

Evaluation of Tritium Content and Release from Pressurized Water Reactor 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 tritium labelled water (THO) or T₂O. 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, so the removal of tritium in the liquid streams throughout the plant may not be required. The fraction of tritium remaining in the cladding may be reduced 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. These recycle processes could release the tritium in the 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 documented¹ 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. Samples of Surry-2 and H.B. Robinson pressurized water reactor cladding were heated to 1100–1200°C to oxidize the zirconium and release all of the tritium in the cladding sample. Cladding samples were also heated within the temperature range of 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.

The tritium content of the Surry-2 and H.B. Robinson cladding was measured to be ~234 and ~500 μCi/g, respectively. Heating the Surry-2 cladding at 500°C for 24 h removed ~0.2% of the tritium from the cladding, and heating at 700°C for 24 h removed ~9%. Heating the H.B. Robinson cladding at 700°C for 24 h removed ~11% of the tritium. When samples of the Surry-2 and H.B. Robinson claddings were heated at 700°C for 96 h, essentially all of the tritium in the cladding was removed. However, only ~3% of the tritium was removed when a sample of Surry-2 cladding was heated at 600°C for 96 h.

These data indicate that the amount of tritium released from tritium pretreatment systems will be dependent on both the operating temperature and length of time in the system. Under certain conditions, a significant fraction of the tritium could remain bound in the cladding and would need to be considered in operations involving cladding recycle.

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ACRONYMS

CETE	Coupled End-To-End
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 to 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 fuel rods from Surry and H.B. Robinson pressurized water reactors (PWR).

The H.B. Robinson fuel rod contained UO₂ enriched to 2.9 wt% ²³⁵U. It was discharged from the reactor in 1995, and the average burnup was 63-67 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 this fuel rod had previously been defueled by mechanically removing the fuel followed by leaching in nitric acid. The defueled cladding was cut into segments approximately 6 mm in length. These were used in tests to determine the material's tensile strength using standard loop tensile testing methods. This is a mechanical test that does not involve heating of the materials, and these cladding samples were then used in tests performed in this study to quantify tritium content.

Tests were also performed on cladding from a fuel rod from the Surry-2 PWR. The fuel rod from the Surry-2 PWR contained UO₂ enriched to 3.1 wt%. It was discharged from the reactor in 1981, and the average burnup was 36 GWd/MTU. The cladding was Zircaloy-4. 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 Experimental System

A high-temperature furnace was used to heat the metal clad specimens. The released tritium was transported as T_2 /HT and HTO using a carrier gas through a heated CuO catalyst, and subsequently the water vapor was trapped in a series of water-filled bubblers for counting using liquid scintillation.

A Carbolite Combustion Tube Furnace, Model MTT 12/38/850, was used to determine the tritium content in irradiated clads. 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 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.

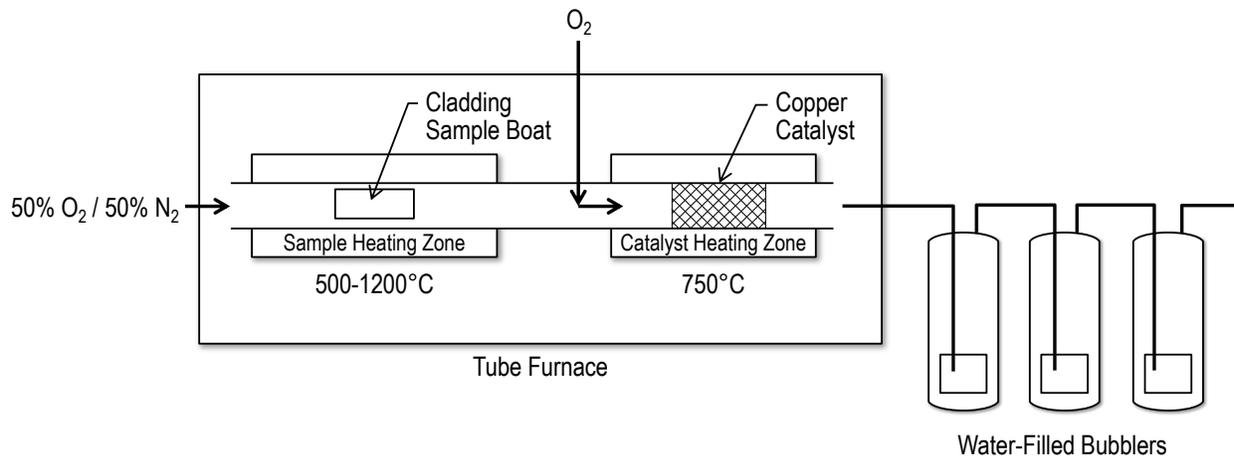


Fig. 1. Schematic of experimental test system.

3.2 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 individual pieces were weighed and then subjected to different simulated tritium pretreatments. One of the samples of cladding from each ring was heated to 1100–1200°C to oxidize the zirconium and release all of the tritium in the cladding sample. The tritium pretreatment conditions applied to each of the remaining test segments were as follows:

- Heated at 500°C for 24 - 96h,
- Heated at 600°C for 24 - 96h,
- Heated at 700°C for 24 - 96 h.

After simulated tritium pretreatment, the specimens were heated to 1200°C for 4 h and 1100°C for up to 20 h to totally oxidize the zirconium and release all remaining tritium. This 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. The initial test results indicated that the majority of the remaining tritium is released within the first 4 h of heating at the higher temperatures of 1100–1200°C required for oxidizing the samples. Thus a minimum of 4 h of heating at 1200°C was used in each test.

These tests were performed over a two-year period. Although the results² from the 2014 tests have been previously reported, they were also included in the data evaluation in this report.

4. EXPERIMENTAL RESULTS

Three rings of cladding were tested in this study: two Surry-2 rings and a ring of H.B. Robinson cladding. One segment from each ring (approximately 1/3 of the ring) of cladding 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 of the two Surry-2 cladding segments was measured to be 239 and 228 μCi/g for an average of 234 μCi/g. The tritium content of the H.B. Robinson cladding segment was measured to be 500 μCi/g.

The results of tests to simulate tritium pretreatment are summarized in Table 1. The table shows the amount of tritium released during the simulated tritium pretreatment condition (500–700°C for 24–96 h), the amount of tritium released during the subsequent heating at 1100–1200°C which oxidized the remaining tritium in the sample, the total amount of tritium, and the percentage of tritium released during the simulated pretreatment step. The tritium pretreatment conditions of 500 and 700°C for 24 h removed ~0.2 and 9% of the tritium in the Surry-2 cladding, respectively. Similarly, heating H.B. Robinson cladding at 700°C for 24 h removed ~11% of the tritium. Increasing the time the samples were exposed to heating at 700°C from 24 h to 96 h, significantly increased to amount of tritium removed during the pretreatment step: 99.4% and 99.0% for the Surry-2 and H.B. Robinson claddings, respectively. However, only 3% of the tritium was removed from a Surry-2 sample when it was heated to only 600°C for 96 h.

Table 1. Tritium in pressurized water reactor cladding

Cladding sample	Simulated tritium pretreatment condition (°C)	Tritium released during simulated tritium pretreatment (μCi/g)	Tritium in cladding sample during oxidation ¹ (μCi/g)	Total tritium recovered from cladding sample (μCi/g)	Tritium removed during simulated tritium pretreatment (%)
Surry-2 Ring 1	500 for 24 h	0.55	247.2	247.7	0.2
Surry-2 Ring 1	700 for 24 h	19.2	201.7	220.9	8.7
H.B. Robinson	700 for 24 h	59.9	478.0	537.9	11.1
Surry-2 Ring 2	600 for 96 h	7.1	230.8	237.9	3.0
Surry-2 Ring 2	700 for 96 h	193.3	1.2	194.5	99.4
H.B. Robinson	700 for 96 h	631.8	6.7	638.5	99.0

¹ Oxidation of cladding at 1100–1200°C to release residual tritium.

The impact of heating time and temperature on the amount of tritium released is shown in Tables 2 and 3 and Figs. 2 and 3. They show that ≤20% of the tritium contained in the clad is released when heating at 500–700°C for tritium pretreatment for 24 h. Essentially 100% of the tritium is released when the heating time at 700°C is extended to 96 h. However, less than 3% of the tritium was released when cladding is heated at 500–600°C for 24–96 h.

Table 2. Tritium in Surry-2 cladding released as a function of heating time and temperature

Time (h)	Surry-2 Ring 1			Surry-2 Ring 1			Surry-2 Ring 2			Surry-2 Ring 2		
	Temperature (°C)	Cumulative tritium released		Temperature (°C)	Cumulative tritium released		Temperature (°C)	Cumulative tritium released		Temperature (°C)	Cumulative tritium released	
		($\mu\text{Ci/g}$)	%		($\mu\text{Ci/g}$)	%		($\mu\text{Ci/g}$)	%		($\mu\text{Ci/g}$)	%
Low-Temperature Heating to Simulate Tritium Pretreatment												
8	500	0.29	0.1	700	1.9	0.9						
24	500	0.55	0.2	700	19.2	8.7	700	12.6	6.5	600	1.5	0.6
48							700	192.9	99.2	600	2.6	1.1
72							700	193.0	99.2	600	4.9	2.1
96							700	193.3	99.4	600	7.1	3.0
High-Temperature Heating to Oxidize Cladding												
4	1200	246.7	99.6	1200	220.0	99.6	1200	193.3	99.4	1200	237.9	100
20 - 24	1100	246.9	99.7	1100	220.3	99.7						
Final		247.7	100		220.9	100		194.5	100		237.9	100

Table 3. Tritium in H.B. Robinson cladding released as a function of heating time and temperature

Time (h)	H.B. Robinson			H.B. Robinson		
	Temperature (°C)	Cumulative tritium released		Temperature (°C)	Cumulative tritium released	
		($\mu\text{Ci/g}$)	%		($\mu\text{Ci/g}$)	%
Low-Temperature Heating to Simulate Tritium Pretreatment						
8	700	11.0	2.0	700	8.1	1.3
24	700	59.9	11.1	700	117.0	18.3
48				700	631.2	98.9
72				700	631.8	99.0
96						
High-Temperature Heating to Oxidize Cladding						
4	1200	536.5	99.7	1200	634.7	99.4
20 - 24	1100	537.7	100	1100	634.7	99.4
Final		537.9	100		638.5	100

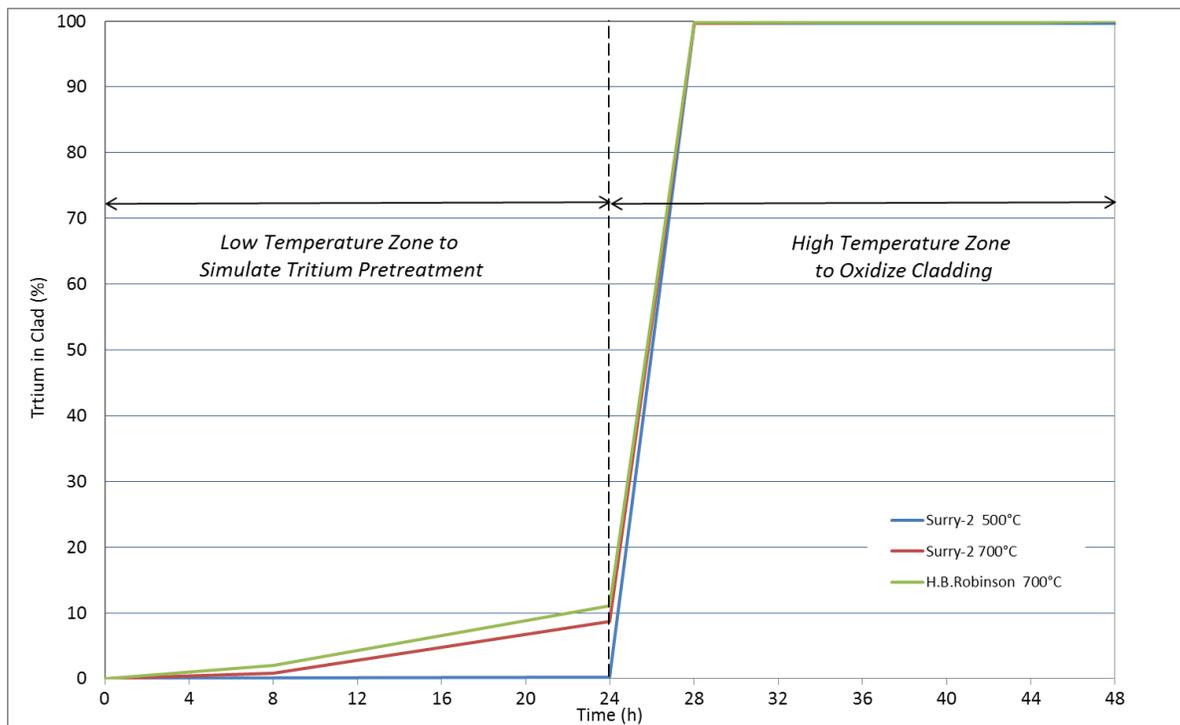


Fig. 2. Tritium released as a function of heating time and temperature: low-temperature for 24 h.

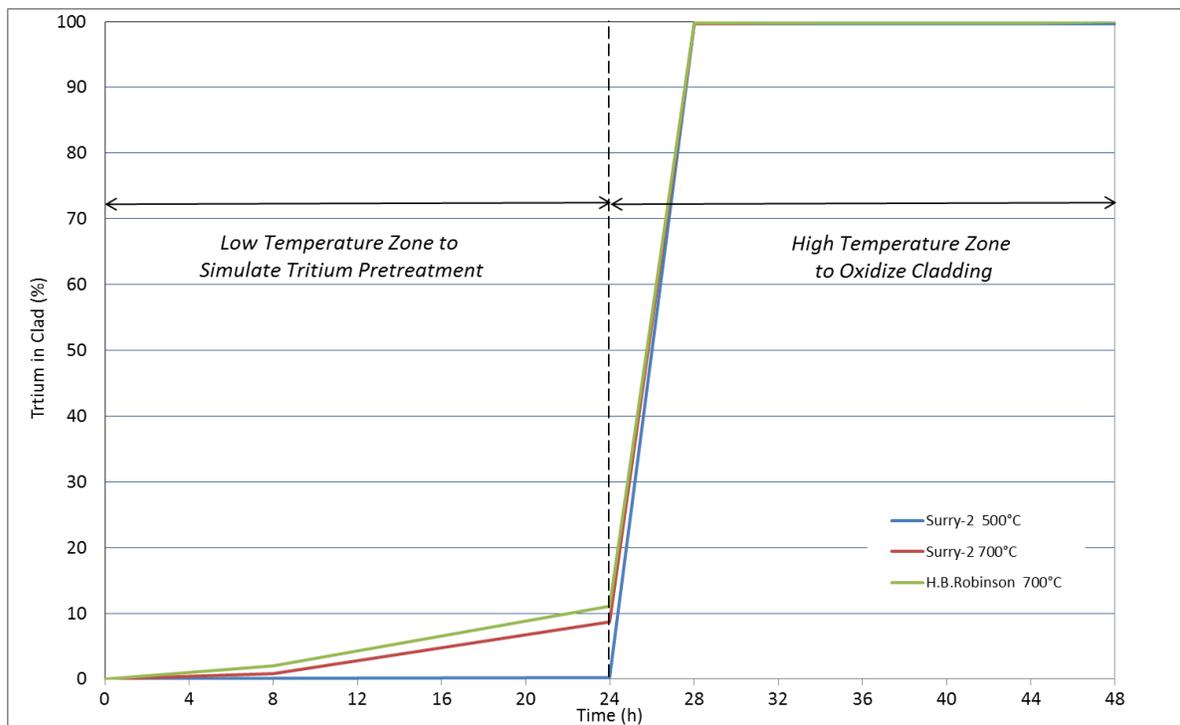


Fig. 3. Tritium released as a function of heating time and temperature: low-temperature for 96 h.

5. SUMMARY/CONCLUSIONS

Test results for tritium in Surry-2 and H.B. Robinson PWR cladding indicate that the cladding that received no heat treatment had a tritium concentration of ~235 and 500 $\mu\text{Ci/g}$, respectively. The average total tritium found in the cladding samples varied less than 15% between the samples. The data indicate that <20% of the tritium in PWR cladding will be removed by pretreatment at 500–700°C for 24 h. Essentially 100% of the tritium is released if the heating time at 700°C is extended to 96 h. Small amounts of tritium are expected to be released if the cladding is heated at $\leq 600^\circ\text{C}$ for up to 96 h.

These data indicate that the amount of tritium released from tritium pretreatment systems will be dependent on both the operating temperature and length of time in the pretreatment system. Under certain conditions, a significant fraction of the tritium could remain bound in the cladding and would need to be considered in any subsequent processing of the cladding to recover/recycle the zirconium.

6. REFERENCES

1. S. Robinson et al., *Review of Tritium in Zircaloy Cladding from Liquid Water Reactors*, FCRD-SWF-2013-000288, UT-Battelle LLC, Oak Ridge National Laboratory, August 2013.
2. S. Robinson et al., *Evaluation of Tritium Content and Release from Surry-2 Fuel Cladding*, FCRD-SWF-2014-000417, UT-Battelle LLC, Oak Ridge National Laboratory, September 2014.