement by a CNSC staff member, if Bruce Power has "*done more work*" and provided the CNSC with an acceptable and experimentally verified root cause of these elevated [Heq] values?

Addendum 2:

I believe that the most important outcome of today's Public Hearing would be that it determines the *root cause* of the high [Heq] first reported in July 2021 for several pressure tubes operating in Bruce Units 3 & 6. Indeed, it is very troubling that it is now over a year since this problem with Bruce pressure tubes was first discovered and, remarkably, the Canadian nuclear industry, and its paid supporters in academia, have only offered a very sketchy qualitative, not quantitative, theory as to the cause of Bruce Units 3 & 6 high [Heq}that is totally lacking in supporting evidence.

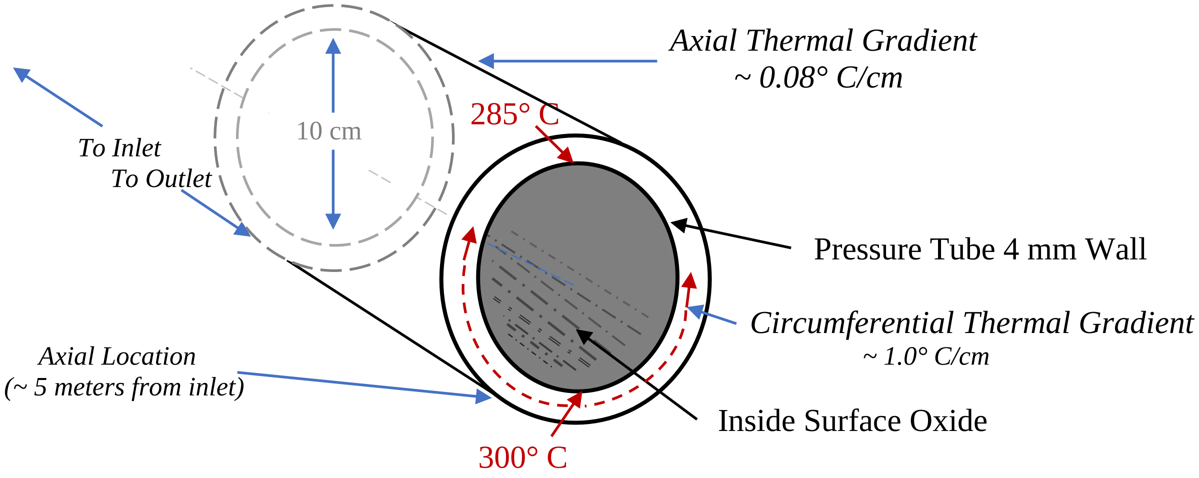
The basis of the nuclear industry's current theory is twofold:

(i) Deuterium, produced by zirconium corrosion in the PHTS, enters a pressure tube at the highest rate at the hottest region of a tube which is at, or near to, the lower (6 o'clock) outlet rolled joint

(ii) The ingressed deuterium subsequently migrates to the cooler regions of the pressure tube located at the top (12 o'clock position) of the tube

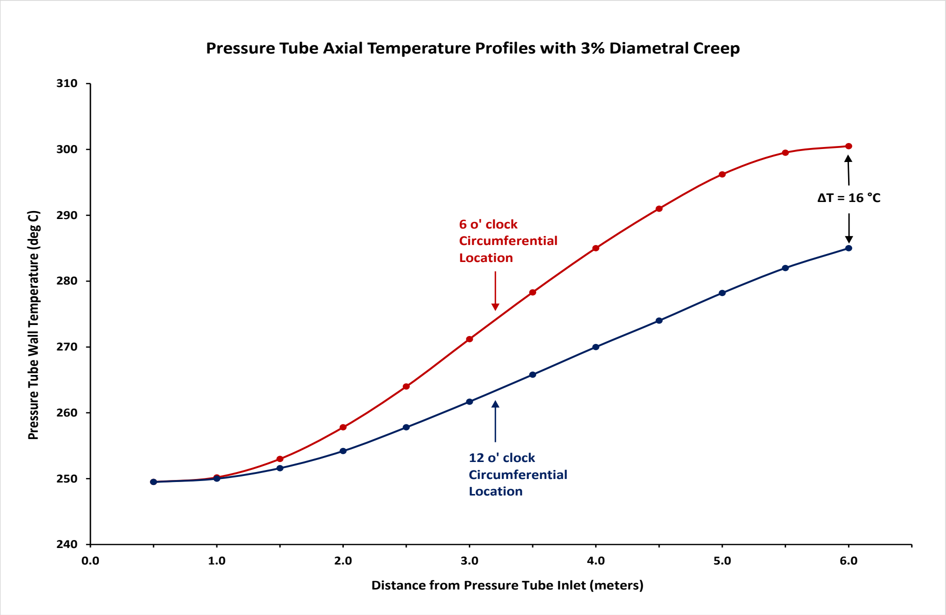
At power, pressure tubes exhibit *two* types of thermal gradients: axial and circumferential, as shown in Figure 1 below. The axial gradient stems from the difference in the inlet and outlet temperatures of the D_2O coolant and equals approximately 0.08 °C/cm along the length of a pressure tube. The circumferential thermal gradient is caused by the off-axis location of the fuel bundles within a fuel channel, especially when the pressure tube wall is subject to neutron-induced diametral creep. As discussed below, the temperature gradient around the circumference of a pressure tube near its outlet end is usually assumed to be about 1.0 °C/cm.

Figure 1: Schematic Illustration of a Pressure Tube near its Outlet End



Thus, for example, D. Rogers et al. at CNL published a plot of the calculated temperature profiles at the 6 o'clock and 12 o'clock circumferential locations for a typical mature pressure tube as shown in Figure 2, below, (See CNL Nuclear Review Vol 5, Number 1, June 2016).

Figure 2: CNL Calculated Temperature Profiles for a Mature Pressure Tube



These plots predict a ΔT – defined as the temperature difference between the bottom and the top of a pressure tube at its outlet end – of about 16 °C. Unfortunately, the methodology used by the CNL to determine these temperature profiles is not provided by the CNL report noted above, from which Figure 2 is derived. Nevertheless, it is possible to predict the basic features of these profiles based on the fact that there are two main contributing factors that determine ΔT:

(i) A contribution, ΔT_6, from *the localized heating of a pressure tube* in the vicinity of the 6 o'clock location, caused by the direct physical contact of fuel bundles with the pressure tube wall at the bottom of a tube

(ii) A contribution, ΔT_{12}, from *the localized cooling of a pressure tube* in the vicinity of its 12 o'clock location, caused by coolant flow bypass due to pressure tube diametral expansion from neutron induced creep

It is assumed that:

$$\Delta T(x) \;=\; \Delta T_6(x) \;+\; \Delta T_{12}(x)$$

Where x is the axial distance (in meters) from the pressure tube inlet, (x = 0), to its outlet, (x = 6).

1. Determination of ΔT_6:

ΔT_6 depends on the bundle power, usually expressed in kW, at a given axial location. I have used bundle power data from a Bruce B Safety Report for a high power, (7.5 MW), channel to derive a dimensionless axial power profile, P(x), over the full 6-meter reactor core, with the data points normalized to the maximum channel power of 1035 kW at the 3-meter axial location. It is assumed that ΔT_6 may be approximated by the simple relationship:

$$\Delta T_6(x) = C_1 \times P(x)$$

Where C_1 is a proportionality constant, (in units of °C), between the excess pressure tube wall temperature and the local fuel bundle output power – a conversion factor to be determined.

Using published data derived from CANDU reactor thermal hydraulic codes such as ASSERT-PV, C_1 is estimated to be 10 °C.

2. Determination of ΔT_{12} :

ΔT_{12} depends on the amount of pressure tube diametral expansion induced by neutron induced creep. CNL has published plots of the amount of diametral expansion, D(x), along the axial length of a pressure tube, (See R. B. Adamson et al. in Journal of Nuclear Materials Vol. 521, 167 – 244, (2019). It is assumed that ΔT_{12} may be approximated by the simple relationship:

$$\Delta T_{12}(x) = C_2 \times D(x)$$

Where C_2 is a proportionality constant, (in units of °C), between the amount of pressure tube wall temperature cooling and the neutron-induced pressure tube diametral expansion normalized to its maximum value which is well in-board of the mid-core, 3-meter location. For this intervention I have used a value of 8 °C for C_2.

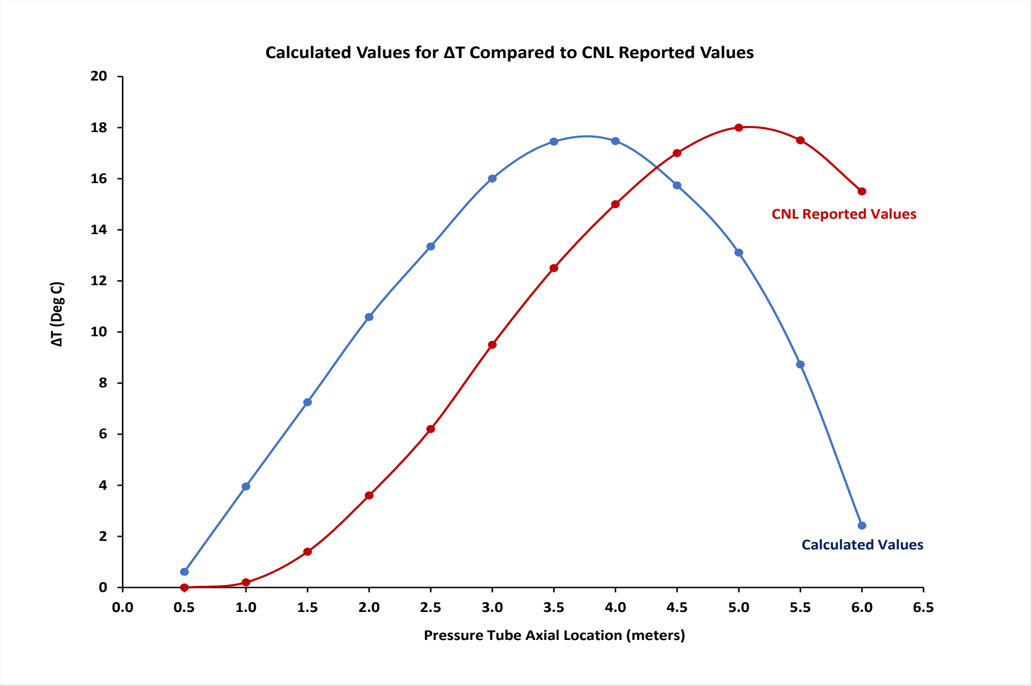
Combining these parameter values with axial power profile and the diametral expansion data noted above we are able to calculate ΔT(x) for a set of axial locations from x = 0 to x = 6.0 meters, as shown in Table 1, below, together with ΔT values taken from CNL's 2016 report.

Table 1: Calculated ΔTs at Different Axial Locations vs. CNL's Published Data

Axial Location, x (meters)	ΔT_6 (Deg C)	ΔT_{12} (Deg C)	$\Delta T_6 + \Delta T_{12}$ (Deg C)	CNL ΔT (Deg C)
0.0	0.0	0.0	0.0	0.0
0.5	0.6	0.0	0.6	0.0
1.0	2.4	1.5	4.0	0.2
1.5	4.4	2.9	7.3	1.4
2.0	6.4	4.2	10.6	3.6
2.5	8.0	5.4	13.4	6.2
3.0	9.5	6.6	16.0	9.5
3.5	10.0	7.5	17.5	12.5
4.0	9.5	8.0	17.5	15.0
4.5	8.0	7.8	15.7	17.0
5.0	6.4	6.7	13.1	18.0
5.5	4.5	4.2	8.7	17.5
6.0	2.4	0.0	2.4	15.5

It is instructive to plot the data in columns 4 and 5 of Table 1 to directly compare the ΔT values determined by the methodology described above, with the results reported by CNL, as shown in Figure 3 below.

Figure 3: Calculated vs. CNL Reported Values for a Pressure Tube 6 to 12 o'clock ΔT



The most striking feature of my calculated values of ΔT compared to CNL's values, as seen in Figure 3, is the large divergence between the data sets at the pressure tube outlet region near the 5-to-6-meter axial location. In this outlet region of the reactor core the neutron flux drops off rapidly with increasing x, as the bundle power declines by about 200 kW/meter from its mid-core output of about 1000 kW. Because diametral creep is a function of the neutron fluence, the pressure tube diametral expansion also falls to a minimum value of about 15% of its peak value at the 6-meter location. This trend is clearly seen in my calculated ΔTs, but is barely evident in CNL's calculated values which is therefore difficult to explain.

I believe that my calculated ΔTs are much closer to reality than CNL's and as a consequence it appears that the ΔTs for the Bruce Unit 3 and 6 pressure tubes with elevated [Heq] near their respective outlet rolled joints are most probably less than 5 °C – a value that is incompatible with the observed [D_{12}]/[D_6] ratio of about 3, which requires a physically unrealistic value > 50 °C for the corresponding ΔT, (See Figure 10, page 25, of this intervention).

Addendum 3:

Part 1:

On August 22nd, 2022, the CNSC issued CMD: 22-M37, entitled "*To All Nuclear Power Plant Licensees*", which provides an update on the latest findings with regard to the issue of elevated

Heq in the pressure tubes of reactors after extended operation. While previous CNSC documents related to this issue dealt exclusively with elevated Heq measurements at *outlet* rolled joints, results of Heq measurements at *inlet* rolled joints, first reported in December 2021, showed elevated Heq levels, exceeding 120 ppm, at this location for the B6S13 surveillance tube. CNSC refers to these and other inlet rolled joint measurements in their CMD: 22-M37 document as follows:

> *The region of elevated Heq in this case was more localized in axial extent than was observed near the outlet rolled joint burnish mark and is referred to as a "blip" because of the appearance of the Heq profiles.*
>
> *Further examination of the B6S13 tube material containing the blip also revealed that there was a significant through thickness gradient of Heq. The punch sample provides the average value of Heq in the volume of the sample, but when the through thickness profile of Heq was evaluated, it was determined that near the outer diameter (OD) surface of the tube the Heq reached a value of over 400 ppm, while at the inner diameter (ID) surface the Heq was below 50 ppm.*
>
> *These observations led to the development of a different theory for the formation of inlet rolled joint blips compared to the outlet rolled joint elevated Heq. The weight of the pressure tube will cause the tube to sag between the end fitting and the first spacer. As the pressure tubes elongate in service due to the irradiation induced creep, the amount of bending increases leading a small region of localized contact with the tapered section of the end fitting, which creates a local cold spot that can attract hydrogen in the tube material.*

Here we have another example of the nuclear industry's penchant to invoke an *ad hoc* hypothesis whenever there is a new finding that does not fit to the existing paradigm. In the present case, it is clear that OPG and Bruce Power are alarmed that a through-thickness profile of Heq near the inlet of tube B3S13 showed that at the outer diameter (OD) surface of the tube, Heq reached a value of over 400 ppm. As a result, to explain high Heq values at a pressure tube's inlet rolled joint, a "*different theory*" was invoked. But I feel compelled to ask: Is there really a need for yet another theory of the root cause of a case of high Heq concentrations in an ex-service pressure tube?

Unfortunately, the CNSC's CMD: 22-M37 document does not include any information as to *how* a "through oxide thickness profile" of the B6S13 inlet sample was measured, but I would suspect that SIMS, (Secondary Ion Mass Spectrometry), was used. In the past, I have taken advantage of the SIMS technique to derive depth profiles of selected isotopes, including hydrogen and deuterium, for many ex-service pressure tube samples. And, in particular, I reported SIMS depth profiles for deuterium in pressure tube samples from *outside* surface oxides from Pickering and Bruce fuel channels in a paper published in the *Journal of Nuclear Materials*, Vol. 226, pp 263 – 271, (1995). The Figure below shows the reported outside oxide depth profiles in samples removed from different axial locations of seven different pressure tubes.

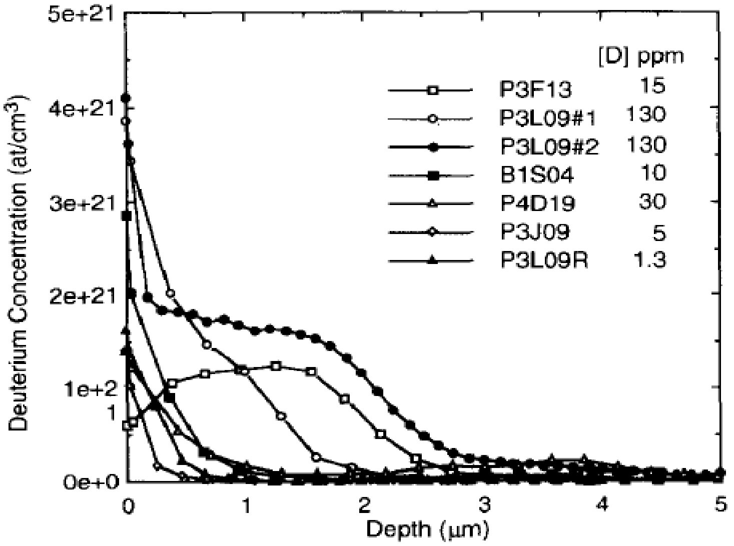


Fig. 9. Concentration depth profiles for deuterium in the oxides exposed to nitrogen (P3 and P4) and carbon dioxide (B1) in the annulus in reactor; deuterium concentrations measured in the alloy are listed.

By way of comment on this Figure it was noted in the *Journal of Nuclear Materials* paper that:

> *The concentration depth profiles of deuterium obtained for the oxides on the outside surfaces of the specimens are shown in Fig. 9. The deuterium concentration and the changes in it with depth in the oxide do not bear an obvious relation to the deuterium uptake by the alloy.*

What is most noteworthy about these profiles is that, with one exception, (sample P3F13), the profiles show a significant *increase* in the concentration of deuterium at the outside surface of the sample. Conversely, the concentration of deuterium *decreases*, by a factor of at least four, from the OD surface to a depth of about 1 micron below the OD surface. This outside surface enrichment of deuterium is most probably caused by a combination of the following phenomena:

(i) The adsorption of D_2O from the reactor's annulus gas system, (AGS), at a pressure tube's OD oxide surface

(ii) The so-called "knock-on" ion implantation of adsorbed deuterium by fast neutron irradiation, combined with subsequent diffusion of deuterium into the ZrO_2 matrix

(iii) The formation of mixed oxy-deuteroxy zirconium species, $ZrO_{2-x}(OD)_{2x}$, within the pressure tube OD oxide layer

Water adsorption on annulus gas system surfaces was reviewed in OHRD Report No: 92-2-K where it was shown that, at the average AGS operating temperature of about 150 °C, a maximum of 0.016 grams of H_2O may be physisorbed per gram of exposed ZrO_2. This implies that the saturated loading of deuterium on a pressure tube OD oxide is about 3500 mg/kg. The average atomic concentration of deuterium at the pressure tube OD surface of the seven samples, (as shown in the Figure above), is ~ 2×10^{21} at/cm^{2}, which is equal to 1140 mg/kg, and corresponds to about 1/3rd of saturation adsorption for the D_2O/ZrO_2 system.

Clearly, these results, derived from studies carried out 25 years ago, show that a Heq in excess of 1000 mg/kg at the OD surface of a pressure tube, (such as B6S13), *is not exceptional*, and certainly not sufficient reason to invoke a new H/D pickup mechanism involving pressure tube contact "*with the tapered section of the end fitting*". However, it is important to also recognize that high OD surface concentrations of deuterium – sometimes in excess of 1000 mg/kg – have very little impact on the overall through-wall concentration of deuterium in a pressure tube because the OD surface enrichment is confined to an oxide layer that is less than 4 µm thick on a 4 mm thick pressure tube.

Part 2:

The occurrence of a "blip" in the [Heq] of a Darlington pressure tube near its inlet rolled joint is discussed in OPG's CMD 21-H11.1 submission to the CNSC, dated September 10th, 2021, where we find the following data for [Heq] vs. axial location for pressure tube D3S13:

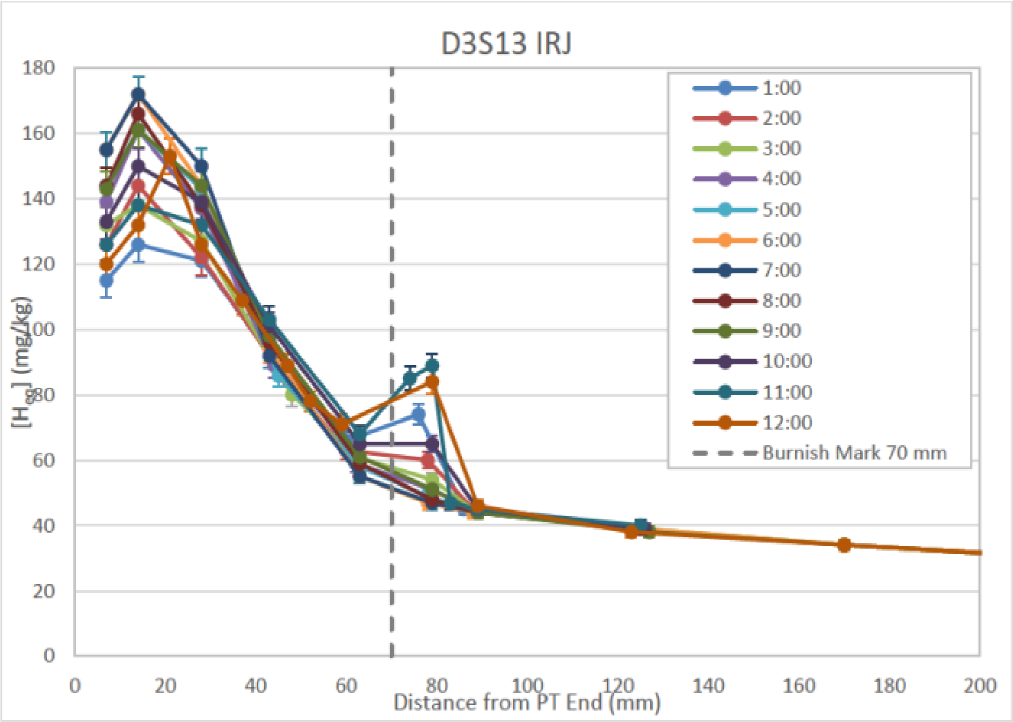
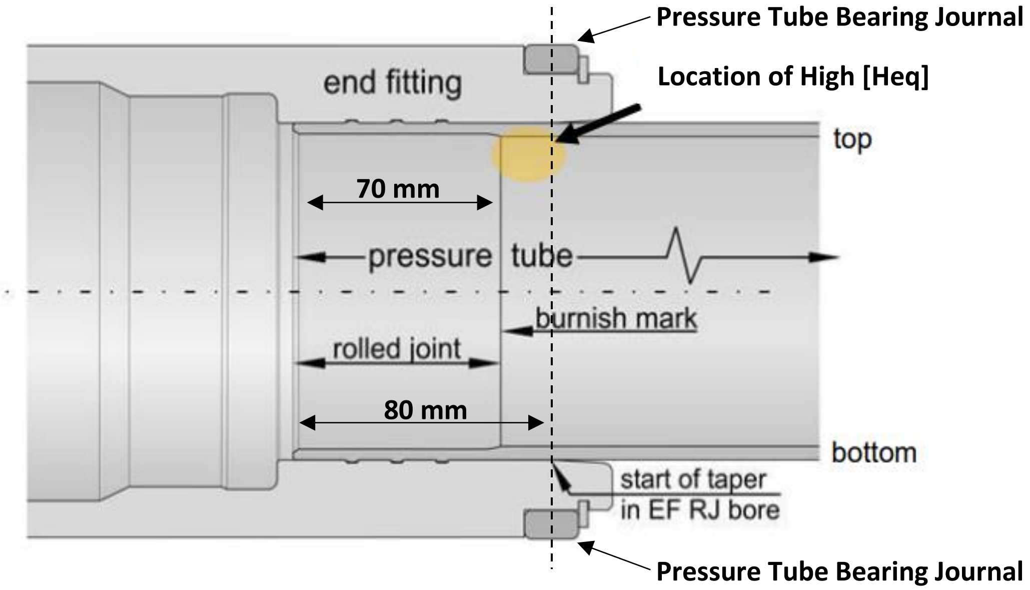


Figure 2 – D3S13 Inlet RJ Measurements from All Clock Positions

The "blip" in Heq for this pressure tube is observed at a distance of about 80 mm from the D3S13 inlet. As shown in Figure 1b below, 80 mm from a pressure tube inlet corresponds precisely to the location of the pressure tube bearing journal where the end fitting and lattice tube make contact – See also Figures 7 and 9a in the main Section of this Intervention.

Figure 1b: Schematic of a Pressure Tube-End Fitting Assembly Showing the Location of the Burnish Mark and the Pressure Tube Bearing Journal



The pressure tube bearing journal is made from tool steel which has a much higher thermal conductivity than any of the other alloys used in this region of an AGS, as shown in Table 1b; this has consequences for the behavior of ingressed H/D that are discussed below.

Table 1b: Some Properties of AGS Components Near an Inlet Rolled Joint

Component	Material	Thermal Conductivity (W/mK)	Estimated Operating Temperature (°C)	
			6 o'clock	12 o'clock
Pressure Tube	Zr-2.5%NB	17.1	260	245
End Fitting	403 SS	21.4	250	235
Bearing Journal	Tool Steel	27.0	210	190
Lattice Tube	304L SS	16.2	75	70

As noted above, a pressure tube bearing journal makes direct contact with a bearing sleeve about 80 mm from the end of the tube. The bearing sleeve is itself directly connected to a lattice tube which is fabricated from 304L stainless steel. A CANDU AGS lattice tube forms part of the reactor's end shield cooling system which recirculates light water at a temperature maintained below 70 °C. Because of this configuration, a bearing journal and sleeve behave as a heat sink at this location, creating a cold spot in the wall of a pressure tube where ingressed deuterium tends to accumulate.

It appears that the cooling effect of these bearing journals is not included in Bruce Power's explanation of the occurrence of a "blip" in the [Heq] at this location. Bruce Power invokes instead a "different" H/D pickup mechanism involving pressure tube contact "*with the tapered section of the end fitting, which creates a local cold spot that can attract hydrogen in the tube material*". However, Bruce Power's proposed mechanism does <u>not</u> explain why the pre-existing contact area of the end fitting, 70 to 80 mm from the end of a pressure tube, doesn't also create a cold spot.

It is significant that a "blip" in [Heq] is also observed at the equivalent *outlet* position – namely 80 mm from the outlet end of pressure tube B6S13. See the Figure below:

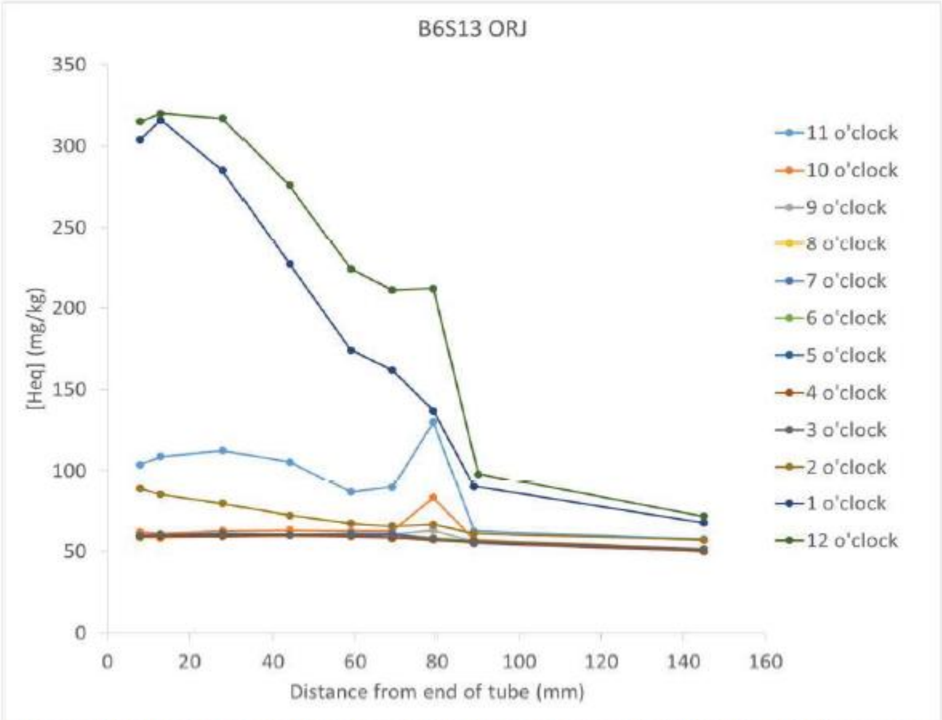


Figure 1: Hydrogen equivalent concentration measurements (obtained to date) from the outlet end of the B6S13 surveillance tube plotted as a function of axial location for the various clock positions.

Interestingly, the original data showing high Heq concentrations near the B6S13 outlet rolled joint is to be found in CNL's Report B-03644.4 LOF NSAS, issued September 17th, 2021, which inexplicably makes no mention of any "blips" in Heq ~ 80 mm from the end of the tube, but simply states:

> *The highest hydrogen isotope concentrations are observed in the upper few clock positions: 12:00, 1:00, and to some extent 11:00. Also evident, (*see the data in the Figure above*), is the beginning of the convergence of the profiles for each circumferential position for sampling locations inboard of the roll transition (i.e., burnish mark) of the joint.*

In spite of Bruce Power's inability to provide an explanation for the presence of blips in these [Heq] profiles, I have considered the effects of heat transfer on the formation of blips near the 80 mm axial location of a pressure tube in the following way:

Let the rate of heat transfer through a pressure tube bearing pad be represented by Q_{BP}(Watts), and assume that:

$$Q_{BP} = k.A.\Delta T/\Delta x \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where,

k is the thermal conductivity of the bearing material in units of Watts/meter.°C
A is the contact surface area of the bearing in units of $(\text{meters})^2$
ΔT is the temperature difference across a pressure tube bearing in °C
Δx is the thickness of the bearing in meters

I have used the following values for the fixed parameters in this equation:

$k = 27$ Watts/m.°C
$A = 30 \times 10^{-4}\ \text{m}^2$
$\Delta x = 2 \times 10^{-2}\ \text{m}$

From which we obtain:

$$Q_{BP} = 4.05 \times \Delta T \text{ Watts} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Calculations reported in the literature show that a value ~ 180 Watts is a reasonable estimate for Q_{BP}. It follows from Equation (2) that the associated ΔT is about 44 °C. This ΔT is separate and apart from the ΔT estimated in Section 7.0 of this intervention for the diffusional redistribution of deuterium at the outlet of the B6S13 pressure tube. Furthermore, Q_{BP} constitutes a heat *loss* term, while the ΔT described in Section 7.0 represents heat *gained* from contact with a fuel bundle. This observation suggests that there is non-uniform heat transfer from a pressure tube to the end fitting through both inlet and outlet bearing assemblies. Evidently, Bruce Power and OPG need to identify and quantify *all* processes that contribute to the observed distribution of H/D in a pressure tube in order to provide a meaningful explanation for the "blips" observed in [Heq] near the 80 mm axial location of some tubes.

Part 3:

The CNSC noted in their 2018 *Record of Decision* for Pickering's Licence Renewal that their confidence in OPG's scrape data stems from the fact that H/D pickup is: "*occurring at the predicted rates*". However, and most unfortunately for OPG, pressure tube scrape data for some Pickering pressure tubes show otherwise. Thus, the H/D concentrations measured in 2017 and 2018 are clearly at odds with earlier data for the same tubes, for example:

1. OPG undertook a pressure tube scrape campaign during the P1711 outage of Pickering Unit 1 in 2017 and the resulting body-of-tube data for a number of samples exhibited *decreased* or unaltered D pickup concentrations compared to previous measurements – a physically impossible result.

2. OPG also undertook a pressure tube scrape campaign during the P1861 outage of Pickering Unit 6 in 2018 and once again obtained data that showed *decreased* or unaltered D pickup concentrations compared to previous measurements – again, a physically impossible result.

OPG initially suggested that these two examples of anomalous D pickup behavior were caused by the influence of a hypothesized *hydride denuded zone* below the surface oxide layer on these pressure tube scrape samples. The possible existence of such a *denuded zone* in Zr-2.5Nb pressure tubes has been invoked since the 1990s. Thus, for example, in Ontario Hydro Report OH A-FC-97-113-P, entitled *Review and Predictions of Corrosion and Deuterium Uptake in the Body of Operating Reactor Pressure Tubes*, (issued in July 1998), we read:

> *Metallurgical cross-sections ... revealed the presence of a hydride layer immediately below the oxide-metal interface and a hydride denuded zone near the surface oxide layer. The presence of this denuded zone is suggested to account for the significant variability in [D] observed during scraping of these regions to determine bulk alloy [D].*

Nevertheless, in spite of OPG's speculation that hydride denuded zones could explain the low H/D concentrations measured in some of its recent scrape samples, this hypothesis has never been experimentally verified. However, it is noteworthy that similar problems have also been encountered with pressure tube scrape data collected during recent Bruce Power scheduled outages such as the Unit 7, B1761, 2017 scrape campaign. Thus, it is abundantly clear that H/D data obtained by currently employed pressure tube scrape techniques are not reliable and therefore are of no use in confirming that H/D pickup rates are "*occurring at the predicted rates*". It follows that OPG's and BP's currently operating reactors *do not meet the acceptance criteria for monitoring H/D pickup as specified by the applicable Standards CSA N285.4 and CSA N285.8*.

For the case of Heq data for Darlington Units we have the following information: OPG Confidential August 7, 2021 Report: NK38-CORR-31100-0940953

Fitness-for-Service Justification to Support Darlington Units 1&4 Restart

> *The results from D3S13 material surveillance demonstrate the [Heq] measurements 20mm inboard of the BM (relevant to deterministic fracture protection) meet the requirements of CSA N285.4 and all tube measurements satisfy the validity limits of the Revision 2 cohesive zone fracture toughness model. Based on the extensive material surveillance [Heq] sampling results to date in numerous tubes and at multiple clock and axial positions, the Darlington [Heq] models utilized in FFS assessments provide conservative upper bound predictions of [Heq] measurements.*

Thus, according to OPG, Darlington [Heq]] levels, measured by both scrape and ex-service punch procedures, satisfy model predictions of [Heq] because the vast majority of the data obtained from past outages remains between the upper and lower bound predictions at each axial location, thereby providing confidence that the [Heq] models are supported in FFS assessments.

However, in Bruce Power's March 11th, 2022 Report: BP-CORR-00531-02589, we read:

Dear Mr. Sigouin: *Bruce A and B: Defense-in-Depth Approach for Addressing Elevated Hydrogen Equivalent Concentration ([H]eq) in the Inlet Rolled Joint*

> *The purpose of this letter is to provide CNSC staff with supplementary information on Bruce Power's defense-in-depth approach to ensure the overall risk of a tube rupture due to elevated hydrogen equivalent concentration ([H]eq) in the inlet rolled joint region of pressure tube remains low. The defense-in-depth approach was communicated to the CNSC in the following Reference:*
>
> *• Letter, M. Burton to L. Sigouin, "Bruce A and B: CNSC Review of Industry Pressure Tube Surveillance Program – Inlet, Hydrogen Equivalent Measurements on PT from Unit Shutdown for Major Component Replacement (MCR), Action Item 2021- 07-24426", February 9, 2022, BP-CORR-00531-02495. Bruce Power recognizes that ongoing technical work is required to further understand the longer-term considerations and mechanisms related to elevated [H]eq in the inlet rolled joint region of ex-service pressure tubes from both Bruce Power and OPG through a joint industry program.*

Thus, we see that in a little over 6 months, Bruce Power and OPG go from having "*a high degree of confidence that pressure tube [Heq] values are within the appropriate licensing limits*", to acknowledging that "*technical work is required to further understand the longer-term considerations and mechanisms related to elevated [H]eq*".

Part 4:

On the topic of the reliability of pressure tube data reported by OPG, I should mention there are additional problems relating to data provided by OPG in its report: NK30-CORR-31100-0941210 P, "*Fitness-for-Service Justification to Support Pickering Unit 5-8 Restart*", issued in August 2021. This OPG report includes a series of Tables, numbered 3 through 6, described as "*conservatively calculated end of life target operating Hot Hour values for Pickering Units 5 to 8*". These Tables also include calculated Hot Hours from July 2021 to the "next planned outage" for all Pickering B Units. From these Tables it is possible to calculate the annual increase in each Unit's Hot Hours from July 2021 to the projected Unit End of Life in December 2024. The resulting data are presented in the table below:

Table 1c: OPG Data Reported for Pickering B Cumulative Hot Hours

Pickering B Unit	Total Hot Hours (As of July 2021)	Total Hot Hours (As of Dec 2024)	Accumulated HH Jul '21 – Dec '24	Average Annual Hot Hours
P5	268000	302000	34000	9951
P6	274000	310000	36000	10537
P7	267000	301000	34000	9951
P8	250000	288000	38000	11122

Unfortunately, there is a very good reason to question the validity of the data in Table 1c, and that is the fact that, even if a Unit operates with a capacity factor of 100 %, it is not possible for its annual Hot Hours to exceed 24 × 365 or 8760 Hot Hours. Thus, we see that *all* of the annual Hot Hour values listed in column 5 of Table 1c are significantly *greater* than 8760 hours – a physical impossibility.

It is also useful to compare the OPG data in Table 1c, to similar data published by the CNSC. Thus, Table 1d, below, contains Hot Hour data for Pickering B Units – derived from the equivalent EFPH data – taken from CNSC report CMD: 22-M34: "*Regulatory Oversight Report for Canadian Nuclear Power Generating Sites for 2021*", issued July 2022.

Table 1d: CNSC Data Reported for Pickering B Cumulative Hot Hours

Pickering B Unit	Total Hot Hours (As of Jan 2021)	Total Hot Hours (As of Dec 2024)	Accumulated HH Jan '21 – Dec '24	Average Annual Hot Hours
P5	270940	301875	30935	7734
P6	278063	309750	31687	7922
P7	269073	301350	32277	8069
P8	254461	288225	33764	8441

It is noteworthy that the "Average Annual Hot Hour" data in Table 1d are all significantly *less* than the theoretical maximum value of 8760 Hot Hours and are therefore preferable to OPG's dubious predictions found in Table 1c. But this conclusion is not only important in keeping track of a Pickering Unit's performance, but also in assessing the associated pressure tube ΔHeq values as explained below.

Why is ΔH_{eq} an important parameter in assessing the fitness for service of a pressure tube? Because all Canadian CANDU Units must satisfy the criteria set out in CSA Standard N285.4 for the maximum acceptable rate of change in H_{eq} – namely a maximum rate of increase in H_{eq} per 10,000 Hot Hours, or $\Delta H_{eq}/10^4$ HH, of 3 ppm, 2 ppm and 1 ppm, for Units at Darlington, Bruce and Pickering respectively. However, in order to make a realistic estimate of $\Delta H_{eq}/10^4$ HH for a particular Unit, it is necessary to have reliable estimates of the average annual Hot Hours of operation for the Units in question. Clearly, OPG and the CNSC need to resolve the differences in their estimates of the average annual Hot Hours for Pickering Units 5 to 8 in order to demonstrate these Unit's compliance with CSA Standard N285.4.

It should also be noted that similar issues with ΔH_{eq} predictions are apparent in Bruce Power's data for pressure tubes in its Units 5 – 8 when compared to values of this parameter quoted in a number of reports by CNSC, which are themselves inconsistent. Thus, for example, Table 1e, below, presents data taken from a number of the CNSC's *Regulatory Oversight Reports for Canadian Nuclear Power Generating Sites* issued in the period 2018 to 2022. Table 1e provides predictions of the End of Life (EOL) date, and the associated EFPHs for Bruce Units 5 to 8. Also included in Table 1e are extrapolated EFPH data taken from CNSC reports published in 2019 and 2022; column 5 of the Table lists the differences in the predicted vs. extrapolated EOL EFPHs.

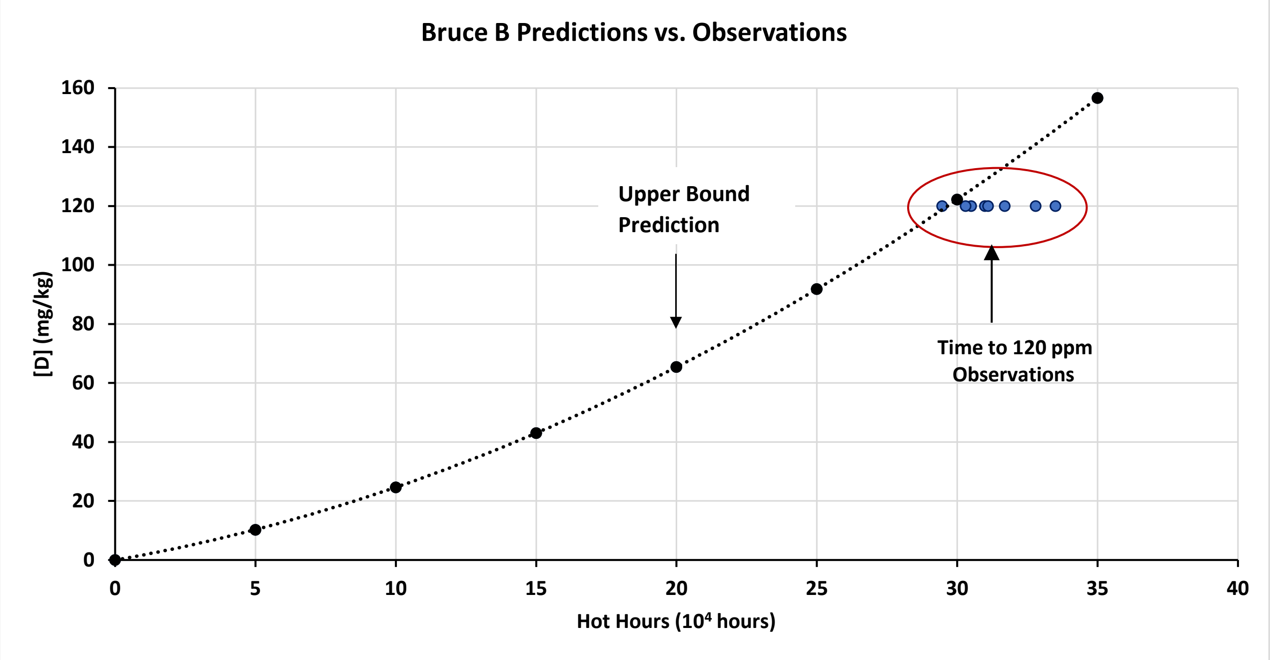
Table 1e: Data Reported by the CNSC for Bruce B Effective Full Power Hours

Bruce B Unit	Predicted EFPH at EOL	Predicted Date for EOL	Extrapolated EFPH at EOL	(Predicted – Extrapolated) at EOL
B5	274800	Sept 2023	286000	11200
B6	245000	Dec 2020	243773	−1227
B7	272000	Jul 2024	290000	18000
B8	275000	Jan 2027	300000	25000

Table 1e shows there are large differences between the predicted and extrapolated EFPHs at the EOLs of Bruce B Units. These differences are well known to the CNSC and led one of its Regulatory Program Directors, Dr. A. Viktorov, to note the following in a December 2019 letter to nuclear industry executives:

> *[Heq] predictions to EOL are important since they are directly related to the 120 ppm limit for (pressure tube) fracture toughness. At the same time, differences in methodologies and continuous updates, create difficulties for CNSC staff to have a clear understanding of [Heq] predictions to EOL.*

In his December 2019 letter, Dr. Viktorov provides some examples of contradictory EOL data, as shown in the Figure below:



I certainly would agree with this comment by Dr. Viktorov and ask OPG and Bruce Power to please explain and remedy these discrepancies in their $\Delta H_{eq}/10^4$ HH predictions.

Part 5:

As previously reported, [Heq] data show that for analyses conducted on samples from the same *axial location*, the D concentration at the 12 o'clock circumferential position is usually ***higher*** than the D concentration at the 6 o'clock circumferential position. This is somewhat unexpected because the D-pickup rate should increase as the temperature increases, and the bottom of a pressure tube is known to be hotter than the top at the same axial location. However, this tendency is countered by the fact that ingressed deuterium will diffuse away from a hot location towards a cooler location. Thus, any inferred D-pickup rate based on measurements on samples collected at a particular location is governed by the combined effects of time-dependent temperature and concentration gradients.

This means, for example, that if a pressure tube is resampled after 4-years, as required by CSA N285.4, the *true* D-pickup rate cannot be determined without knowledge of the relative contributions from corrosion and diffusion which are difficult, if not impossible, to disentangle. The additional influence of neutron-induced diametral creep only serves to exacerbate this problem. Simply put, the concentration of deuterium at a particular location in a pressure tube is subject to many highly variable factors including the reactor operating power; the Zr-2.5Nb corrosion rate and percent pickup; the degree of oxide spalling; the local temperature and concentration gradients; the terminal solute solubility and the deuterium diffusion rate.

However, as recently pointed out by Dr. A. Victorov, a Director General at the CNSC, there is an additional problem specific to scrape sample data, and that is the fact that during a scrape campaign pressure tube scrapes may be performed at any selected axial location, but only at circumferential locations near the top of the tube. In addition, in order to obtain an oxide-free sample, the CWEST scrape tool actually performs *two* scrapes, one to remove the pressure tube inner surface oxide layer, and a second scrape to collect an oxide-free base metal sample for analysis. This process leads to localized damage, ~ 3 cm^2 in area, and leaves a permanent flaw on the inside surface of the scraped pressure tube – See Bruce Power Report: B-REP-31100-00033, issued December 2021.

It follows that, for so-called "repeat scrapes" during some future campaign, the scrape must be carried out either at a different *axial location*, or at a different *circumferential location*. This means that the so-called "repeat analyses" used to determine values of $\Delta H_{eq}/10^4$ HH are actually *not true repeats*, and are therefore potentially not representative of any real changes in [Heq], especially in cases of large circumferential, or through-wall radial concentration gradients.

Based on these facts, I believe that the current practice of predicting the end-of-life performance of pressure tubes by relying on the measurement of D concentrations, derived from "repeat" scrape samples collected at "nominally the same location", is unacceptable because such measurements are not true repeats because they are *not* measured at the same location. Furthermore, because of the previously mentioned redistribution of ingressed deuterium, using the difference between two successive scrape measurements is not a measure of the true H/D pickup rate and therefore does not provide meaningful data for the evaluation and prediction of the present and future fitness-for-service of pressure tubes.

Part 6:

In addition to the problems with repeat scrapes discussed in Part 5 of this intervention, there is also a problem with the efficacy of the CWEST scrape tool in collecting an oxide-free sample. The issue here is that if a scrape is too shallow it will result in the second, base metal, scrape not being representative of the bulk pressure tube [D] as required. In practice it is observed that inside oxides on mature pressure tubes are up to 35 µm thick, and to be conservative, OPG has specified that the oxide scrapes must be at least 95 µm thick, although various OPG and COG reports published in the period 2015 to 2020 have specified oxide scrape minimum thicknesses up to 130 µm.

It is difficult and impractical to directly measure the thickness of an oxide scrape sample, therefore a surrogate measurement is used – namely, the oxide scrape *mass* m_{sc}, usually quoted in units of milligrams. This scrape mass is related to the sample thickness, d, measured in microns, by the simple relationship:

$$d(\mu m) = [10 \times m_{sc}(mg)]/A\rho$$

Where,

A is the oxide scrape sample area in cm^2
ρ is the oxide sample density in g/cm^3

Since an oxide scrape is essentially pure ZrO_2 with a density of about 6 g/cm^3, and the scraped area of a pressure tube is about 3 cm^2, we conclude that for a 100 mg oxide scrape sample, d is approximately equal to 50 µm. Since OPG has specified that oxide scrapes must be at least 95 µm thick, we also conclude that the minimum acceptable mass of an oxide scrape is about 200 mg.

However, oxide scrape samples collected from CANDU reactors over the past 25 years have exhibited a wide range of thicknesses especially for samples collected during different scrape campaigns. Thus, for example, the average oxide scrape thickness for the 1994 scrape campaign on Bruce Unit 3 was 103 µm, while the average oxide scrape thickness was only 66 µm for the 1996 campaign. However, third scrape campaign on Bruce Unit 3 conducted in 1998, using a modified scrape tool, generated oxide scrapes with an average mass of 494 mg and scrape thicknesses well over 200 µm – See OPG Report No. NK21-REP-31110-00001. This variability in sampling depth resulted in questionable H/D concentration data and the associated $\Delta H_{eq}/10^4$ HH predictions.

Nevertheless, both Bruce Power and OPG now claim that the latest version of the CWEST scrape tool generates oxide scrape samples that are "*much deeper than those obtained by the tools of the past*", implying that current scrape samples are at least 100 µm thick and weigh at least 200 mg. Unfortunately, perusal of some recent scrape data suggests otherwise. Thus, consider the data for the 2020 Pickering Unit 6 scrape campaign listed in OPG's April 2021 submission to the CNSC in Report: CD# NK30-CORR-00531-08205. Table 1, of Attachment 1, of this report lists data for 40 body of tube scrapes and 40 rolled joint scrapes. The oxide scrape masses, (neglecting obviously damaged samples), were in the range 50 to 80 mg. Similarly, in Appendix B of OPG's April 2021 Report, we have data for the Pickering Unit 7 2019 scrape campaign where the oxide scrape masses are in the range 36 to 55 mg. These results indicate that current oxide scrapes are certainly less than 50 µm thick, which one could hardly describe as satisfying the minimum oxide scrape depth requirement of 100 µm.

Part 7:

Canadian Nuclear Standard CSA N285.8, which covers "*Technical Requirements for In-service Evaluation of Zirconium Alloy Pressure Tubes in CANDU Reactors*", is quite explicit about the need to acquire "hydrogen equivalent concentration data" as stipulated in Clause 8.2, item d of the Standard:

> *When the measured pickup rate of hydrogen equivalent concentration exceeds the predicted upper-bound pickup rate of hydrogen equivalent concentration, the owner/operator shall satisfy the following technical requirements, ... etc*

What is most important to note here is the use of the term "*measured pickup rate*", as discussed further below. However, first we note that the related Standard, CSA N285.4, entitled *Periodic Inspection of CANDU Nuclear Power Plant Components*, states in Clause 12.3.5.2, item b of the Standard:

> *The measured rate of change in Heq shall be less than, ,,, etc,*

Thus, we see that CSA Standard N285.4 refers to limits on the *rate of change of Heq*, while Standard N285.8 refers to *limits on the hydrogen pickup rate*. This begs the question: Is the rate of change of Heq the same as, or different from the hydrogen pickup rate? To answer this question, consider the definition of the rate of change of Heq used in CSA N285.4:

$$\Delta \text{Heq}/10^4 \text{ Hot Hours} = 10{,}000 \times [\text{Heq}(t_2) - \text{Heq}(t_1)] / (t_2 - t_1)$$

Where,

t_1 is an initial Heq measurement time (in Hot Hours)
t_2 is a later Heq measurement time (in Hot Hours)

Now, until very recently, it has been tacitly assumed that:

$$\Delta H_{\text{Pickup}} = [\text{Heq}(t_2) - \text{Heq}(t_1)] / (t_2 - t_1)$$

Where,

ΔH_{Pickup} is the hydrogen pickup rate over time interval $(t_2 - t_1)$

This assumes that the change in the measured concentration of hydrogen at times t_1 and t_2, divided by the time interval $(t_2 - t_1)$, is equal to the hydrogen *pickup rate*. However, if we accept Bruce Power's explanation of the high levels of hydrogen isotopes in the outlet rolled joint region of pressure tubes B6S13 and B3F16, it follows that:

$$\Delta H_{\text{Pickup}} \neq [\text{Heq}(t_2) - \text{Heq}(t_1)] / (t_2 - t_1)$$

And this inequality is because of the postulated *redistribution of ingressed hydrogen isotopes* caused by thermal diffusion. Thus, we may write for the top and bottom of a pressure tube:

$$\text{Heq (top)} = H_{\text{Pickup}}\text{ (top)} + H_{\text{Diff;}}; \quad \text{Heq (bottom)} = H_{\text{Pickup}}\text{ (bottom)} - H_{\text{Diff}}$$

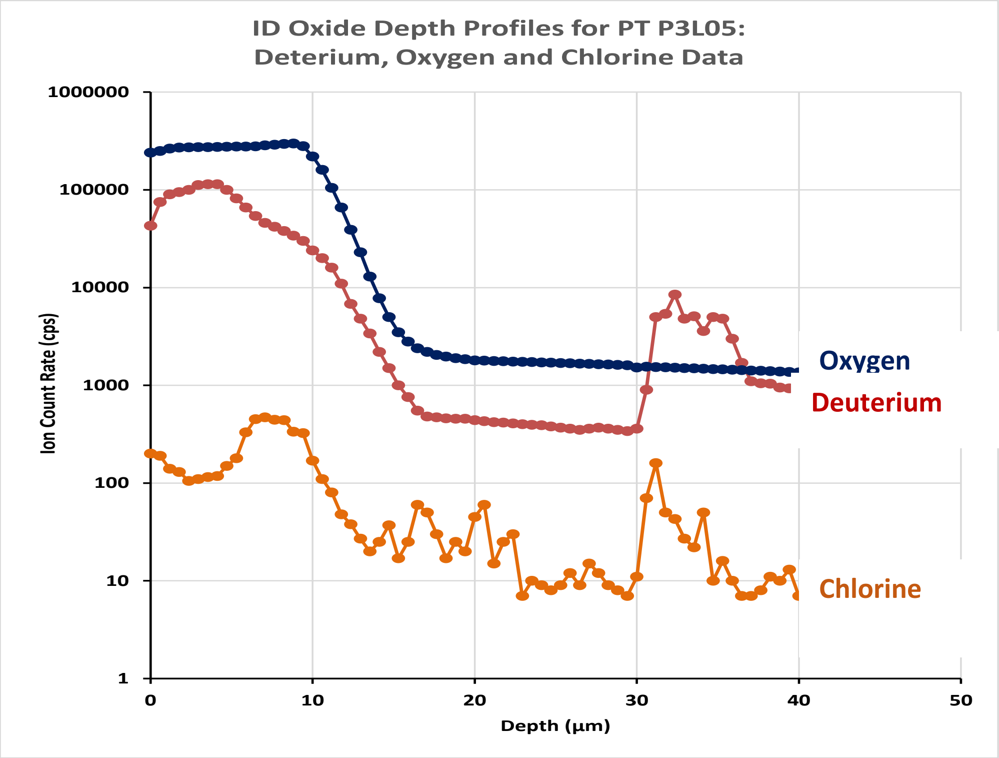
But this implies that CSA Standard N285.8 is not being properly applied by Bruce Power.

Part 8:

As previously discussed in this intervention, OPG suggested many years ago that cases of anomalous D pickup are due to the presence of a *hydride denuded zone* below the inside surface oxide layer of a pressure tube. Nevertheless, in spite of OPG's speculation that a hydride denuded zone could explain anomalous H/D concentrations, this hypothesis has never been experimentally verified.

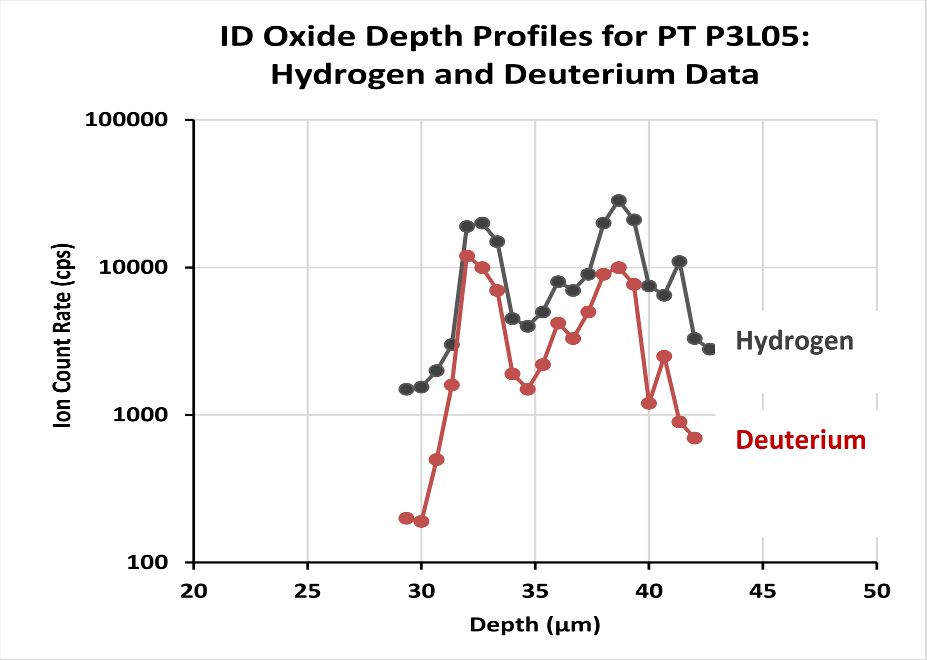
As discussed by Dr A. Viktorov in his December 2019 letter, a so-called "*denuded zone*" is a hypothesized near-surface region adjacent to the oxide/metal interface which is *free* of hydride inclusions. However, Dr. Viktorov also notes in his letter that a recent metallographic analysis of seven samples from Pickering Unit 6, *showed no denuded zones*.

In an effort to find supporting evidence for the presence of a denuded zone in near-surface regions of CANDU pressure tubes, I have reviewed available Secondary Ion Mass Spectrometric (SIMS) data for this region of interest. Surprisingly, rather than finding confirmation of the existence of this "denuded" region, I have found data exhibiting quite the opposite behavior, namely SIMS depth profiles in a number of Pickering pressure tubes showing clear evidence for sub-surface deuterides. Furthermore, these deuterides were observed in pressure tubes showing elevated levels of [Heq], such as the LSFCR surveillance tube P3L05, as shown in the SIMS data below:



These SIMS data show an oxide layer approximately 15 µm thick with a deuterium profile exhibiting deuteride inclusions in a zone well below the surface oxide layer, at a depth of about 30 – 40 µm; with a similar chlorine inclusion, (detected by the m/e = 35 peak), at the same depth.

A clue to the origin and nature of these inclusions may be found by comparing these depth profiles to depth profiles measured at essentially the same location, but for deuterium and hydrogen, as shown below:



These profiles show a remarkable concordance between the distributions of hydrogen and deuterium in the P3L05 inside oxide, but with the concentrations being about 4 times higher for hydrogen than for deuterium. We know all pressure tubes begin life with essentially no deuterium, but pick up deuterium during reactor operation, so we need to consider when and how hydrogen entered the tube? Is it possible that the hydrogen was already present in the tube at reactor startup as a residual trace impurity? I believe that the presence of chlorine at the same location as the hydrogen and deuterium sub-surface inclusions provides an answer to these questions.

The chlorine inclusions detected by SIMS analysis of the P3L05 pressure tube no doubt stem from the fact that chlorine is used in the Kroll Process to extract zirconium metal from zirconium ores. Multiple vacuum arc melting cycles are utilized for the production of Zr-2.5Nb pressure tubes to reduce the chlorine concentration to trace levels throughout the ingot. For pressure tubes manufactured in the 1980’s or earlier, the maximum permissible level of chlorine was 5 mg/kg, which was reduced to 0.5 mg/kg in 1992.

It is known that residual chlorine, at concentrations greater than 3 mg/kg, results in the formation of small precipitates, which are particularly damaging because they tend to cluster and become elongated voids – a process known as decohesion or fissuring. A high density of fissures is associated with low fracture toughness. Cracks and pores have been suggested as preferential pathways for the diffusion of H/D through a surface oxide and into the base metal where it accumulates at pre-existing voids. It is recommended that additional SIMS analyses of ex-service pressure tubes should be undertaken to investigate the occurrence of sub-surface inclusions of chlorine, hydrogen and deuterium in regions below the inside surface oxide.

Part 9:

Before concluding this intervention, I wish to point out that the high Heq levels recently observed in a number of Bruce Units is yet another example of how little is really understood about H/D ingress into operating pressure tubes. And how OPG, and more recently Bruce Power, have struggled to make reliable predictions concerning the fitness for service of aging pressure tubes.

As an example of this problem, I present below part of my submission to a Public Hearing, *held in March 2011*, on the topic of OPG's Darlington New Build Project where I wrote:

Pressure tube problems have plagued CANDU reactors since the early days of Pickering NGS in the mid-1970s. OPG, NBP, AECL and other members of COG, the CANDU Owners Group, have collectively spent over $100 million on pressure tube research and development in the past 20 years but achieved only marginal improvements in pressure tube performance. There have been problems with leakage at the pressure tube rolled joints, neutron induced creep of in-core pressure tube sections (leading to sagging), pressure tube embrittlement and hydride blister formation caused by excessive hydrogen pickup, and localized fretting corrosion.

Starting in 1974 many individual pressure tubes were replaced in Pickering and Bruce Units, typically involving outages of several months and a dose commitment of about 10 man-rem per tube. In August 1983 pressure tube G16 in Pickering Unit 2 suffered a catastrophic rupture and the decision was made to replace the full complement of 390 pressure tubes in all four Pickering "A" Units.

One would expect that after OPG and AECL fixed all these early problems, CANDU pressure tubes would provide many years of trouble-free service. Indeed, the CNSC stipulates that nuclear pressure boundary materials meet stringent inspection codes as a licensing requirement. Unfortunately, the complexity and inconsistent results of pressure tube inspections over the past 25 years leave the question of future CANDU pressure tube performance still very much in doubt. For example, in the CNSC's 2004 *Reason for Decision* on Bruce 'A' there is a section, albeit a very short one, that discusses the issue of pressure tube integrity. The perfunctory discussion offered by the CNSC fails to deal with, or even mention, some very important observations concerning Bruce 'A' pressure tubes. Just a small sampling of these observations is given below:

- Anomalous eddy current (EC) scans for a number of Unit 4 pressure tubes during SLAR inspections carried out in 1993.

- Some EC scans near the center of channel B4O13 that were so noisy it was impossible to reliably locate the spacers. The noisy EC signal was attributed to *either* very thick oxides *or* magnetite deposits.

- SLAR UT blister detection inspections, also carried out in 1994, produced highly variable signals that were shown to be caused by interferences from lubricant and/or adhesive contaminants.

- Metallographic sectioning of removed tubes carried out in 1993 - '94 showed *some* very thick patches of oxide on ID surfaces close to mid-bundle positions. Other sections that were predicted to have thick patchy oxides on the basis of EC inspections, were found to have thin uniform oxides.

• Data on deuterium uptake by Bruce pressure tubes are largely derived from scrape samples taken from “scrape campaigns” first undertaken on Unit 3 in October 1988. By 1993 it was realized that all previous scrape data were essentially worthless because of oxide contamination of the samples.

• Scrapes taken from pressure tube outlet regions of Unit 3 in 1994 were higher than predicted by the current AECL/OPG deuterium uptake model. The model was therefore revised to accommodate the new data.
• Re-scraping of Bruce 3 tubes in 1996 showed a *decline* in deuterium levels. AECL/OPG declared that the 1994 data were obviously in error and should not be included in deuterium uptake prediction calculations.

These observations raise serious concerns about the reliability of the inspection procedures used for pressure tubes in Bruce Units and undermine any belief in the long-term integrity of pressure tubes in all CANDU reactors. Certainly, as a veteran of many years of research into pressure tube corrosion and hydrogen pickup, I can attest to the poor level of mechanistic understanding of pressure tube behavior inside a CANDU fuel channel in spite of the efforts of literally hundreds of scientists and engineers worldwide. I have also been witness to the reporting of falsified data for some of OPG’s pressure tubes from Pickering NGS - a situation I reported to OPG management in 1995 that is yet to be rectified.

The CANDU research community is also unable to account for another unexpected problem observed in a number of Bruce “A’ fuel channels: namely, thick oxide patches in high flux regions of the core. Unfortunately, the true extent of this problem is largely unknown and this ignorance is compounded by the phenomenon of oxide spalling, which is known to have occurred in some Bruce ‘A’ Units. Measurements on heat transport system particulate from Bruce Unit 3 indicate that several *kilograms* of pressure tube oxide have been released to the coolant over 15 years of operation.

An additional observation that should give added cause for concern to the operators and regulators of CANDU reactors is the detection of lithium-6 *enrichment* and beryllium deposition in oxide patches formed in high-flux areas of some tubes removed from Bruce reactors.

Based on this intervention from 2011 it is clear that OPG and Bruce Power have collectively failed to explain anomalous Heq data that have been observed many times over the years. However, what most concerns me is how the CNSC has reacted to such an ongoing problem with data quality. And, in this regard it is useful to consider certain statements on this issue made by CNSC Commissioners and Staff going back almost *two decades*, as in the following example taken from the Commission Hearing on OPG’s application for renewal of Pickering A (May 21, 2003):

Discussion of Written submission from Dr. Frank Greening: 03 H7.16 / 03 H7.16.A / 03 H7.16.B / 03 H7.16.C:

COMMISSION MEMBER BARNES: I find it important that a seemingly competent senior scientist in an organization, a specialist in corrosion problems in a critical area that we are looking at for Pickering A, which is the corrosion of the feeder pipes and pressure tubes, has seemingly progressively felt that senior management were disregarding his comments.

Then, when seeing a scientific paper by members of Ontario Hydro, University of Western Ontario and Chalk River incorporate data that was inappropriate, the normal pattern in any kind of science surely would have been for the authors to have made a public retraction,

There seems to have been efforts on the part of Ontario Hydro in a sense to not encourage, if that is the right word, the public admission. Dr. Greening makes this point in virtually all of the four or five letters that we have had.

If this is true, I think it is a disturbing pattern here inasmuch as we are looking at a key aspect of the safety of the Pickering plant. Here is a specialist who is pointing out a very serious issue and perhaps indicating that we don't know enough about the issue. There seems, at least in his interpretation, to be some suppression of that. Does staff have any comment on these issues that Dr. Greening is raising?

Mr. BLYTH (Director General of Power Reactor Regulation): For the record, Jim Blyth. Yes, we do have comments. My first comment is that I have no doubt about Dr. Greening's competence or expertise in this area, but my interpretation from the documentation is that Dr. Greening does not understand the licensing process and does not understand how the CNSC or the AECB works. We base future performance of pressure tubes and most other components based on inspection results; samples collected from the pressure tubes in situ. We don't license based on a long-term prediction of how a component might perform. That is very important to OPG. We license on the basis of: Is this pressure tube or feeder going to function safely until the next inspection?

In terms of science, I do not propose to take issue with Dr. Greening by what I am saying. But it is important to understand that we deal with this differently. We are not interested in the science that is producing long term projections of a system or equipment performance. We are interested in inspection results. We are looking for frankly engineered solutions and engineered answers to these problems, not science.

MEMBER BARNES: So unlike Dr. Greening, who had a title of senior research engineer scientist, who was concerned about balancing the causes of potential corrosion, you are not interested in the causes of the corrosion but rather just the estimated wall thickness or thinness from inspection to inspection.

I would be inclined to agree with Mr. Blyth, (then Director General of Power Reactor Regulations), that pressure tube inspection data are of prime importance – rather than relying on theoretical models and predictions – *but only if the inspection data are consistent, reliable and reproducible, which, at the present time, is simply not the case*.

I therefore ask the CNSC Commissioners to recognize this uncomfortable truth about pressure tube inspection data and request that:

(i) OPG and Bruce Power stop relying on questionable *in situ* wet scrape measurements and use only Heq data derived from the analysis of punched samples from removed pressure tubes.

(ii) OPG and Bruce Power provide an explanation for the elevated levels of *light hydrogen*, and the accompanying high H/D ratios, (> 0.1), observed in some pressure tubes near their rolled joints

(iii) Bruce Power *proves* that the annulus gas systems of each of its Units, B3, B4, B5, B6, B7 and B8, are *not* the main source of light hydrogen observed in the pressure tubes in these Units, and if these AGS are not the source, could Bruce Power please explain what it believes the source is?

(iv) Bruce Power and OPG *prove* that iron and nickel carbonyls are *not* present in the annulus gas systems of any of their Units when they are shutdown

(v) Bruce Power and OPG *prove* that levels of NO_x/HNO_x species that are detrimental to the integrity of pressure tube outside oxides have never been present in any of their Unit's AGS

(vi) Bruce Power, rather than simply claiming otherwise, *proves* that the elevated levels of deuterium observed near the outlet rolled joints of pressure tubes B6S13 and B3F16 are *not* caused by accelerated D pickup

(vii) As pointed out in this intervention, the possibility of the redistribution of hydrogen isotopes in pressure tubes was first investigated by the Canadian nuclear industry ~ 25 years ago – See for example, OPG Report No; OH A-FC-97-113-P by D. Metzger et el: *Influence of Temperature and Concentration Gradients on the Redistribution of Hydrogen Isotopes*). Given this fact, could Bruce Power and OPG please explain why this phenomenon is only now being included in their deuterium uptake models?

(viii) Bruce Power and OPG acknowledge that many pressure tubes in Units at Darlington, Bruce and Pickering exhibit deuterium pickup rates, $\Delta H_{eq}/10^4$ HH, that are non-compliant with the CSA Standard N285.4 requirements for the maximum acceptable rate of change in H_{eq}

(ix) Bruce Power explain how it is in compliance with CSA N285.8 with regard to the measurement of the *hydrogen pickup rate*, when it also claims there is significant hydrogen diffusion to the top of a pressure tube leading to elevated hydrogen concentrations that are not representative of the true hydrogen pickup rate.

(x) Bruce Power please explain why *every* measurement ever made of [Heq] at the 12 o'clock location of an ex-service pressure tube is *not* elevated by thermal diffusion to the top of the tube and therefore *not* a true measure of the hydrogen pickup rate.

(xi) Bruce Power and OPG please provide experimental evidence proving that pressure tube scrapes collected with the current CWEST scrape tool are sufficiently thick to provide meaningful [Heq] data.

Dr. F. R. Greening

October 1st, 2022