Tritium Behavior in Zircaloy Cladding from Used Light Water Reactor Fuel Rods – 14087

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ABSTRACT

Zircaloy cladding makes up roughly 25% by mass of used nuclear fuel (UNF) in the United States. Treatment options for Zircaloy cladding include recycling to recover the significant cost of the zirconium. For Zircaloy-clad fuels from light water reactors (LWRs), the tritium produced from ternary fission and other sources is expected to be divided between the fuel, where it is generated, and the cladding. It has been previously documented that a fraction of the tritium produced in uranium oxide fuel from LWRs can migrate and become trapped in the cladding. Addressing the tritium in the cladding could be an important step in the development of cladding-recycle treatment processes.

Examination of the literature indicates that data characterizing tritium content of actual samples of Zircaloy-clad fuel rods and cladding irradiated in LWRs are rather sparse and scattered. The estimates of the percentage of tritium in the cladding typically ranged from 0% to 96%, and very few data points are available for high-power-density burnups. The primary variables that are thought to influence the tritium concentration in cladding are cladding temperature, linear heat rating (power density), burnup, and/or the physical condition of the fuel rod or fuel pellets. Correlations with several of these variables have been attempted with limited success. More in-depth analysis of the existing published data and/or additional experimental studies are needed to understand the behavior of tritium in cladding.

In order to obtain a better understanding of how tritium in cladding will behave during processing, scoping tests were performed to determine the tritium content in the cladding before and after tritium pretreatment. Initial test results for tritium in H. B. Robinson pressurized water reactor cladding indicate that the cladding that received no heat treatment had a tritium concentration of ~5 µCi/g and that heating at 500°C to 600°C for 24 h removes approximately 65% of the tritium from the cladding. These tritium levels are low compared to those reported in the literature for cladding with similar histories. Additional studies will be needed to address the differences.

INTRODUCTION

In the future, reprocessing may be the option of choice for disposition of UNF from LWRs. Currently, various chemical pre-treatment processes are under development to simplify and increase the safety of the reprocessing plant [1]. For Zircaloy-clad fuels from LWRs, recycle of the zirconium is also an option being considered to reduce the mass and volume of transuranic waste (transuranic-contaminated Zircaloy cladding) since zirconium is 98.5% of mass of the used UNF zirconium alloy cladding [2].

For Zircaloy-clad fuels from LWRs, the tritium produced from ternary fission and other sources is expected to be divided between the fuel, where it is generated, and the cladding. It has been previously documented that a fraction of the tritium produced in LWR uranium oxide fuel can migrate and become trapped in the cladding.

Understanding the tritium content of the fuel and the cladding is important for the design of the reprocessing plant. In the baseline processing flowsheet (no pre-treatment or zirconium recycle), the UNF will be dissolved in nitric acid, and the tritium originally in the fuel matrix will remain in the dissolved fuel and will be spread throughout the plant. The tritium originally in the cladding should remain in the cladding which will be disposed of as transuranic waste. Pre-treatment steps are under investigation that could remove the tritium from the fuel matrix prior to dissolution, potentially avoiding the need for recovery of tritium throughout the plant. The requirements for treatment of the tritium in the pre-treatment step and the balance of the plant will be dependent on the extent of tritium removal during the pre-treatment step. The tritium content in the cladding also needs to be understood should cladding recycle be implemented. Tritium treatment requirements for the recycle operations will be dependent on the levels of tritium contained in the cladding. Those levels are presently unknown, and the impact of pre-treatment on the levels is also unknown.

This study was undertaken to gain a better understanding of the tritium content in Zircaloy-clad LWR fuel rods as a function of burnup and fuel history (e.g., temperature, power) and how the tritium concentration varies within a single fuel pin due to variations in its history (e.g., temperature profiles, heat rates). Once the tritium content in fuel rods is understood, the impact (if any) of tritium pre-treatment and zirconium recycle on the reprocessing plant design can be determined.

LITERATURE REVIEW

Examination of the literature indicates that tritium data from samples of Zircaloy-clad fuel rods and cladding irradiated in LWRs are rather sparse. The data describing the tritium content of UNF as reported in the available references were very scattered. Estimated percentages of tritium in the cladding typically ranged from 0% to 96%. The limited amount of data and the variety of methods used to obtain the data make interpretation very difficult. Most papers only analyzed the tritium in the cladding or the fuel. They calculated the total tritium in the fuel rod

using computer models, such as ORIGEN, to estimate the uranium and plutonium content remaining in the rod and calculated the resulting amount of tritium from ternary fission; the percentage of tritium in the cladding was estimated from the ratio of the amount measured in the cladding to the total amount of tritium calculated with the model. In some cases, the researchers took multiple samples of cladding near the same longitudinal cross section on the fuel rod for analysis. The scatter in the data typically ranged from ±10% to ±30% of the average tritium concentrations. Some researchers took samples at different points down the length of the fuel rod for analysis. The scatter in those data typically ranged from ±15% to ±65% of the average tritium concentrations.

Only three papers, by Goode and Cox [3], Gross and Hegland [4], and Bleir et al. [5], were found that measured the tritium levels in both the fuel and the cladding and attempted tritium mass balances. Their mass balances ranged from 19% to 99%. Gross and Hegland [4] was also one of the few papers based on the analysis of samples obtained along the length of the entire fuel rod.

Gross and Hegland's paper is a good example of the type of information that is available in the literature. They measured the tritium distributions for fuel and cladding in two ~1.8 cm diameter Zircaloy-2–clad UO_2 fuel elements. One rod was irradiated in the Big Rock Point (BRP) boiling water reactor (BWR) and obtained an average burnup of 12,000 MWd/tU at an average linear power density of 580 W/cm (17.6 kW/ft), and at one point along the length of the rod achieved a maximum burnup of 15,500 MWd/tU at a maximum linear power density of 735 W/cm (22.3 kW/ft). The second rod was irradiated in a General Electric Test Reactor (GETR) pressurized water loop. It obtained an average burnup of 21,000 MWd/tU at an average linear power of 1030 W/cm (31.4 kW/ft) with maximum burnup of 23,500 MWd/tU at a maximum linear power density of 1640 W/cm (49.7 kW/ft). The tritium distribution along the length of the rods is shown in Figure 1. The tritium concentrations are the highest in the middle of the rods and taper off on the ends, as would be expected from typical burnup profiles. The tritium concentrations in the fuel for both rods were rather uniform. There was scatter in the data on tritium content in the cladding, particularly for the GETR rod**.** The scatter in the data on the tritium content in the fuel was ±10% of the average values; the average scatter in the cladding data was ±30% for the BRP BWR rod and was too large to measure for the GETR rod. The closure on the tritium mass balances was poor, 47% and 19%, respectively. Gross and Hegland assumed that the unaccounted-for tritium was in the cladding and that their sampling/analytical methods had been inaccurate. Analytical data indicated that 26% of the theoretical amount of tritium was in the BWR fuel and that 9% of the tritium was in the cladding, but the calculated amount in the cladding (based on the difference between the theoretical amount and that measured in the fuel) was 74%. Similarly, they measured 4% of the tritium in the fuel and 15% of the tritium in the cladding for the GETR rod. The calculated amount of tritium in the cladding was 96%. The longitudinal distribution of tritium in the fuel for both rods followed the burnup profiles. For the BWR rod, the tritium in the cladding also followed the burnup profile. The longitudinal tritium distribution in the cladding of the GETR rod indicated thermal migration. The differences in

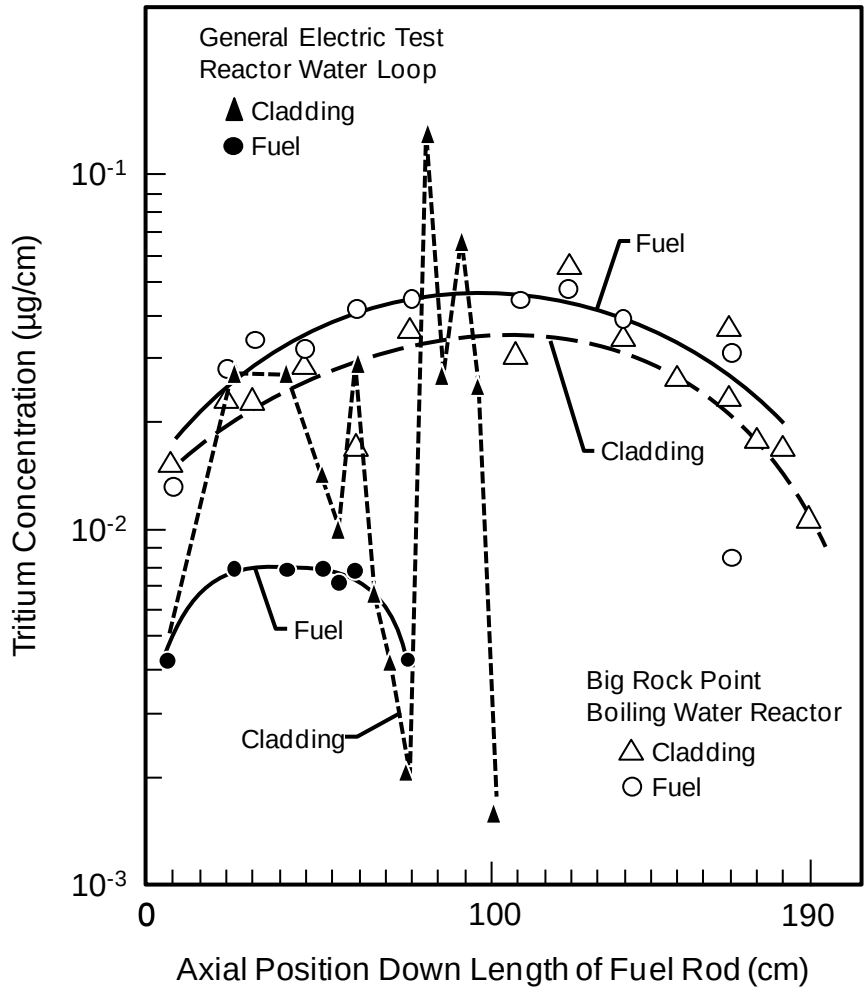

Fig. 1. Tritium Release Data from Fuel Rods (adapted from Gross and Hegland, 1971).

longitudinal tritium migration behavior were believed to be due to the different temperature gradients experienced by each rod. The BWR rod was irradiated in a reactor where the longitudinal temperature extremes did not exceed 50°C; the GETR rod experienced temperature differences of 150°C between the plenum and the active part of the fuel rod.

The primary variables that are thought to influence tritium concentration in cladding are cladding temperature, linear heat rating (or linear power density), burnup, and/or the physical condition of the fuel rod. Correlations between tritium concentration in the cladding and these variables have been attempted by various researchers as summarized below.

Goode and Vaughn [6] and Goode and Cox [3] evaluated data for pressurized water reactors (PWRs) and found no correlation between the linear heat rating (linear power density) and the percentage of tritium in the fuel. They speculated that the tritium concentration in the fuel was a function of the temperature of the fuel rods during reactor operations.

Megerth [7] reported tritium release data for the Zircaloy-2 cladding from fuel rods that were irradiated in the Vallecitos Boiling Water Reactor and that had attained average rod exposures as high as 10,000 MWd/tU prior to being incorporated in a special assembly that was irradiated in the Dresden Reactor Unit No. 1 for 5 years. The tritium content ranged from 2% to 16% of the tritium generated during operation. Megerth noted that cladding tritium content correlated quite well with the fuel burnup and with the average power rating over the total operating time. The ratio of cladding tritium content to burnup and time-averaged power increased rather markedly with increasing burnup and power, both among samples from different rods and between two samples from individual rods.

Grossman and Hegland [4] evaluated the data from Figure 1 along with Goode and Cox's [3] and Melehan's [8] data. They concluded that there was a strong relationship between tritium retention in the cladding and linear heating rate (linear power density), and that it was much stronger than the relationship with burnup.

Neeb et al. [9] studied tritium distribution in high-power Zircaloy fuel elements. They found a depletion of tritium in the center of the UO_2 pellet and postulated that the tritium migrates to the cooler surface. This effect is more pronounced at higher power densities and leads to an increase in the fraction of tritium in the Zircaloy cladding with increasing power density.

Wolfe et al. [10] evaluated their experimental data from a PWR and BWR along with data from Goode and Cox [3], Meleham [8], Grossman and Hegland [4], Broothaerts et al. [11], and Andriessen [12]. They found a correlation between tritium concentration and linear heat rate (linear power density). They noted that their references had found a depletion of tritium in the center of uranium fuel pellets and postulated that the tritium migrates to the cooler surface. This effect would be more pronounced at higher power densities, thus leading to an increase in the fraction of tritium in the Zircaloy cladding with increased power density. However, they noted that the possible dependence of the total tritium content on the linear heat rate (power density) can probably only be answered when more data obtained at higher linear heat rates (power densities) are available. Furthermore, they noted that it seems necessary to use samples from specific locations along an individual fuel rod.

Jenkins et al. [13] examined several batches of cladding hulls from a PWR and a BWR. They could not correlate the tritium content of the hulls with the linear power ratings of the fuel.

Uchiyama et al. [14] reported that the distribution of tritium between fuel and cladding seems to be dependent on temperature distribution in the fuel rod, which is influenced by the linear heating rate (power density) of the fuel but is much less dependent on the average burnup. This was based on reference papers by Bleir et al. [5] and Brucher [15]. Bleir et al. concluded that the distribution of tritium between fuel and cladding seemed to be independent of local burnup; rather, it depended on thermal conditions that influence diffusion from the fuel to the cladding. The 10% difference in tritium release between the PWR and BWR rods was attributed to the different dimensions and densities of the pellets.

Babenko et al. [16] did extensive measurements of tritium in N-1 alloy (Zr + 1% Nb) cladding from spent fuel rods from Vodo-Vodyanoi Energetichesky Reactor 440 fuel assemblies. They concluded that the tritium concentration did not correlate with the fuel depletion or fuel rod temperature. Significant nonuniformity was observed in the tritium distribution over both the length and circumference of the fuel rod. The nonuniformity was attributed to the accumulation in the form of hydrides near areas where the zirconium protective oxide film was damaged.

One of the most recent reviews was performed by Crowder et al. [17], where they evaluated data from their own experimental work as well as published data. They indicated that their data agreed well with the relationship described by Wolfe et al. [10] between the percentages of tritium in the fuel and the linear heat rate (power density), as shown in Figure 2a. Crowder et al. concluded that the relationship appears to work well for fuel with elevated linear power ratings (power densities), but fuels burned below ~200 W/cm showed a wide range of tritium retention values. The variability in tritium retention at low linear power density was attributed in part to the range of tritium retention values observed at different longitudinal positions along a fuel rod. They also noted that with only two data points available for high linear burnups, more data are needed to determine whether tritium content is dependent on linear heat rate (power density). The percentage of tritium in the cladding versus linear heat rate for the data reported by Crowder et al. [17] is plotted in Figure 2b. In this case, the model does not fit the data as well [18].

EXPERIMENTAL

In order to obtain a better understanding of how tritium in cladding will behave during processing, scoping tests are being performed to determine the tritium content of unheated and heated samples of cladding [19]. Tests are being performed on cladding from a fuel rod from the H. B. Robinson PWR. The fuel rod contained UO_2 enriched to 2.9 wt % uranium-235. It was discharged from the reactor in 1995, and the average burnup was 63 to 67 GWd/MTU. The cladding is Zircaloy-4.

Experimental Technique

Samples taken from near the center of the fuel rod were defueled by mechanical means after which the cladding was given a leaching treatment in~8M nitric acid at 80°C to 90°C to remove any loose particles on their surfaces. The defueled cladding was cut into rings approximately 5 to 6 mm in length. Each ring of cladding was cut into three equal segments by cutting each ring at radial positions (i.e., 0°, 120, and 240°).

The segments from one ring were analyzed to determine the tritium content in the cladding after being exposed to one of three heating conditions. One segment was digested as is with no heating pretreatment. The second segment was weighed, heated to 500°C for 24 h, reweighed,

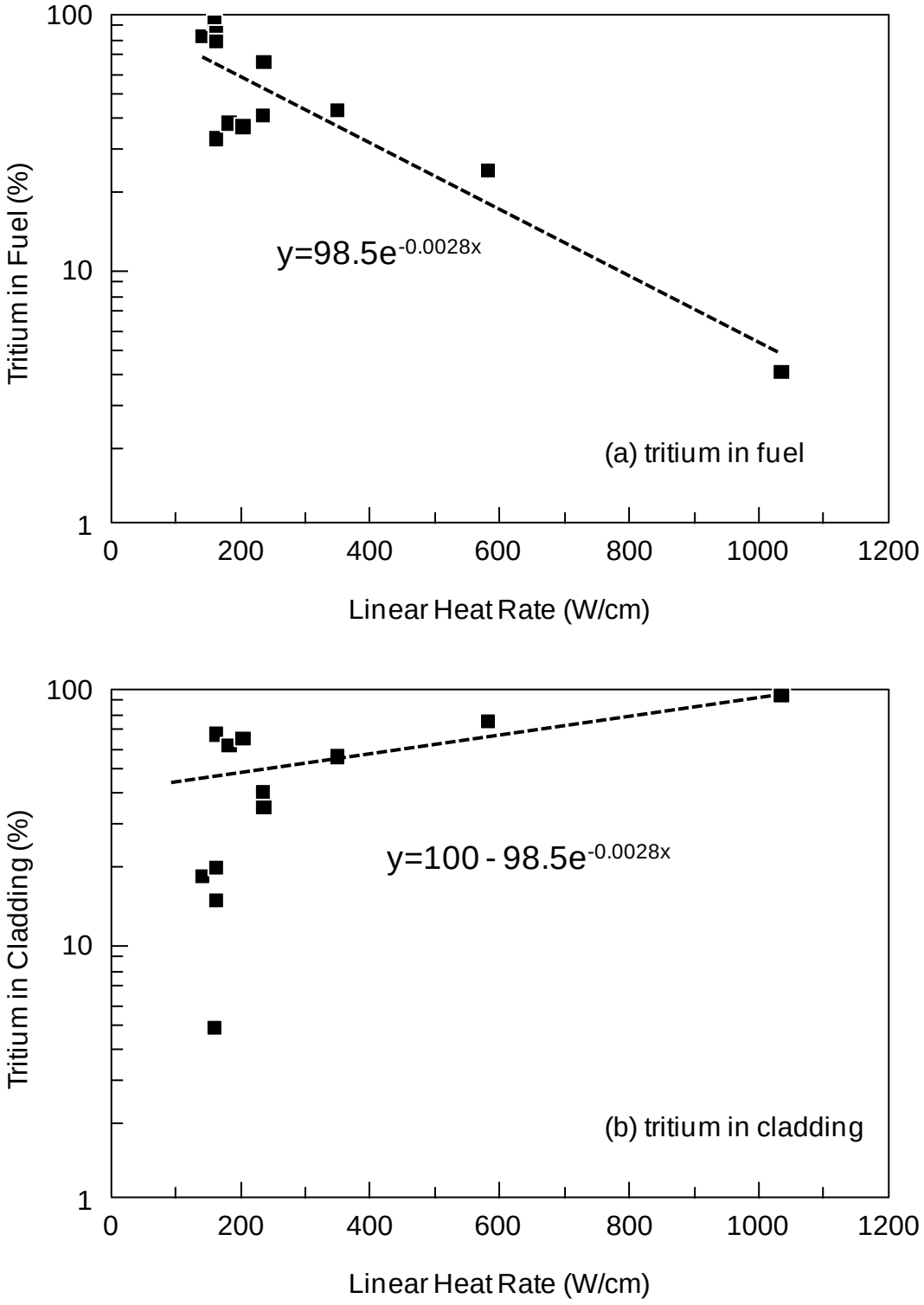

Fig. 2.Tritium as a Function of Linear Heat Rate (adapted from Crowder et al., 2011).

and digested. The third segment was weighed, heated to 600°C for 24 h, reweighed, and digested. The tritium content of each digested sample was then determined.

Closed-vessel microwave technology was used to digest the irradiated cladding specimens. Closed-vessel systems seal the samples within Teflon containers and effectively prevent the loss of tritium as water vapor during the dissolution process, allowing for quantitative recovery. This methodology also allows for digestions at pressures above atmospheric. Therefore, higher temperatures can be used for a more effective dissolution.

For each segment, 8 ml of concentrated nitric acid (15.8M) and 2 ml of concentrated hydrofluoric acid (22.6M) were used for the digestion process. A preparation blank and a tritium laboratory control sample were included with the batch. The microwave run profile is shown in Table 1.

TABLE 1. Microwave Run Profile

Time (min)	Power (W)	Temperature (°C)
10	600	ramp 25 to 100
10	600	hold at 100
15	600	ramp 100 to 175
10	600	hold at 175

After the segments were digested, the vessels were allowed to cool overnight prior to being opened. All sample digests were observed to be clear with no notable solids present. The digests were quantitatively transferred from the Teflon beakers into sample flasks using dilute nitric acid [diluted with Type II laboratory water (resistivity ~18 MΩ•cm @ 25°C)] to a final volume of 20 ml for tritium distillations.

The liquids from the microwave digestion procedures were distilled and counted by the liquid scintillation process to determine the tritium content of the cladding. For the distillations, a 0.100 ml aliquot diluted to 50 ml with water was used. Samples were treated with a small amount of sodium hydroxide and potassium permanganate prior to distillation. The alkaline treatment prevents other radionuclides such as radioiodine and radiocarbon from distilling over with the tritium. The permanganate treatment provides further oxidation of the solution to prevent organics in the sample aliquot, which could distill over and cause quenching interferences. The first 10 ml volume of distillate was collected and discarded. The next ~15 ml of distillate was then collected for counting and determination of tritium. A middle fraction of the distillate was collected for tritium analysis because the early and late fractions are more apt to contain interfering materials for the liquid scintillation counting process. The collected distillate fraction

was thoroughly mixed. Then a 0.100 ml portion was added to and mixed with 15 ml of the Ultima Gold Scintillation Cocktail liquid scintillation solution. After being dark-adapted, the distillates were counted using liquid scintillation counting for tritium beta particle activity.

Experimental Results

Tritium content in the unheated segment was measured to be 3.21 µCi/g. The tritium concentration of two samples that were exposed to heat at 500°C and 600°C was reduced by ~65% to ~1.7 µCi/g, which was near background levels. The amount of tritium in the unheated sample was unexpectedly low. The literature indicates that the cladding from an LWR fuel rod can contain 0% to 95% of the tritium in the fuel rod. Many researchers have reported seeing 30% to 50% of the tritium in the cladding. Many literature references reported tritium concentrations in the cladding in the range of hundreds of microcuries per gram. A rough estimate of the total tritium that would be expected from a fuel rod with an average burnup of 60 to 70 GWd/MTU and cooled for 20 years is ~1000 µCi/g. If only 10% of the tritium was in the cladding, it would have resulted in ~100 µCi/g in the unheated cladding. Additional evaluations will be needed to address the unexpectedly low value of tritium.

CONCLUSIONS

Examination of the literature indicates that data characterizing the tritium content of samples of Zircaloy-clad fuel rods and cladding irradiated in LWRs are rather sparse, and limited details were given on the related fuel history, making interpretation of the reported data difficult. The behavior of tritium in fuel rods and claddings is by no means fully understood, and the presently available data are scattered and sometimes conflicting. The primary variables that are thought to influence the tritium concentration in cladding are cladding temperature, linear heat rating (power density), burnup, and/or the physical condition of the fuel rod or fuel pellets. Various researchers have attempted with limited success to establish correlations between tritium concentration in the cladding and these variables. Literature references indicated that the location of samples along the length of a fuel rod and the analytical procedures used to determine the tritium content could significantly influence the measurement of tritium in the cladding.

In order to obtain a better understanding of how tritium in cladding will behave during processing, scoping tests were performed to determine the tritium content in the cladding. Initial test results for tritium in H. B. Robinson PWR cladding indicates that the cladding that received no heat treatment had a tritium concentration of ~5 µCi/g and heating at 500°C to 600°C for 24 h removes approximately 65% of the tritium from the cladding

It is recommended that alternate analytical techniques be explored and compared to the methods used in this study. Additional experimental data should then be obtained using the most appropriate analytical techniques available to fill in the gaps in existing data.

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