

# ***Evaluation of Tritium Content and Release from Surry-2 Fuel Cladding***

**Fuel Cycle Research & Development**

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## SUMMARY

It is expected that tritium pretreatment will be required in future reprocessing plants to prevent the release of tritium to the environment (except for long-cooled fuels). To design and operate future reprocessing plants in a safe and environmentally compliant manner, the amount and form of tritium in the used nuclear fuel (UNF) must be understood and quantified. Tritium in light water reactor (LWR) fuel is dispersed between the fuel matrix and the fuel cladding, and some tritium may be in the plenum, probably as THO or T<sub>2</sub>O. In a standard processing flowsheet, tritium management would be accomplished by treatment of liquid streams within the plant. Pretreating the fuel prior to dissolution to release the tritium into a single off-gas stream could simplify tritium management, and removal of tritium in the liquid streams throughout the plant may not be required. The fraction of tritium remaining in the cladding may be altered as a result of tritium pretreatment.

Since Zircaloy® cladding makes up roughly 25% by mass of UNF in the United States, processes are being considered to reduce the volume of reprocessing waste for Zircaloy® clad fuel by recovering the zirconium from the cladding for reuse. The recycle process could release the tritium in the cladding. Therefore, it is important to understand the behavior of tritium in both fuel rods and cladding.

For Zircaloy-clad fuels from light water reactors, 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. Estimates of the percentage of tritium in the cladding typically range from 0–96%. There is relatively limited data on how the tritium content of the cladding varies with burnup and fuel history (temperature, power, etc.) and how pretreatment impacts its release. To gain a better understanding of how tritium in cladding will behave during processing, scoping tests are being performed to determine the tritium content in the cladding pre- and post-tritium pretreatment.

A sample of Surry-2 pressurized water reactor (PWR) cladding was heated to 1100–1200°C to oxidize the zirconium and release all of the tritium in the cladding sample. The tritium content was measured to be ~240 µCi/g. Cladding samples were heated to 500°C, which is within the temperature range (480 - 600°C) expected for standard air tritium pretreatment systems, and to a slightly higher temperature (700°C) to determine the impact of tritium pretreatment on tritium release from the cladding. Heating at 500°C for 24 hr removes ~0.2% of the tritium from the cladding, and heating at 700°C for 24 hr removes ~9%. Thus, a significant fraction of the tritium remains bound in the cladding and must be considered in operations involving cladding recycle.

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## ACRONYMS

DI	deionized
GWd/MTU	gigawatt day per metric tonne uranium
LWR	light water reactor
PWR	pressurized water reactor
UNF	used nuclear fuel



# EVALUATION OF TRITIUM CONTENT AND RELEASE FROM SURRY-2 FUEL CLADDING

## 1. INTRODUCTION

Zircaloy® cladding makes up roughly 25% by mass of used nuclear fuel (UNF) in the United States. In the future, reprocessing may be the option of choice for disposition of UNF from light water reactors (LWRs). Treatment options for Zircaloy cladding include recycling to recover the significant cost of the zirconium and eliminate costs associated with the disposal of transuranic-contaminated Zircaloy®. If LWR fuel is reprocessed and the fuel is dissolved without tritium pretreatment, the tritium in the cladding will remain bound to the cladding. If tritium pretreatment is included in the flow sheet, some portion of the tritium in the cladding may be released along with the tritium from the fuel matrix. To design and operate reprocessing plants in a safe and environmentally compliant manner, the amount and form of tritium in the UNF must be understood and quantified.

Estimates of the percentage of tritium originally in the fuel rod that is retained in the cladding typically range from 0–96%. A single sample of post-tritium pre-treated cladding was analyzed as part of the Coupled End-To-End (CETE) project, and no tritium was detected. This single data point was not a definitive test, but the results warranted additional investigation since it indicated that tritium pretreatment could potentially eliminate the presence of tritium in the zirconium recycle step. The present study was undertaken to understand how tritium pretreatment at standard air tritium pretreatment conditions (480 - 600°C) affects the tritium content in the Zircaloy® cladding and the extent to which the tritium content could be reduced with modest increases in the tritium pretreatment temperature. Scoping tests are being performed to determine the tritium content of pre- and post-tritium pretreated cladding.

## 2. FUEL SAMPLE HISTORY

Tests were performed on cladding from a fuel rod from the Surry-2 pressurized water reactor (PWR). The fuel rod from the Surry-2 PWR contained UO<sub>2</sub> enriched to 3.1 wt%. It was discharged from the reactor in 1981, and the average burnup was 36 gigawatt day per metric tonne uranium (GWd/MTU). The cladding was Zircaloy-4, which has a composition of ~ 98% zirconium, 1.8% tin, and small fractions of nickel and iron. Samples of the fuel rod were defueled and cut into segments ~5 mm in length to test for tritium content.

## 3. EXPERIMENTAL TECHNIQUES

### 3.1 Literature Review

There is not a national standard test method for measurement of tritium content in irradiated clads. Prior to the establishment of an experimental technique at ORNL for this work, a comprehensive literature review<sup>1</sup> was conducted to determine the protocols that have historically been used to quantify tritium content in clads. It is well documented that destructive techniques will liberate tritium as a gas, T<sub>2</sub>/HT, and vapor, HTO, both of which must be accounted for in the final analytical measurement.

High-temperature combustion of clads is the most common destructive technique noted. Capture of the off-gas and water vapor for counting by liquid scintillation was accomplished by various experimental techniques. Wolfe<sup>2</sup> and Kunz<sup>3</sup> documented a combustion system in which the tritium was carried via a gas

stream through water-filled bubblers to trap tritium released as water vapor. For tritium that was released as a gas, Wolfe<sup>2</sup> used a collection train comprising an in-line molecular sieve, an activated charcoal bed, and a gas chamber for proportional counting, in that order. Kunz<sup>3</sup> captured the released tritium using an in-line water trap followed by a heated CuO catalyst and trapped the condensed water vapor via a cold trap for counting. Broothaerts<sup>4</sup> and Grossman<sup>5</sup> described combustion using hot vacuum extraction. Broothaerts<sup>4</sup> employed a mechanical pump to transport the released T<sub>2</sub>/HT gas and HTO vapors over a heated CuO catalyst to convert any remaining gas to vapor followed by trapping in a liquid-nitrogen cold trap. Grossman<sup>5</sup> collected the gas and then converted it to HTO off-line.

Some authors reported using acid dissolution of the clad similar to that described by Goode.<sup>6</sup> For that work, the gases released during dissolution were converted to HTO using an in-line heated CuO catalyst and trapping the resultant vapor onto a molecular sieve. The contents on the sieve were then desorbed and counted by liquid scintillation counting. The dissolver solution was distilled and the distillate counted using liquid scintillation counting.

### 3.2 Experimental System

From the literature review, it was determined that the most effective experimental protocol would employ a high-temperature furnace to heat the metal clad specimens. The released tritium would then be transported as T<sub>2</sub>/HT and HTO using a carrier gas through a heated CuO catalyst, and subsequently the water vapor would be trapped in a series of water-filled bubblers for counting using liquid scintillation.

For the characterization of tritium content in irradiated clads, ORNL set up a Carbolite Combustion Tube Furnace, Model MTT 12/38/850. The furnace can operate at a maximum combustion zone temperature of 1200°C and utilizes a copper metal catalyst in a separate heated zone for conversion of tritium gas to water for trapping. The sample carrier gas consisted of a 50:50 mixture of oxygen and nitrogen, and a 100% oxygen gas flow was used for the catalyst zone. Three bubblers containing ~60 mL of deionized (DI) water each were connected in series to the outlet of the furnace. The first two bubblers were routinely sampled during the tests, and the third bubbler only sampled at the end of the test. The experimental system is shown schematically in Fig. 1.

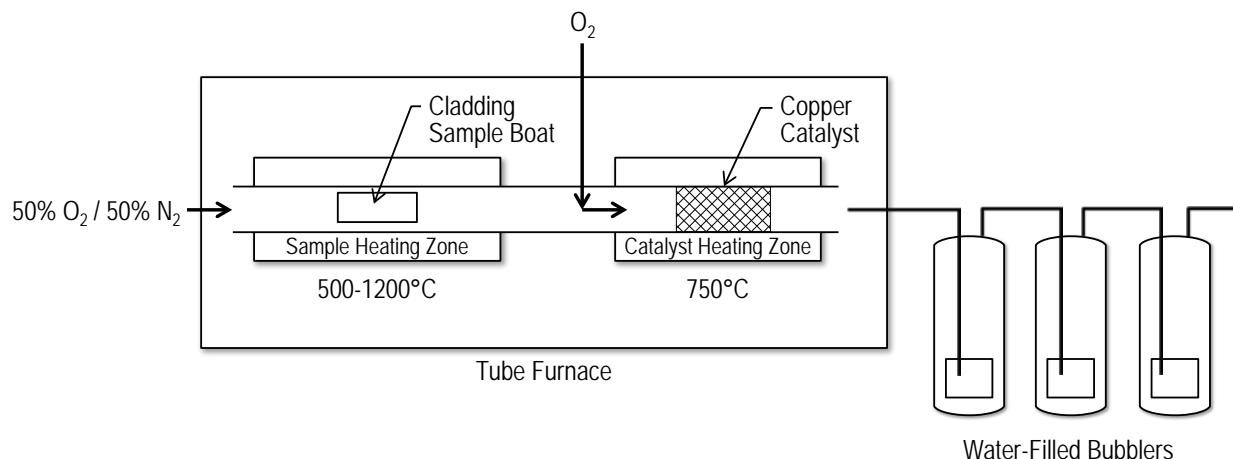


Fig. 1. Schematic of experimental test system

### 3.3 Experimental Tests

For the experiments, 5–6 mm wide rings of cladding were cut into three equal segments by cutting each ring at radial positions (i.e., 0, 120, and 240 degrees). The three pieces (1A, 1B, and 1C) were weighed. The weights are given in Table 1.



**Table 1. Weights of cladding samples**

<b>Sample ID: 5950</b>	<b>Surry-2 1A</b>	<b>Surry-2 1B</b>	<b>Surry-2 1C</b>
Sample + Vessel (g)	1.4197	1.3855	1.5013
Vessel tare Wt.(g)	1.1941	1.2079	1.2069
Sample Net Wt. (g)	0.2256	0.1776	0.2944

The segments of cladding were subjected to different simulated tritium pretreatments. The tritium pretreatment conditions applied to each test segment were as follows:

- Segment Surry-2 1A was not subjected to simulated tritium pretreatment conditions,
- Segment Surry-2 1B was heated at 700°C for 24 hr, and
- Segment Surry-2 1C was heated at 500°C for 24 hr.

After simulated tritium pretreatment, the specimens were heated to 1100 - 1200°C for 45 – 53 hr to totally oxidize the zirconium and release all remaining tritium. This latter high temperature heating step was performed to determine the total or residual amount of tritium in the sample with the objective of closing the tritium mass balance.

#### **Surry-2 Cladding Sample 1A (No Tritium Pretreatment)**

Three clean bubblers with ~60 mL of DI water each were clamped in line with the Carbolite tube furnace rig. Clad piece Surry-2 1A was placed into a quartz boat, and the boat was loaded into the quartz working tube. Both the 50% oxygen/nitrogen-to-sample flow path (200 mL/min) and oxygen-to-catalyst flow path (100 mL/min) were capped and clamped, and the bubblers were started. The catalyst zone temperature was preheated to 750°C. The sample zone was then heated at 1200°C for 4 hr. After heating for 4 hr at 1200°C, samples were collected from each of the first two bubblers. Two fresh bubblers were filled with DI water and placed in the experimental system. The sample zone temperature was reduced from 1200°C to 1100°C. The furnace was held at 1100°C for 18 hr. Again, the bubbler liquids were collected as two separate samples, and two fresh bubblers were filled with DI water and placed in the system. The bubblers were swapped again after 7 hr. The furnace was then turned off and cooled to 25°C overnight with continuous gas purging of the entire system flow path. After cool-down, the water samples from the final set of bubblers were retrieved for analysis.

#### **Surry-2 Cladding Sample 1B (Simulated Tritium Pretreatment at 700°C)**

Three clean bubblers with ~60 mL DI water each were clamped in line with the Carbolite tube furnace rig. Clad piece Surry-2 1B was placed into a quartz boat, and the boat was loaded into the quartz working tube. Both the 50% oxygen/nitrogen-to-sample flow path (200 mL/min) and oxygen-to-catalyst flow path (100 mL/min) were capped and clamped, and the bubblers were started. The catalyst zone temperature was preheated to 750°C. The sample zone was heated to 700°C and held for a total of 24 hr. After heating for 8 hr at 700°C, the bubbler liquids were collected as two separate samples. Two clean bubblers were filled with DI water and placed into the system. The sample zone temperature was held at 700°C for an additional 16 hr. Again, the bubbler liquids were collected as two separate samples. Two more bubblers were filled with DI water and placed in the system. The furnace temperature was then raised to 1200°C and held for 4 hr. The bubblers were swapped once more. The temperature was then reduced to 1100°C and held there for 15 hr. The bubblers were swapped once more. The temperature was held at 1100°C for an additional 6 hr. The bubblers were swapped once more. The temperature was held at 1100°C for an additional 20 hr. Then the furnace was turned off and cooled to 25°C overnight, with gas flow paths to the

bubblers purging overnight. After cool-down, the water in the final set of bubblers was retrieved for analysis.

### Surry-2 Cladding Sample Piece 1C (Simulated Tritium Pretreatment at 500°C)

Three clean bubblers with ~60 mL DI water each were clamped in line with the Carbolite tube furnace rig. Clad piece Surry-2 1B was placed into a quartz boat, and the boat was loaded into the quartz working tube. Both the 50% oxygen/nitrogen-to-sample flow path (200mL/min) and oxygen-to-catalyst flow path (100 mL/min) were capped and clamped, and the bubblers were started. The catalyst zone temperature was preheated to 750°C. The sample zone was heated to 500°C and held at temperature for a total of 24 hr. After heating for 8 hr at 500°C, the bubbler liquids were collected as two separate samples. Two clean bubblers were filled with DI water and placed in the system. The sample zone temperature was held at 500°C for an additional 16 hr. Again, the bubbler liquids were collected as two separate samples. Two more bubblers were filled with DI water and placed in the system. The furnace temperature was then raised to 1200°C and held for 4 hr. The bubblers were swapped once more. The temperature was then reduced to 1100°C and held there for 15 hr. The bubblers were swapped once more. The temperature was held at 1100°C for an additional 6 hr. The bubblers were swapped once more. Then the furnace was turned off and cooled to 25°C overnight, with gas flow paths to the bubblers purging overnight. After cool-down, the water in the final set of bubblers was retrieved for analysis.

## 4. EXPERIMENTAL RESULTS

Sample 1A received no simulated tritium pretreatment; it was heated to 1100–1200°C to oxidize the zirconium and release all of the tritium in the cladding sample. The tritium content was measured to be ~240 µCi/g.

The tritium concentrations in the off-gas from cladding samples 1B and 1C that were exposed to simulated tritium pretreatment conditions at 500 and 700°C were 0.55 and 19.2 µCi/g, respectively. The residual tritium released during subsequent oxidation of the cladding samples was 247.2 and 201.7 µCi/g for the 500 and 700°C pretreated samples, respectively. Based on the sum of the tritium released during these two heating periods, the tritium pretreatment conditions of 500 and 700°C removed ~0.2 and 9% of the tritium in the cladding. The results are summarized in Table 2.

**Table 2. Tritium in Surry-2 cladding**

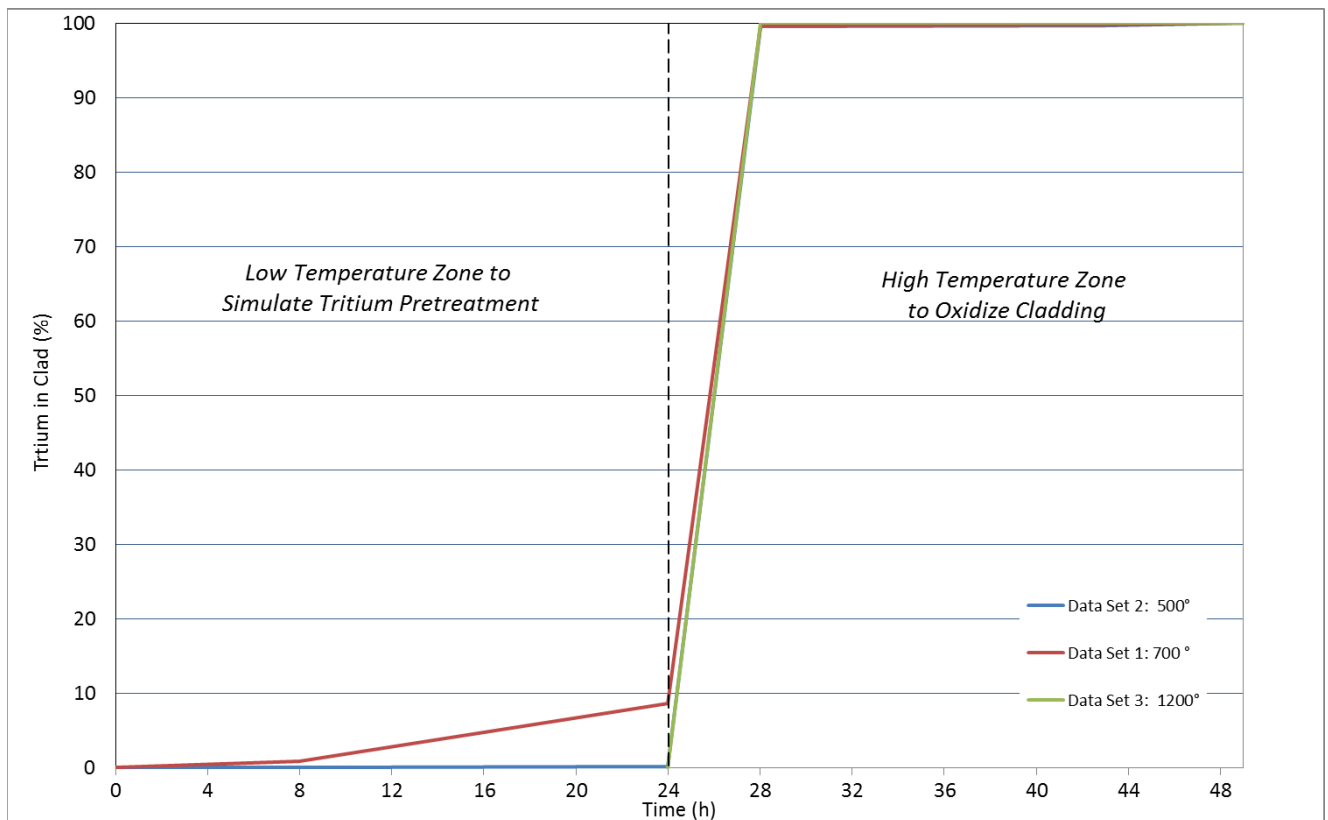
Sample	Simulated tritium pretreatment condition (°C)	Tritium released during simulated tritium pretreatment (µCi/g)	Tritium in cladding sample during oxidation <sup>1</sup> (µCi/g)	Total tritium recovered from cladding sample (µCi/g)	Tritium removed during simulated tritium pretreatment (%)
1B	500	0.55	247.2	247.7	0.2
1C	700	19.2	201.7	220.9	8.7

<sup>1</sup> Oxidation of cladding @ 1100–1200°C to release residual tritium

The impact of heating time and temperature on the amount of tritium released is shown in Table 3 and Fig. 2. They show that less than 10% of the tritium contained in the clad is released when heating at 500–700°C for tritium pretreatment and that the majority of the tritium is released within the first 4 hr of heating at the higher temperatures of 1100–1200°C required for oxidizing the samples.

**Table 3. Tritium released as a function of heating time and temperature**

Time (hr)	Sample 1A			Sample 1B			Sample 1C		
	Temperature (°C)	Cumulative tritium released		Temperature (°C)	Cumulative tritium released		Temperature (°C)	Cumulative tritium released	
		( $\mu$ Ci/g)	%		( $\mu$ Ci/g)	%		( $\mu$ Ci/g)	%
<b>Low Temperature Heating to Simulate Tritium Pretreatment</b>									
8	NA			700	1.9	0.9	500	0.29	0.1
24	NA			700	19.2	8.7	500	0.55	0.2
<b>High Temperature Heating to Oxidize Cladding</b>									
4	1200	238.0	99.7	1200	220.0	99.6	1200	246.7	99.6
19				1100	220.3	99.7	1100	246.9	99.7
22	1100	238.3	99.8						
25				1100	220.8	99.9	1100	247.7	100
29	1100	238.7	100						
45				1100	220.9	100			
Cool Down		238.7	100		220.9	100		247.7	100
Final Sample		238.8	100		220.9	100		247.7	100



**Fig. 2. Tritium released as a function of heating time and temperature**

## 5. SUMMARY/CONCLUSIONS

Test results for tritium in Surry-2 PWR cladding indicate that the cladding that received no heat treatment had a tritium concentration of  $\sim 240$   $\mu\text{Ci/g}$ ; heating at  $500\text{--}700^\circ\text{C}$  for 24 hr removes  $\sim 0.2$  and 9% of the tritium from the cladding, respectively. The average total tritium found in the cladding samples was  $\sim 235$   $\mu\text{Ci/g}$ , varying less than 6% between the samples. Based on these data, it would appear that a significant fraction of the tritium contained in the cladding would remain within the cladding structure at the temperatures used for standard air tritium pretreatment. This indicates the residual tritium must be factored into any subsequent processing of the cladding to recover/recycle the zirconium.

These data are consistent with that found in the literature, which indicates that the cladding from a LWR can contain 0–96% of the tritium in the fuel rod.<sup>1</sup> Many of these references reported tritium concentrations in the cladding in the range of hundreds of  $\mu\text{Ci/g}$ . ORIGEN models predict a total tritium content of  $\sim 280$   $\mu\text{Ci/g}$  for cladding of Surry-2 fuel that has been out of the reactor for 33 years. This value is averaged across the length of the fuel rod. Given that the tritium distribution along the length is not uniform and that only a fraction of the tritium would be found in the cladding, the data obtained in this study are consistent with the ORIGEN models.

## 6. REFERENCES

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