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Secondary Startup Neutron Sources as a Source of Tritium in a Pressurized Water Reactor (PWR) Reactor Coolant System (RCS)

MW Shaver
DD Lanning

February 2010

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Summary

Currently there are large uncertainties in the attribution of tritium in a Pressurized Water Reactor (PWR) Reactor Coolant System (RCS). The measured amount of tritium in the coolant cannot be separated out empirically into its individual sources. Therefore, to quantify individual contributors, all sources of tritium in the RCS of a PWR must be understood theoretically and verified by the sum of the individual components equaling the measured values. The traditional accounting for tritium in the RCS assumes there are two main contributors. The first is soluble species in the RCS, and the second is release from fuel. This stems from the historical knowledge that when fuel had stainless steel cladding it was a major contributor. When the fuel cladding was changed to zirconium alloys in the 1970s, it was assumed that fuel was still the remainder of the source not attributable to the soluble species. Current investigation indicates that this may not be the case. The hypothesis of this paper is that the Zircaloy clad fuel source is minimal and that secondary startup neutron sources are the significant contributors of the tritium in the RCS that was previously assigned to release from fuel.

Secondary startup neutrons sources are made of cold-pressed antimony-beryllium pellets in stainless steel cladding. Beryllium is a source of tritium when irradiated with neutrons. Because the secondary source pellets have high porosity and stainless steel has a high permeability for tritium, the tritium that is made in the secondary sources permeates to the coolant. This secondary source contribution of tritium in the coolant is calculated computationally and statistically shown to account for all tritium in the coolant previously assigned to the fuel. Nine reactor cycles from three reactors were analyzed, and the results support the hypothesis of the paper.

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1.0 Introduction and Background

Currently, there are large uncertainties in the attribution of tritium in a Pressurized Water Reactor (PWR) Reactor Coolant System (RCS). The measured amount of tritium in the coolant cannot be separated out empirically into its individual sources. Therefore to quantify individual contributors, all sources of tritium in the RCS of a PWR must be understood theoretically and verified by the sum of the individual components equaling the measured values. The traditional accounting for tritium in the RCS assumes there are two main contributors. The first is soluble species in the RCS, and the second is release from fuel. The hypothesis of this paper is that the fuel source is minimal and that secondary startup neutron sources are the significant contributors of the tritium in the RCS that was previously assigned to release from fuel.

1.1 History of Accounting for Tritium Sources in the RCS

It is well documented that a large fraction of the tritium in the RCS is from neutron interactions with soluble boron in PWR coolant. Neutron reactions with a few other minor soluble species such as lithium and deuterium are also minor contributors to tritium in PWR coolant (Locante and Malinowski 1973; Liu et al. 2003; UK-EPR 2006). It has been traditionally assumed that the remainder of the tritium in the coolant is coming from the fuel rods including integral fuel burnable absorber rods (IFBA) that use boron as the burnable absorber. Nuclear fuel originally had stainless steel cladding, which released much of the tritium produced as ternary fission products since the permeability of hydrogen in steel is very high (Locante and Malinowski 1973).

In the early 1970s, as the fuel cladding was being changed from stainless steel to zirconium alloys (Zircaloys), a large decrease in the tritium levels in the coolant was noticed. Following the transition to zirconium alloy cladding, a small residual tritium could still be calculated when soluble tritium sources (mostly boron and lithium) was subtracted from the total measured cumulative RCS tritium, and this residual was again assigned to fuel with the acknowledgement that the tritium diffusion through Zircaloy cladding was unknown. This assignment was not questioned further because even with large uncertainties the cumulative tritium releases at the sites were well under the regulatory release limits. The conventional wisdom in the United States became that Zircaloy clad fuel rods release ~1% of their cumulative tritium production (Locante and Malinowski 1973).

However, more current (and mostly non-U.S.) literature indicates, through experimentation and modeling, that the release rate from Zircaloy clad fuel is actually ~$1 \cdot 10^{-4}$ to $1 \cdot 10^{-2}$%, making fuel a negligible tritium source and leaving hundreds of curies in the RCS unaccounted for (Liu et al. 2003; UK-EPR 2006; Andrieu et al. 2005). Documentation submitted to the British regulatory agency states that the unaccounted for tritium source in the coolant could be attributed to secondary source rods (UK-EPR 2006).

1.2 Background on Secondary Startup Neutron Sources

Neutron sources provide a flux of neutrons that are used to support reactor startup. Primary startup neutron source rods made of ^{252}Cf are inserted into the reactor during the first cycle of a new nuclear

reactor. The primary neutron sources are used to produce enough neutrons through spontaneous fission to create a sufficient neutron flux to be seen by the ex-core neutron detectors and facilitate reactor startup. Antimony-Beryllium secondary startup neutron sources are also inserted in the first reactor cycle to provide a neutron source for startups in future cycles. The secondary sources must be irradiated for a cycle to build up enough neutron emissions to support start up of the next cycle. A diagram, taken from Hawkes (1994), of a typical secondary source is shown in Figure 1. The main reaction chains in the secondary sources that produce the neutrons are:

$$
\begin{aligned}
&{}^{121/123}_{51}Sb + {}^{1}_{0}n \rightarrow {}^{122/124}_{51}Sb \\
&{}^{122/124}_{51}Sb \xrightarrow{t_{1/2} \sim days} {}^{122/124}_{51}Sb + \gamma \\
&{}^{9}_{4}Be + \gamma \rightarrow {}^{8}_{4}Be + {}^{1}_{0}n
\end{aligned}
\tag{1}
$$

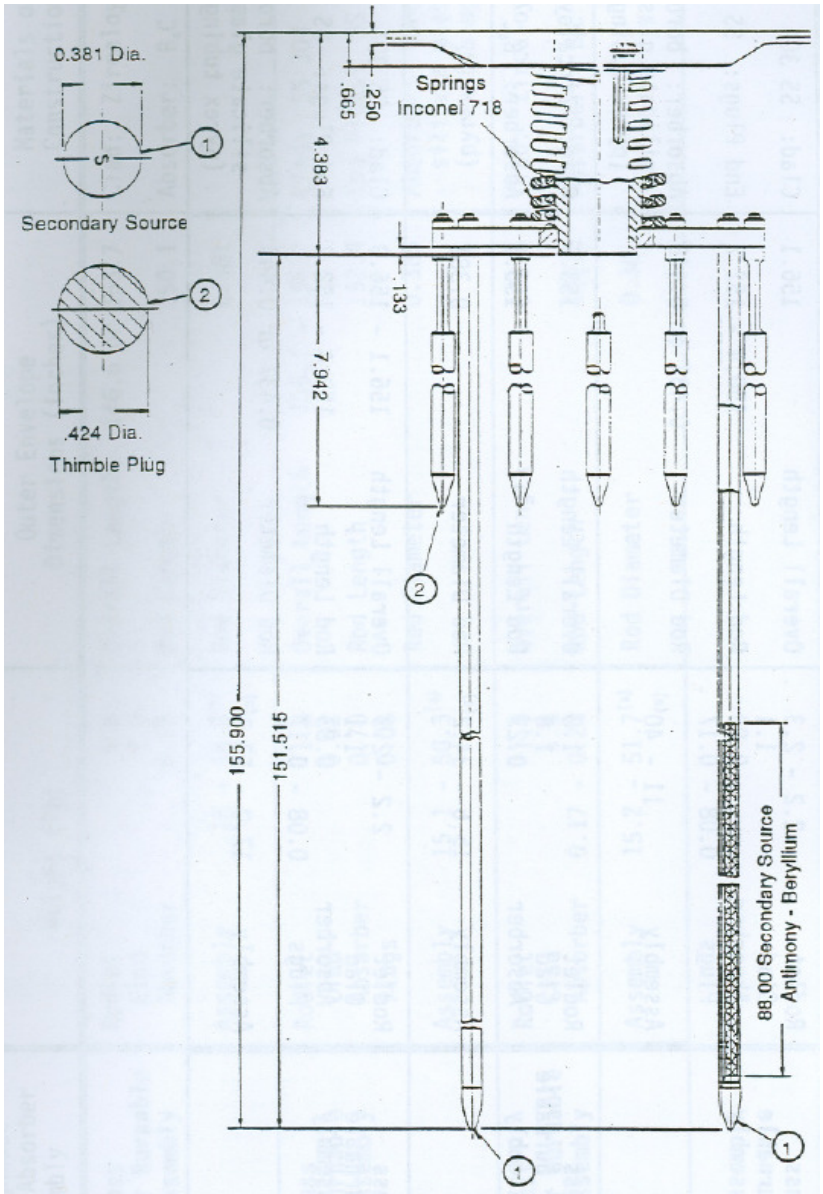

Figure 1. Diagram of a Standard Secondary Startup Neutron Source (Hawkes 1994)

2.0 Methods Discussion

This paper details the investigation and analysis quantifying the contribution of the secondary sources to the tritium in a PWR RCS. First, the degree to which secondary sources produce tritium and release it to the coolant is investigated. This is done by describing the tritium-producing reactions in the secondary sources and calculating their contributions. If they are found to be a major source, then it should be determined if they are the only major source besides the soluble species in the coolant. To do this, the two sources (i.e., total soluble species source and secondary neutron rod source) are subtracted from the total measured tritium in the coolant, and the unaccounted for tritium is quantified.

2.1 Secondary Source Physical Design Details

Because secondary sources are made from cold-pressed pellets of 50% antimony and 50% beryllium, half of the material by volume is made of a tritium-producing isotope when irradiated in a neutron flux (Van Engen and Ainsworth 1983). The tritium-producing reactions are shown below. The tritium produced in the secondary sources is primarily from the reaction chain:

$$\begin{aligned} &{}^{9}_{4}Be + {}^{1}_{0}n \rightarrow {}^{4}_{2}\alpha + {}^{6}_{2}He \\ &{}^{6}_{2}He \xrightarrow{t_{1/2}=807\,ms} {}^{0}_{-1}\beta^{-} + {}^{6}_{3}Li \\ &{}^{6}_{3}Li + {}^{1}_{0}n \rightarrow {}^{4}_{2}\alpha + \underline{{}^{3}_{1}H} \end{aligned} \tag{2}$$

Plots of the neutron cross sections for these two reactions are shown below in Figures 2 and 3, respectively.

There is also a small cross section for two other reactions, which are:

$$\begin{aligned} &{}^{9}_{4}Be + {}^{1}_{0}n \rightarrow {}^{10}_{4}Be + \gamma \\ &{}^{10}_{4}Be + {}^{1}_{0}n \rightarrow {}^{8}_{3}Li + \underline{{}^{3}_{1}H} \end{aligned} \tag{3}$$

As well as:

$$\begin{aligned} &{}^{9}_{4}Be + {}^{1}_{0}n \rightarrow {}^{7}_{3}Li + \underline{{}^{3}_{1}H} \\ &{}^{7}_{3}Li + {}^{1}_{0}n \rightarrow {}^{4}_{2}\alpha + {}^{1}_{0}n + \underline{{}^{3}_{1}H} \end{aligned} \tag{4}$$

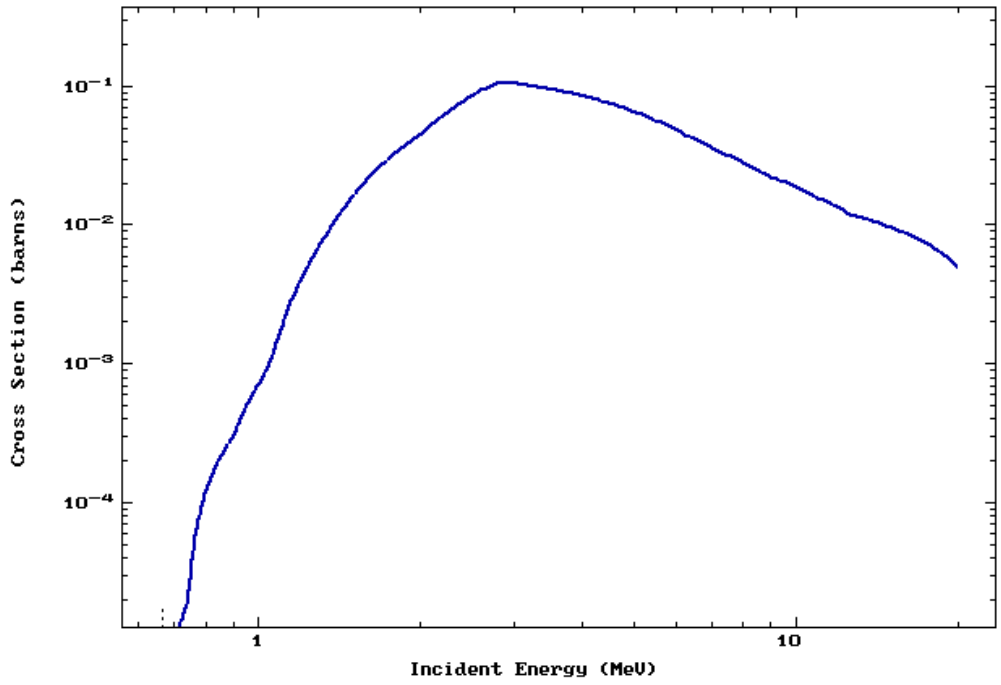

Figure 2. ^{9}Be(n,α) Microscopic Neutron Cross Section (ENDF/VI) (AEA Technology 1999)

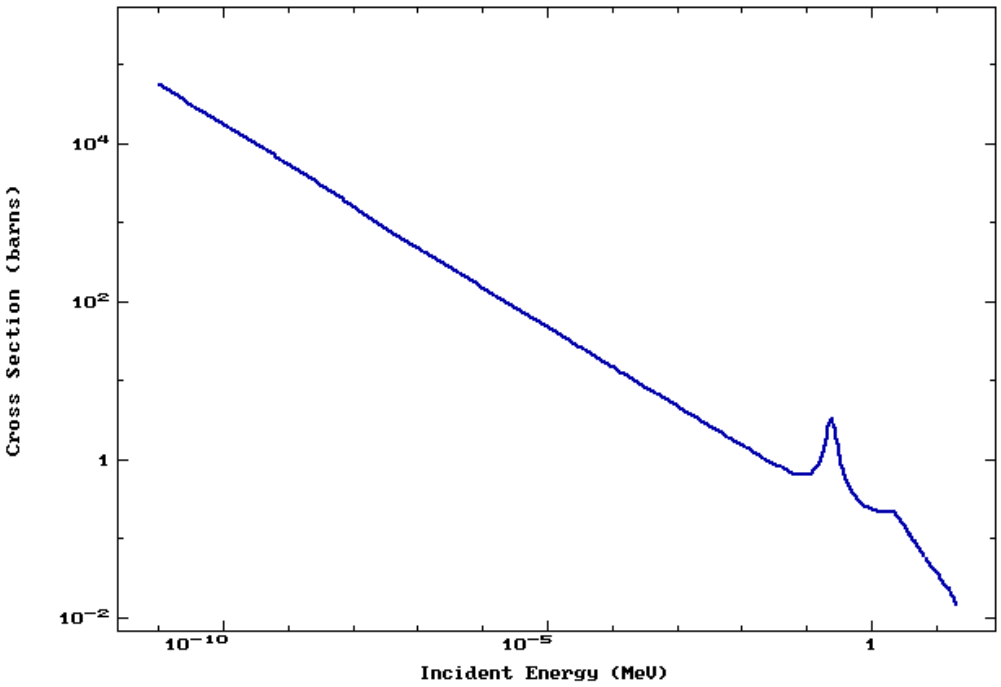

Figure 3. ^{6}Li(n,t) Microscopic Neutron Cross Section (ENDF/VI) (AEA Technology 1999)

Because the pellets are cold pressed, they have large and open porosity (Van Engen and Ainsworth 1983). In fact, it has been found using a scanning electron microscope that even the lowest porosity in the pellets is open, meaning the voids are interconnected, and therefore are not a barrier for tritium release

(Elmore 2009). Also, the secondary source cladding is made of stainless steel (Hawkes 1994; Van Engen and Ainsworth 1983), which has very high hydrogen/tritium permeability. Therefore, the assumption is made that there is no holdup of the tritium in the pellets and the diffusion through the secondary source cladding after production is instantaneous. Secondary source rods are exposed to less than the average axial core flux because they only span the bottom 88 in. of the active core, as depicted in Figure 1. The actual exposure seen by the secondary source rods can be determined from the axial burnup profile over the cycle.

The Winfrith Improved Mulitgroup Scheme (WIMS) version 8a simulation package, which is a general 2-D lattice cell neutronics code, is used to calculate the tritium production in stainless steel clad, Sb-Be secondary startup neutron sources (Shaver 2009b). WIMS calculates a 172 group flux and uses that to calculate the 172 group reaction rates that produce tritium. The group structure extends up to 20 MeV, which is necessary to account for the high-energy cross sections shown in Figure 2. This calculation is done by modeling a generic 2-D, 17 × 17, assembly with reflective boundary conditions. The methodology is detailed in (Shaver 2009b). Figure 4 provides a plot of the results of the tritium production in an average secondary source rod over its lifetime assuming identical, average 18-month cycles with the same flux and burnup.

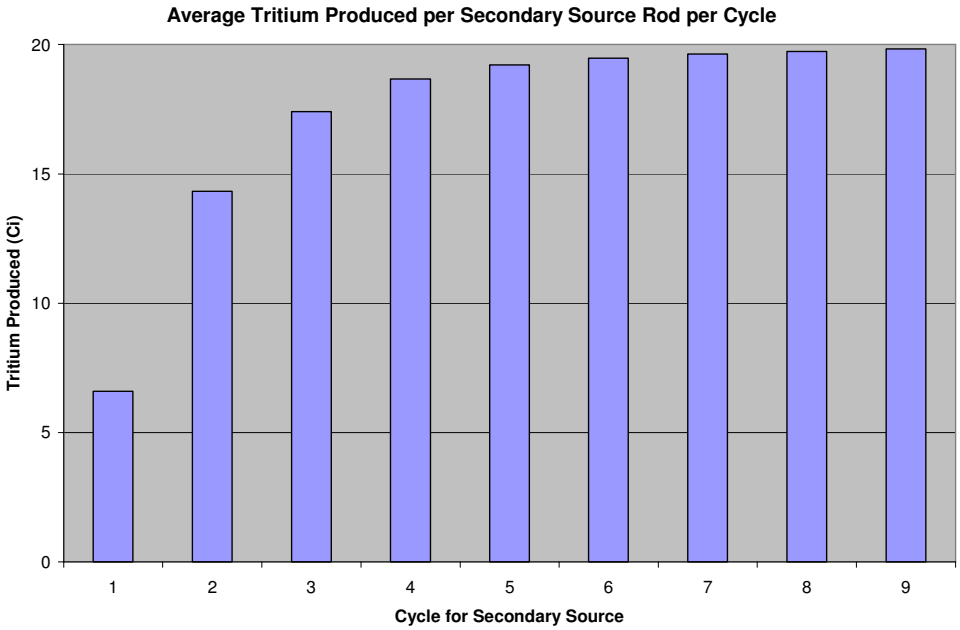

Figure 4. Tritium Production in an Average Secondary Source Rod over its Lifetime

2.2 Reactor Operation Details Related to Secondary Sources

There are usually 12 secondary source rods in an assembly and two secondary source assemblies with secondary sources in the core. The core locations of the secondary source assemblies may change each cycle, as does the relative burnup of each assembly. Each fuel assembly hosting a secondary source has a different relative burnup, which changes cycle to cycle. The host fuel assemblies are usually in symmetric positions in the core, and the production is assumed to be the same in each assembly for that cycle.

Secondary sources take one cycle to "charge" (i.e., become sufficiently activated to produce enough neutrons for the next cycle) and are used for approximately nine reactor cycles. The limiting factor in their lifetime is the pressure buildup from helium gas due to alpha particle production. Therefore, every ninth cycle there is an overlap of old and fresh secondary source assemblies to allow the new ones to charge. This typical loading is shown below in Table 1.

Table 1. Typical Loading of Secondary Source Assemblies for Each Cycle

Secondary Source	Reactor Cycle															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Assembly #1	x	x	x	x	x	x	x	x	x							
Assembly #2	x	x	x	x	x	x	x	x	x							
Assembly #3									x	x	x	x	x	x	x	x
Assembly #4									x	x	x	x	x	x	x	x

Assuming the production shown in Figure 4 per secondary source rod and the loading shown in Table 1, the total tritium in the coolant due to secondary sources can be calculated on a cycle-by-cycle basis. This calculation, which was done using WIMS, is shown in Figure 5 along with a comparison of the current fuel release model of 1.0 ± 0.2 curie per effective full power day (EFPD). The ± 0.2 curies per EFPD was added on because it seemed to take into account the variation of the data. As can be seen, the magnitudes are comparable, but the secondary source method takes into account the varying amount per cycle rather than a constant for all cycles. Knowing specifics of reactor cycles would also allow this analysis to be done for specific reactors and cycles.

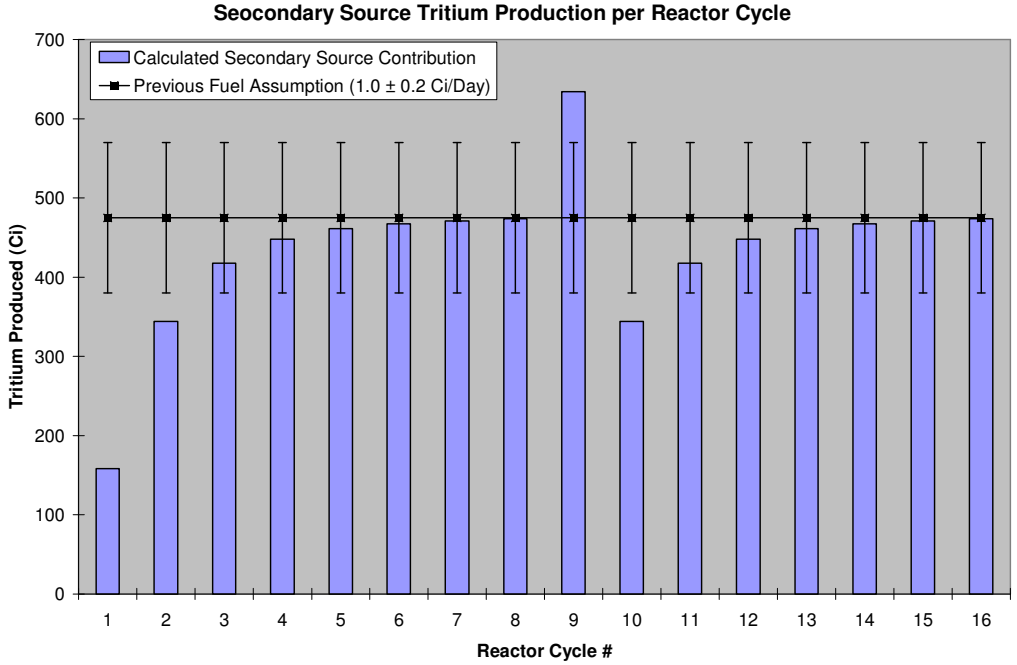

Figure 5. Comparison of Secondary Source and Fuel Release Methods of Accounting for Tritium in the Coolant from Core Components. Assembly loading is shown in Table 1.

2.3 RCS Tritium from Soluble Species

The tritium-producing soluble species in the RCS include boron (as boric acid for reactivity control), lithium (as lithium hydroxide to balance the pH), and deuterium (naturally occurring in water). The tritium production reactions from these species are:

$$ {}^{10}_{5}B + {}^{1}_{0}n \rightarrow 2\,{}^{4}_{2}\alpha + \underline{{}^{3}_{1}H} \tag{5} $$

Chain:

$$ \begin{aligned} &{}^{10}_{5}B + {}^{1}_{0}n \rightarrow {}^{4}_{2}\alpha + {}^{7}_{3}Li \\ &{}^{7}_{3}Li + {}^{1}_{0}n \rightarrow {}^{4}_{2}\alpha + {}^{1}_{0}n + \underline{{}^{3}_{1}H} \end{aligned} \tag{6} $$

Chain:

$$ \begin{aligned} &{}^{10}_{5}B + {}^{1}_{0}n \rightarrow {}^{2}_{1}H + {}^{9}_{4}Be \\ &{}^{9}_{4}Be + {}^{1}_{0}n \rightarrow {}^{4}_{2}\alpha + {}^{6}_{2}He \\ &{}^{6}_{2}He \xrightarrow{t_{1/2}=807\,ms} {}^{0}_{-1}\beta^{-} + {}^{6}_{3}Li \\ &{}^{6}_{3}Li + {}^{1}_{0}n \rightarrow {}^{4}_{2}\alpha + \underline{{}^{3}_{1}H} \end{aligned} \tag{7} $$

Chain:

$$ {}^{10}_{5}B + {}^{1}_{0}n \rightarrow {}^{9}_{4}Be + {}^{2}_{1}H \tag{8} $$

$$ {}^{2}_{1}H + {}^{1}_{0}n \rightarrow {}^{3}_{1}H $$

$$ {}^{11}_{5}B + {}^{1}_{0}n \rightarrow {}^{9}_{4}Be + {}^{3}_{1}H \tag{9} $$

Chain:

$$ \begin{aligned} &{}^{11}_{5}B + {}^{1}_{0}n \rightarrow {}^{3}_{1}H + {}^{9}_{4}Be \\ &{}^{9}_{4}Be + {}^{1}_{0}n \rightarrow {}^{4}_{2}\alpha + {}^{6}_{2}He \\ &{}^{6}_{2}He \xrightarrow{t_{1/2}=807\,ms} {}^{0}_{-1}\beta^{-} + {}^{6}_{3}Li \\ &{}^{6}_{3}Li + {}^{1}_{0}n \rightarrow {}^{4}_{2}\alpha + \underline{{}^{3}_{1}H} \end{aligned} \tag{10} $$

$$ {}^{6}_{3}Li + {}^{1}_{0}n \rightarrow {}^{4}_{2}\alpha + \underline{{}^{3}_{1}H} \tag{11} $$

$$ {}^{7}_{3}Li + {}^{1}_{0}n \rightarrow {}^{4}_{2}\alpha + {}^{1}_{0}n + \underline{{}^{3}_{1}H} \tag{12} $$

$$ {}^{2}_{1}H + {}^{1}_{0}n \rightarrow {}^{3}_{1}H \tag{13} $$

A similar model to the secondary source calculation can be developed in WIMS to calculate the tritium produced directly in the coolant by nuclear reactions with soluble species. Soluble boron accounts for more than 95% of all tritium production in the coolant. A methodology of this calculation is detailed in (Shaver 2009b).

3.0 Results and Discussion

When the tritium production from all sources is calculated over a specific cycle, the estimated secondary source tritium contribution as well as the tritium contribution from the RCS can be subtracted from the measured total tritium in the RCS, showing the unaccounted for tritium in the RCS is statistically negligible. This analysis is done on three cycles of three different reactors, which span the lifetimes and variable loadings of secondary source assemblies. This indicates that this methodology works when there are two or four secondary source assemblies. The results of these analyses are shown graphically for each cycle in Figures 6 through 14. The measured and calculated values are shown with their 2σ (95% confidence) error bars.

The black lines in the plots indicate the measured total tritium in the RCS, while the red and green lines represent the calculated contributions from the soluble species in the coolant and the secondary source rods, respectively. Subtracting out the calculated sources from the measured total, the unaccounted for tritium is represented as the blue lines. The amount of unaccounted for tritium is relatively close to zero in all cases, and the error bars on the unaccounted for tritium points encompass zero at all times. This means that no statistical difference can be found between the calculated unaccounted for tritium and having no unaccounted for tritium.

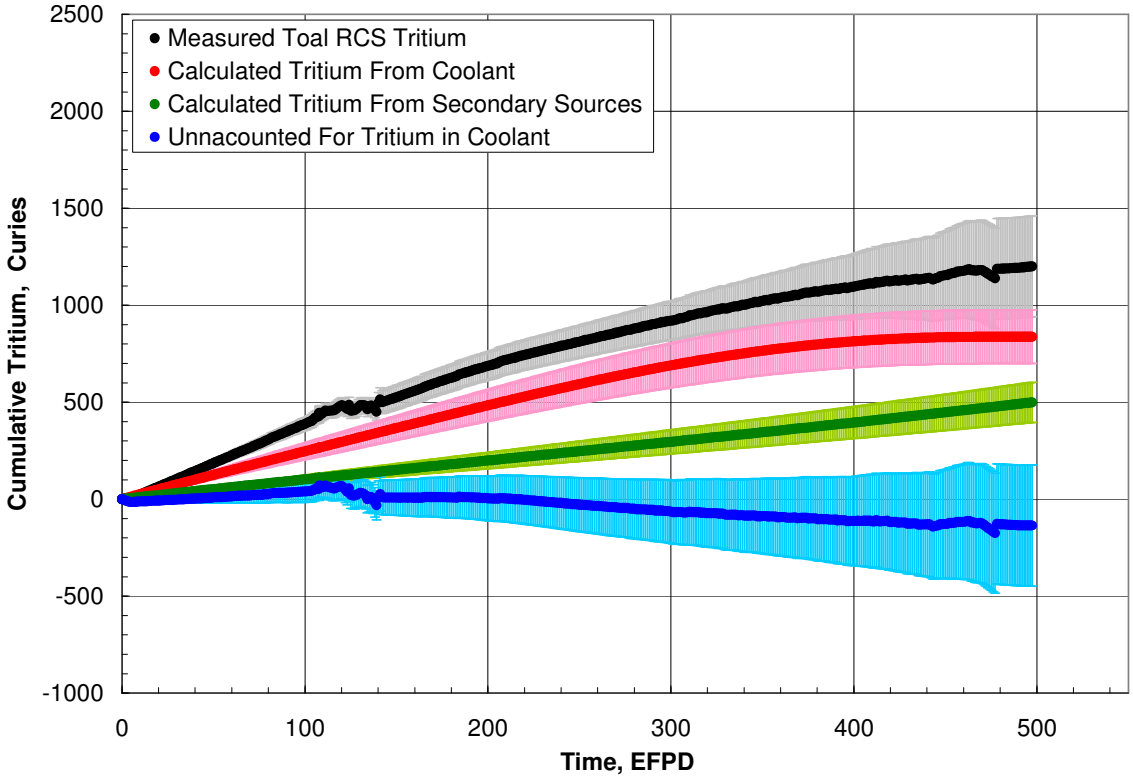

Figure 6. Reactor 1, Cycle A. Two, 8th cycle, secondary source assemblies.

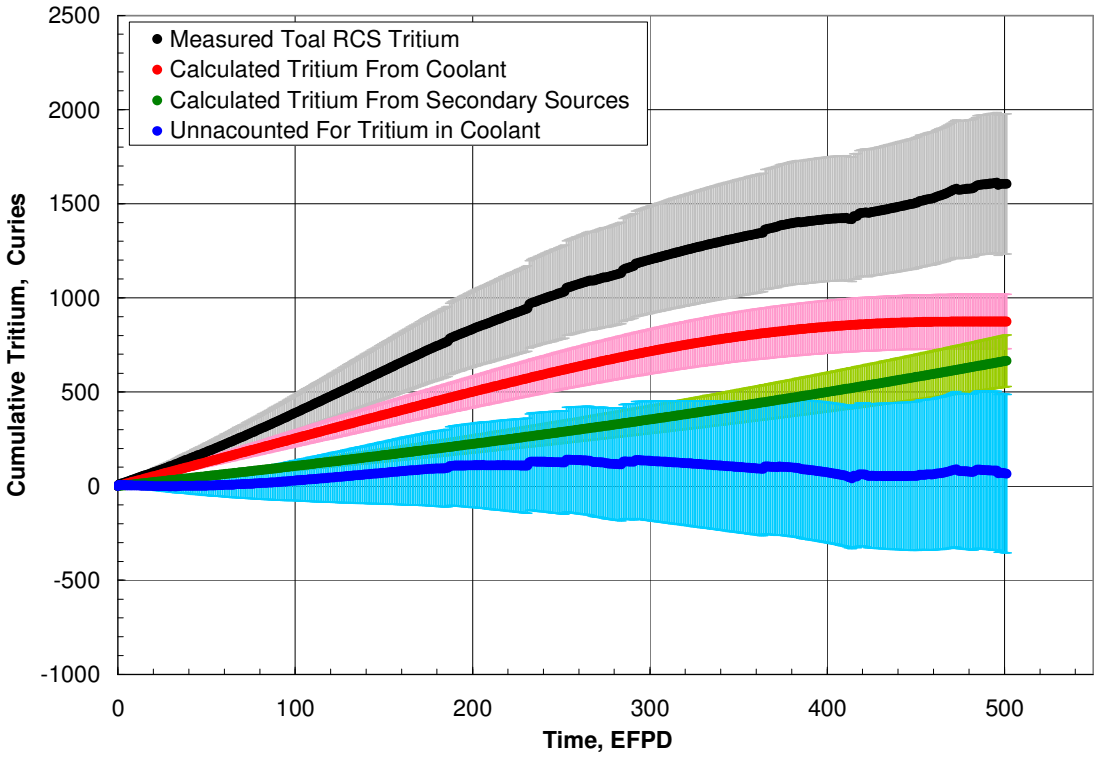

Figure 7. Reactor 1, Cycle B. Two, 9th and two, 1st cycle, secondary source assemblies.

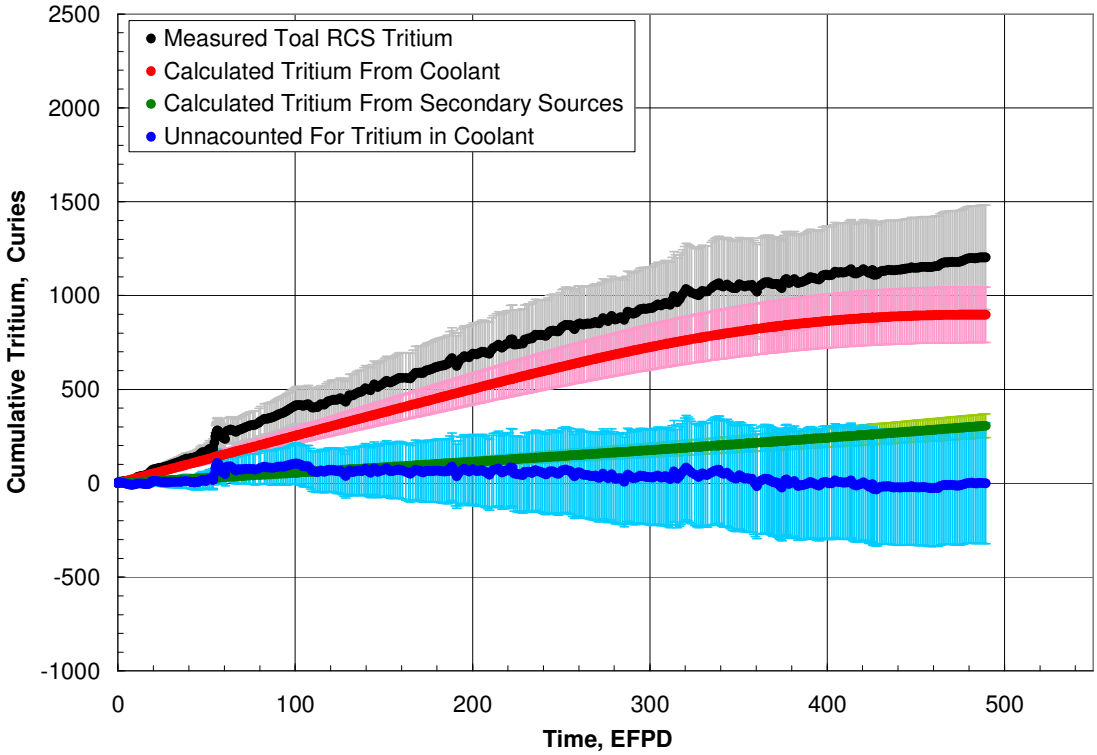

Figure 8. Reactor 1, Cycle C. Two, 2nd cycle, secondary source assemblies.

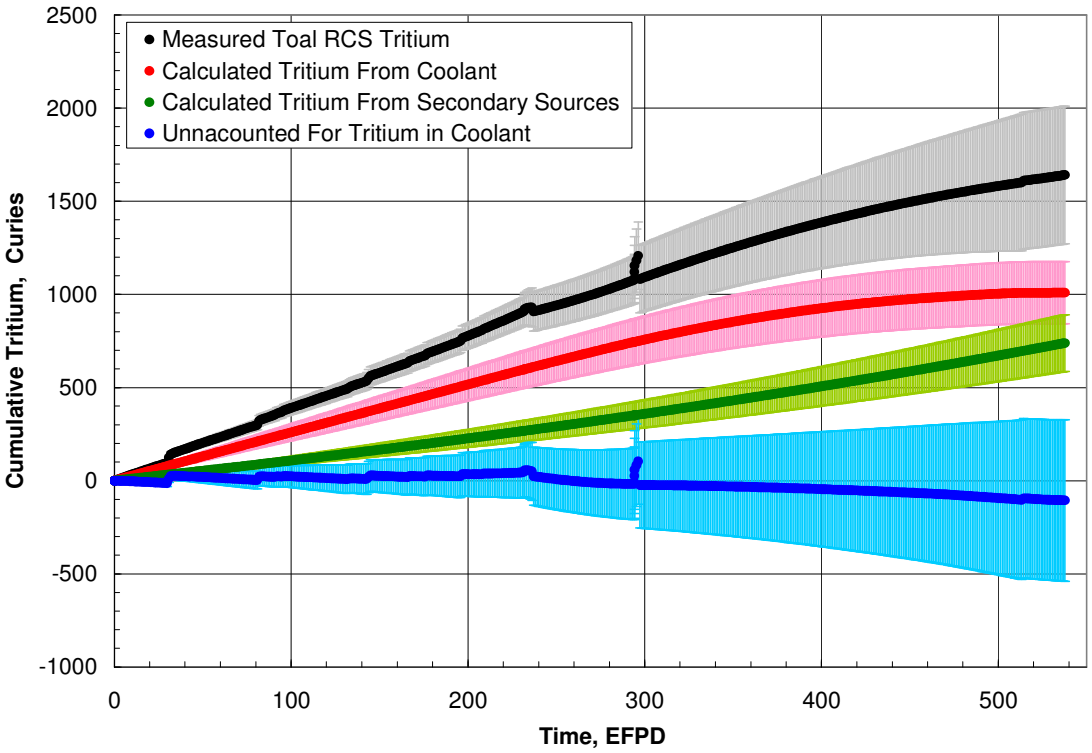

Figure 9. Reactor 2, Cycle A. Two, 9th and two, 1st cycle, secondary source assemblies.

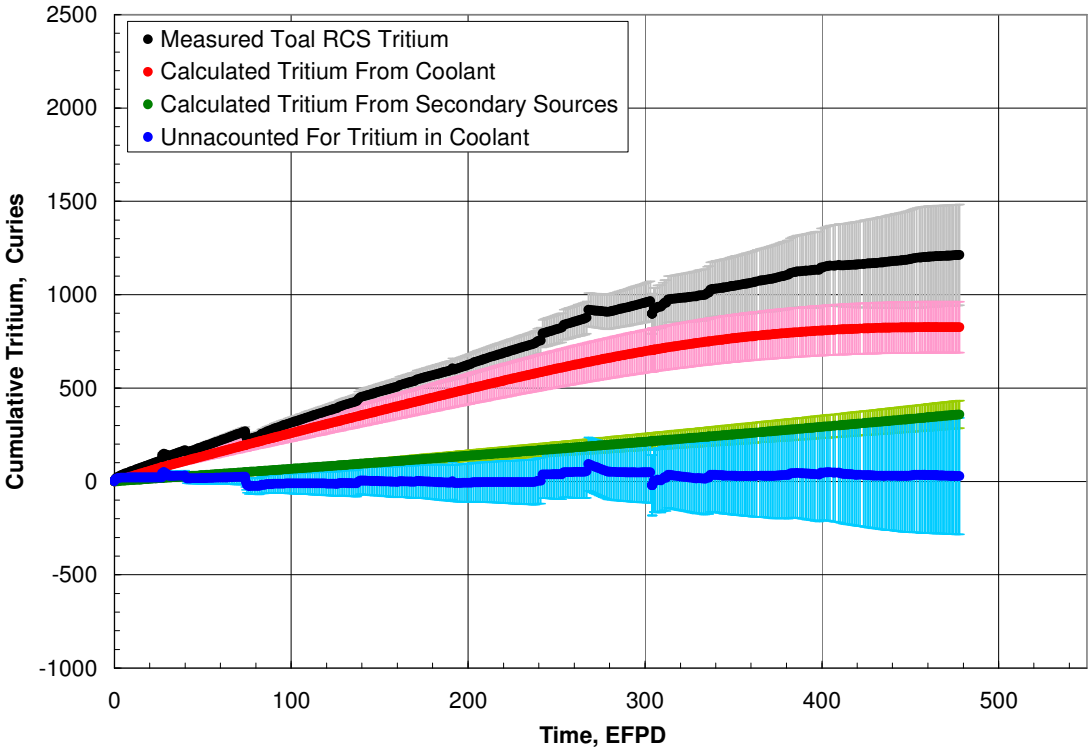

Figure 10. Reactor 2, Cycle B. Two 2nd cycle secondary source assemblies.

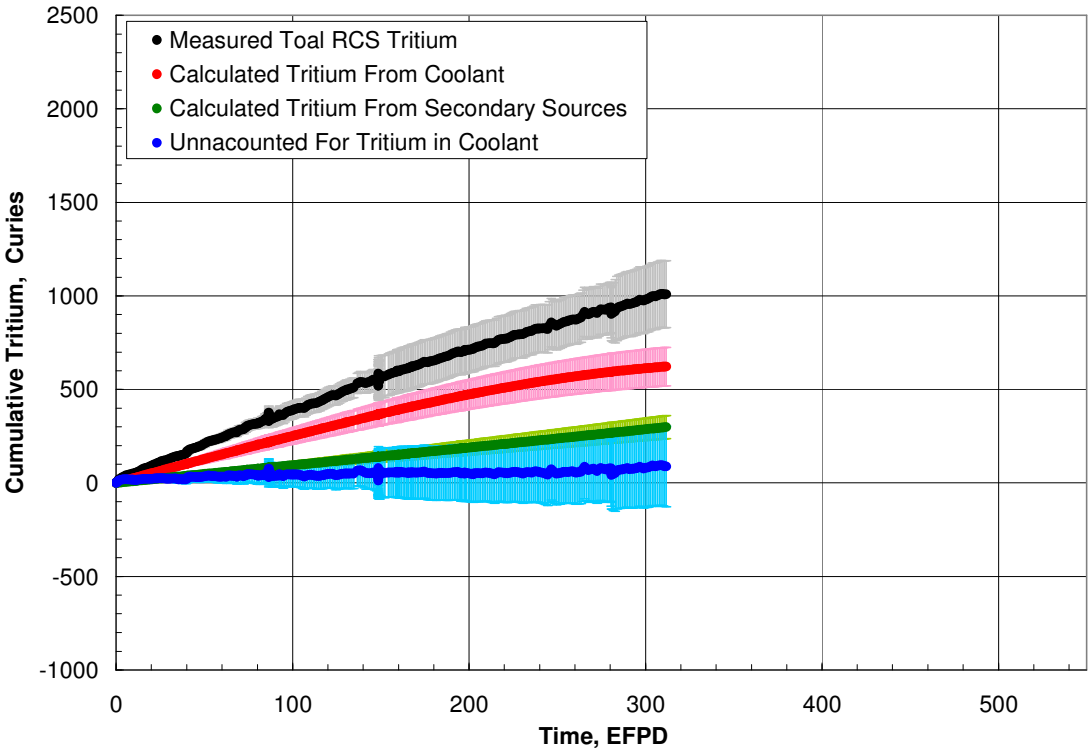

Figure 11. Reactor 2, Cycle C (partial cycle). Two 3rd cycle secondary source assemblies.

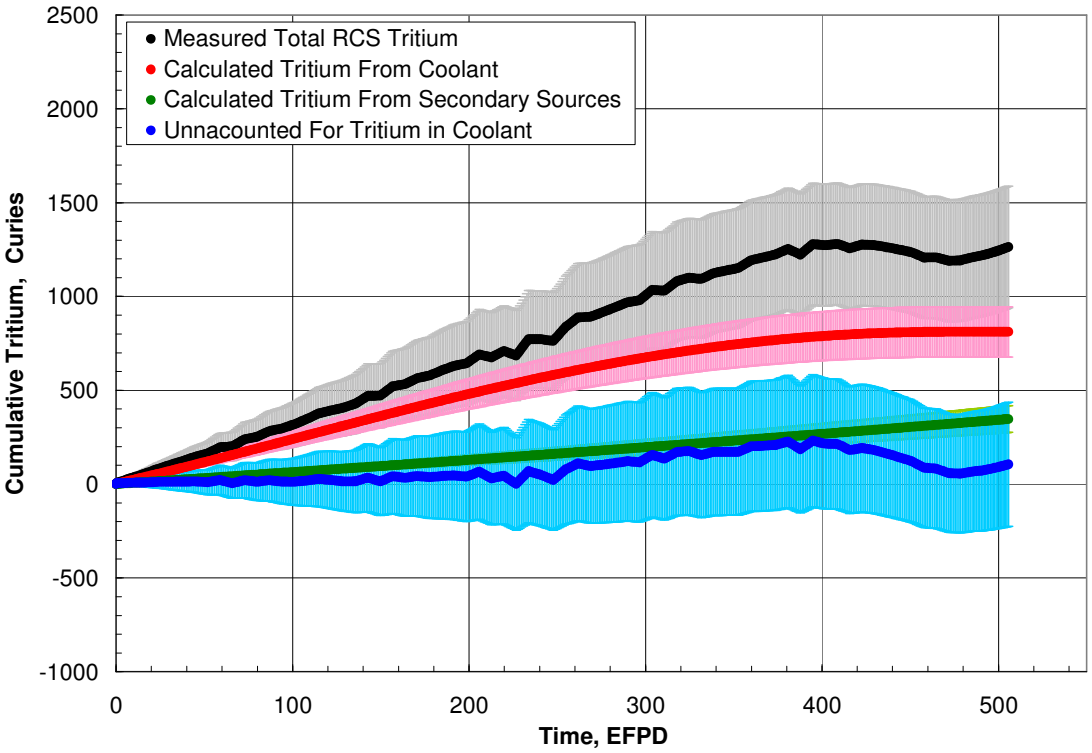

Figure 12. Reactor 3, Cycle A. Two, 3rd cycle, secondary source assemblies.

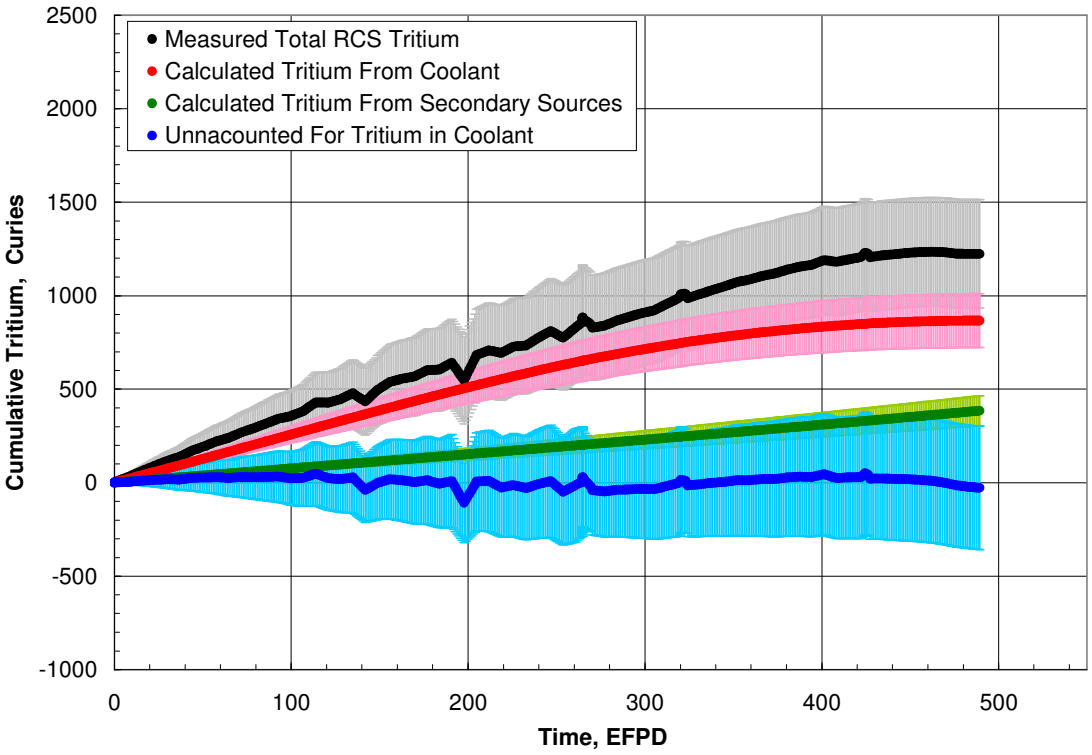

Figure 13. Reactor 3, Cycle B. Two, 4th cycle, secondary source assemblies.

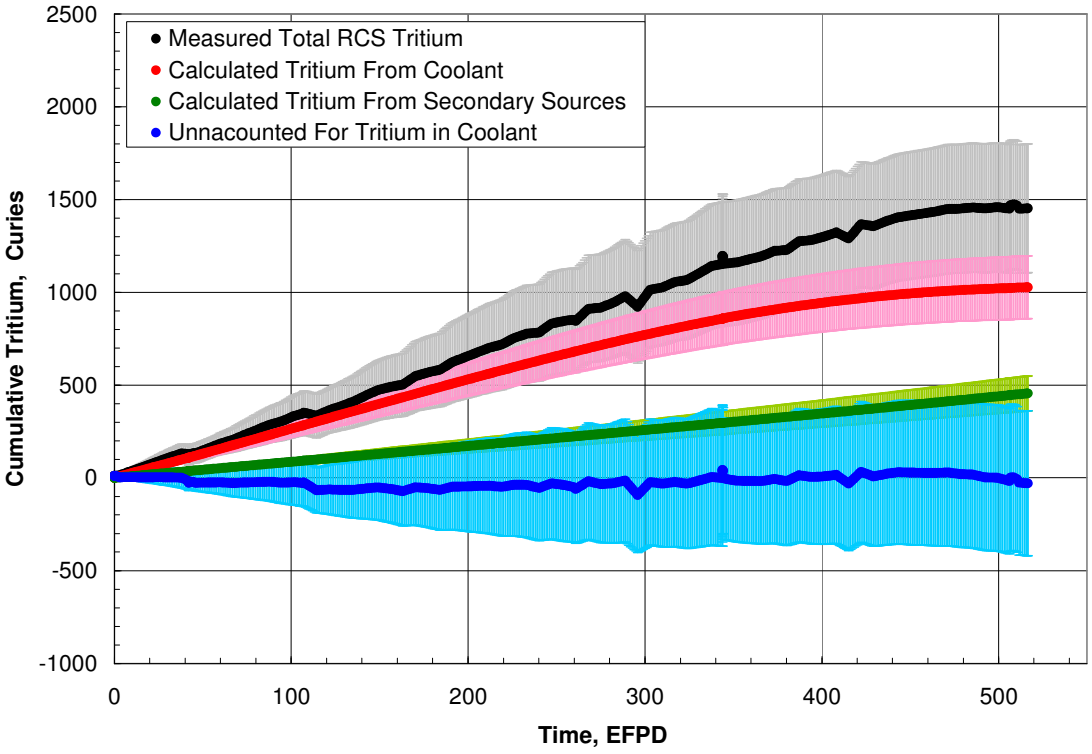

Figure 14. Reactor 3, Cycle C. Two, 5th cycle, secondary source assemblies.

Previous calculations assumed that fuel contributed 1.0 ± 0.2 Ci/EFPD tritium total to the RCS at a fixed rate. This range is picked because it nominally seems to fit the measured data. While this is the same range as the secondary source calculations for most cycles, the cycle to cycle values are less accurate. A plot comparing the two methods as a function of the measured data is shown in Figure 15. The black line is the ideal y=x line, the red line is the linear fit for the current fuel release model, and the blue line is the linear fit for the secondary source method. The secondary source method yields a correlation of y=0.93x+42.73, which is much closer to y=x than the fuel method, which yields y=0.15x+413.17. Also, the R^2 value is a useful metric of how much scatter there is in the data or how well the data fits the correlation. The closer to 1.0 the better the data points fit their correlation, and the closer to 0.0, the worse the data points fit their correlation. The R^2 value of the secondary source method is 0.73, which is a good correlation, and the R^2 value of the fuel method is 0.15, which is just barely any correlation at all. As can be seen, the secondary source points have a better fit to the y=x line (ideal) and a better R^2 value than the constant fuel source. This means that the secondary source calculation is a better fit with the measured data and is also more consistent with less spread in the data about its best fit line.

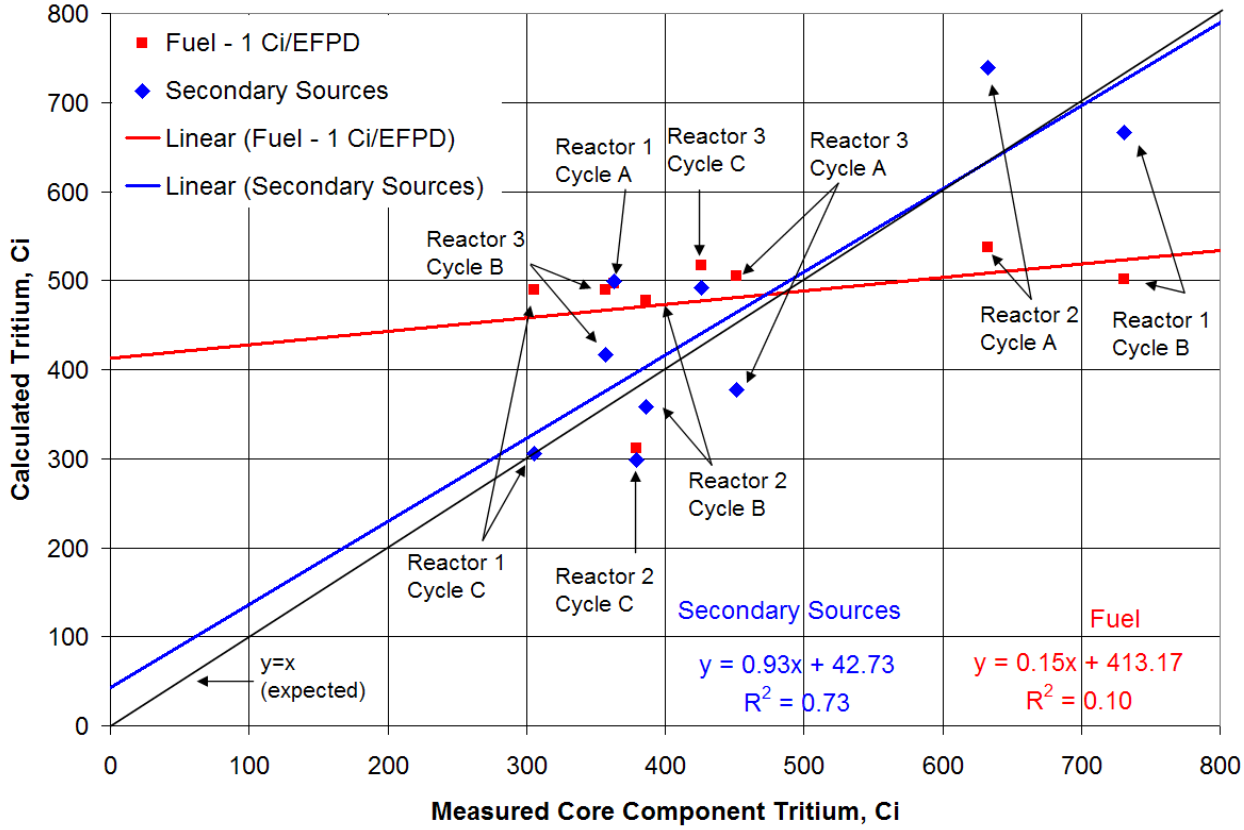

Figure 15. Predicted vs. Deduced ("measured") Core Component Source Tritium. The black line is the ideal y=x line, while the blue data represents the cycle-varying secondary source rod tritium production, and the red data is the constant "fuel source" source rate of 1.0 Ci/core/day.

Besides looking at the linear fits, the mean orthogonal distances can be compared. This is essentially a measure of the difference at every data point between the calculated and measured total values. The secondary source rod data points have a mean distance of 11.0% away from the ideal y=x line, while the

mean distance for the points from the fuel release method is 19.41%. As can be seen, these are both within the 95% confidence bands of ~20% for both methods, but the secondary source method values are still closer. This essentially tells us that the blue data points in Figure 15 are closer, on average, to the black line than the red data points are.

4.0 Conclusions

The hypothesis that tritium production in the secondary sources is a main source of tritium in the RCS of a PWR appears to the validated. When calculating the tritium in the coolant from secondary sources and adding that to the tritium from soluble species, it statistically accounts for all of the tritium in the coolant over a wide range of secondary source loadings. This analysis was done for nine reactor cycles in three reactors, where the total tritium in the coolant over the cycle was known.

5.0 References

AEA Technology. 1999. "WIMS: A Modular Scheme for Neutronics Calculations." *The ANSWERS Software Package, ANSWER/WIMS(99)9*. Dorset, United Kingdom.

Elmore, MR. 2009. *Characterization of Antimony/Beryllium Secondary-Source-Rod Pellets*. TTP-2-195, Rev. 0, Pacific Northwest National Laboratory, Richland Washington.

Locante J and DD Malinowski. 1973. "Tritium in Pressurized Water Reactors." In *Tritium* (AA Moghissi and MW Carter, editors), Messenger Graphics, Phoenix, Arizona and Las Vegas, Nevada, pp. 45–57.

Liu CC, J-H Chao, and CC Lin. 2003. "Tritium Release from Nuclear Power Plants in Taiwan." *Health Physics* 84(3):361–367.

UK-EPR. 2006. Fundamental Safety Overview Volume 2: Design And Safety, Chapter K: Discharges and Waste, Sub-Chapter K.3 Preliminary Estimate of Effluent and Waste.

Andrieu C, S Ravel, G Ducros, and C Lemaignan. 2005. "Release of Fission Tritium Through Zircaloy-4 Fuel Cladding Tubes." *Journal of Nuclear Materials* 347:12–19.

Hawkes EC. 1994. *Physical Characteristics of Non-Fuel Assembly Reactor Components*. PNL-8425, Pacific Northwest Laboratory, Richland, Washington.

Van Engen WR and A Ainsworth. 1983. "Report on Antimony-Beryllium Neutron Sources Examined After 7.45 Effective Full Power Years in the Dodewaard BWR." In *Dimensional Stability and Mechanical Behaviour of Irradiated Metals and Alloys, Volume 2*. In "Proceedings of the conference organized by the British Nuclear Energy Society", London.

Shaver MW. 2009a. *Tritium Production in Secondary Startup Neutron Sources.* TTP-1-3009, Rev. 0, Pacific Northwest National Laboratory, Richland Washington.

Shaver MW. 2009b. *Tritium Production in an LWR Reactor Coolant System.* TTP-1-3001, Rev. 0, Pacific Northwest National Laboratory, Richland Washington.

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