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Measurement of Tritium during Voloxidation of Zircaloy-2 Fuel Hulls

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Abstract

A straightforward method to evaluate the tritium content of Zircaloy-2 cladding hulls via oxidation of the hull and capture of the volatilized tritium in liquids has been demonstrated. Hull samples were heated in air inside a thermogravimetric analyzer (TGA). The TGA was rapidly heated to 1000 °C to oxidize the hulls and release absorbed tritium. To capture tritium, the TGA off-gas was bubbled through a series of liquid traps. The concentrations of tritium in bubbler solutions indicated that tritiated water vapor was captured nearly quantitatively. The average tritium content measured in the hulls was 19% of the amount of tritium produced by the fuel, according to ORIGEN2[1] isotope generation and depletion calculations. Published experimental data show that Zircaloy-2 oxidation follows an Arrhenius model, and that an initial, nonlinear oxidation rate is followed by a faster, linear rate after "breakaway" of the oxide film. This study demonstrates that the linear oxidation rate of Zircaloy samples at 974 °C is faster than predicted by the extrapolation of data from lower temperatures.

Introduction

Zircaloy cladding makes up roughly 25% by mass of used nuclear fuel in the United States. Leading treatment options for Zircaloy-2 cladding include recycle to

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recover the significant cost of zirconium and alloying with other metals to produce a waste form. For separation of tritium and some other volatiles, an attractive initial step in recovery of used fuel is heating in air, or voloxidation, where volatile components are released while the fuel and some of the volatiles are oxidized.[2] During oxidation or melting of Zircaloy hulls, the release of radioisotopes, particularly tritium, is expected.

Several research groups have measured the tritium content of irradiated fuels and Zircaloy hulls by various methods,[3,4,5,6,7] but the reported data at low to moderate linear heat rates are somewhat conflicting. Methods used to determine tritium content in Zircaloy hulls have included dissolution with capture of gaseous tritium,[5,6] heating of hulls up to 1100 °C in H_2 or under vacuum,[7] or both dissolution and heating in H_2 to 1000 °C.[4] However, the use of high temperature hull oxidation for tritium measurement has not been studied. Different methods of tritium capture or measurement have also been used. Kunz et al.[8] showed that below about 350 °C, a small amount of tritium was released from Zircaloy samples heated in Argon with 5 vppm oxygen, and >95% of that tritium was in the form of tritiated water (HTO) vapor. In addition, Kunz showed that at 350 and 500 °C in air, 97% of the tritium is released as HTO. The autoignition temperature of hydrogen isotopes in air is 585 °C. Thus, we expected that by quickly heating samples in air to ~1000 °C, nearly all the tritium released forms HTO and is readily captured in liquid traps, so a catalyst bed to oxidize elemental tritium was not required. In summary, this study employed Zircaloy hull oxidation in dry air followed by capture of gaseous tritium to initiate development of a simple analytical tool for hull characterization and to gain information on the Zircaloy-2 oxidation rate at high temperatures.

Experimental

The Zircaloy-2 hulls used in this study were from the Big Rock Point (BRP) Reactor, a boiling water reactor of General Electric design. Specifically, the hulls were from a fuel pin that was part of an "Extended Burnup Demonstration" program with a burnup of 30,100 MWd/MTU. The hulls were separated from the fuel via an elevated pressure/elevated temperature dissolution in nitric acid, since nitric acid preferentially dissolves uranium oxide fuel but not Zircaloy-2. The hulls still contained significant amounts of radioactivity and were handled in radiological shielded cells with limited glovebox handling at the Savannah River National Laboratory. Sample portions of nominally 0.5-0.6 g were cut using a tubing cutter. Each sample portion, or ring, was transferred to a glovebox and placed in a fired (dried) alumina crucible. The crucible was inserted into the furnace of a Netzsch STA 409 Luxx thermogravimetric analyzer (TGA). The furnace was purged with air at a nominal rate of 50 mL/min. The TGA heated samples to a maximum of 975 °C at nominally 40 °C/min. The TGA offgas stream was routed through insulated tubing and bubbled through a series of three liquid traps, in which the HTO from the hull samples was readily absorbed into either distilled water, 5 wt % HNO_3/10 wt % H_2O_2 made with reagent grade components, or reagent grade ethylene glycol. The sequence of solutions used in the bubblers was altered in different tests to provide an indication of relative sensitivities of different solutions to the components of the offgas.

The first two Zircaloy hull samples tested contained an outer layer of significant radioactivity, typical of used fuel hulls. The third and last hull portion tested had been

partially decontaminated by removing a combined total of 15 wt % of the hull from the inner and outer hull surfaces. The tritium contents of the bubbler solutions were determined by distillation followed by liquid scintillation counting. Samples were acidified prior to distillation.

Results

The Zircaloy samples oxidized readily in the TGA, as expected, and the resulting mass changes indicated essentially complete oxidation. A time-temperature-mass plot for Hull #3 is shown in Figure 1. The plots for the other two hull samples were nearly identical. Mass changes for Hull portions 1-3 at 132 minutes were 34.25, 34.25, and 34.34 wt %, respectively, which compare well to the theoretical mass gain of 35.07% for oxidation of pure zirconium (Zr) and approximately 34.95% for Zircaloy-2. The hull mass gains occurred after an initial mass loss of 0.14 wt %, attributed to release of adsorbed gases, particularly moisture. For all three samples, the autoignition temperature for hydrogen – 585 °C – was reached within 17.5 min, prior to the observation of mass gain by the TGA.

Analysis of Bubbler Solutions

Table 1 lists values for tritium analyses of the bubbler solutions, showing a range of 67-99 μCi tritium/g hull for the samples tested. For all solutions tested, the gross beta values measured by liquid scintillation counting were lower than the equivalent beta activities for tritium as measured by distillation followed by counting. Thus, beta emitters in addition to tritium were either not volatilized or were not captured.

Discussion

For each of the three hulls tested, the first bubbler solution captured 98-99% of the total tritium captured. Similarly, the second bubbler solutions each captured at least ten times more tritium than the final solutions. This expected behavior confirmed the tritium capture effectiveness of the solutions. Interestingly, Hull 3, which had been partially decontaminated prior to this study, contained more tritium than Hulls 1 and 2, which had not been decontaminated. An implication of this results is that tritium in cladding is not confined to the surface layers. Also, an earlier study showed that the tritium content in hulls varies with location of hull portions, with more tritium in hull portions near the middle of the fuel rod.[3] The relative positions of the hull portions used in this study is not known.

Measured Tritium in Hull vs. Calculated Total Fission Tritium

ORIGEN2 calculations were performed using representative numbers for the BRP fuel, which was enriched to 4.6 wt % ^{235}U and contained 1.2 wt % Gd_2O_3 as a burnable poison. The fuel calculations were performed using an ORIGEN2 BWR cross section library and an assumed typical specific heat generation rate for BWR's of 25.9 MW/MTHM,[9] which converts to a linear heat rate of 160 W/cm. For the specific pin burnup at discharge of 30,100 MWd/MTHM, the tritium present at the end of irradiation was 0.0495 g per MT of fuel. Separately, cladding activation calculations were performed using ORIGEN2, but the resulting tritium generation was deemed negligible because it was six orders of magnitude less than that of the fuel. Though ORIGEN2 does

not account for diffusion effects, researchers have demonstrated a very low diffusion rate of tritium through the surface layer of Zircaloy-2.[10,11]

After 23 years of cooling and neglecting diffusion losses, the total ORIGEN2 tritium decays to 442 μCi per g of Zircaloy-2 cladding present. In this study, an average of 86 μCi tritium/ g Zircaloy-2 was found, which corresponds to 19% of the total tritium produced and remaining after 23 years. The value of 19% tritium in the cladding at a linear heat rate of 160 W/cm agrees well with the relation shown by Wölfle in Figure 2, where the dashed line is $y = 98.514e^{-0.0029x}$. Wölfle's relation is similar to one proposed earlier by Grossman and Hegland. Both relations appear to work well for fuel with elevated linear power ratings, but fuels burned below about 200 W/cm still show a wide range of tritium retention values. The variability in tritium retention at low linear power is likely due in part to the range of tritium retention values observed at different positions along a fuel rod.[3]

The results of this study may correspond best with those of Jenkins et al.,[5] where five samples of Zircaloy-2 from a boiling water reactor were found to contain an average of 23% of the total tritium generated by the fuel, as determined by ORIGEN[12] calculations. In that case, the fuel's linear power history was not known.

Oxidation Rate

The oxidation rate for Zircaloy-2 has been measured in separate studies at Hanford[13] and at Oak Ridge.[14] The addition of the tin and other trace elements to the Zircaloy reduces oxidation times by about an order of magnitude compared to that of

pure Zr. For oxidation reactions that exhibit a linear rate, the temperature dependence is described by the Arrhenius equation

$$k = A \exp(-Q/RT)$$

where k is the surface specific rate, A is the surface specific rate constant, Q is the activation energy, R is the gas constant, and T is the absolute temperature. For both Zr and Zircaloy-2, Kendall et al.[13] observed two oxidation rates, an initial nonlinear rate that probably is diffusion-limited, and a subsequent linear rate that occurred after "breakaway" of the oxide film. The linear rate considerably exceeds the initial rate. Kendall demonstrated that Zr and Zircaloy-2 oxidation rates obey the Arrhenius law, due to the linearity of the plot of k vs 1/T. Based on measurements of Zircaloy-2 linear oxidation rates at 500, 600, and 700 °C, Kendall[13] calculated a rate constant of 8.5×10^6 mg/(cm^2 h) and an activation energy of 3.1×10^4 cal/mol.

The TGA analysis in Figure 1 shows that the Zircaloy-2 oxidation rate is linear after a short initiation period lasting no more than about 10 min. The exact duration of the initiation period is difficult to determine in this study due to the fact that the furnace heats to the desired oxidation temperature after the sample is in place. Based on the measured initial total surface area of Hull #3, the oxidation rate over a linear 30-minute range at 974-975 °C was 73.2 mg/(cm^2 h). For the other two hulls, the initial surface area was determined by the sample masses and the average diameters and density of a set of 15 hull samples. The resulting average oxidation rate of the three hulls at 974 ± 1 °C was 75.3 ± 3.0 mg/(cm^2 h). Extrapolating the Arrhenius correlation from Kendall for 500 - 700 °C yields an expected oxidation rate at 974 °C of 31.4 mg/(cm^2 h). Thus, the observed values were more than twice that expected from experimental observations at

500 - 700 °C. A comparison to the Kendall results and extrapolation is provided in Figure 3. The increased oxidation rate observed at 974 °C is likely due to a change in the metallic phase of Zr which occurs between 800 and 900 °C. The β-Zr phase, expected above 950 °C, has a larger oxygen diffusion coefficient than the α-Zr phase, which is the Zr phase at lower temperatures.[15,16]

Conclusions

The experimental design successfully captured tritium. Previous research has shown the release of tritium from Zircaloy at or below 500 °C to be almost entirely in the form of HTO. In this study, the autoignition temperature for hydrogen was reached before appreciable mass gain, causing release of tritiated water vapor, which is readily absorbed. The orders of magnitude decrease in tritium content in succeeding liquid traps demonstrated the effectiveness of the traps in capturing tritiated water vapor. The Big Rock Point hulls tested ranged from 67 – 99 μCi tritium/g Zircaloy-2 hull. The average value, 86 μCi tritium/g hull, corresponds to 19% of the total fission tritium, based on ORIGEN2 calculations for a decay of 23 years. The measured linear oxidation rate of the Zircaloy-2 hull was more than twice as fast as expected based on extrapolation of lower temperature data. The increase in the oxidation rate at higher temperatures is attributed to the increase in the diffusion rate as α-Zr transforms to β-Zr.

Table 1. Tritium Contents of Offgas Bubbler Solutions

Hull #	Bubbler #-Solution	Tritium µCi/mL	Tritium µCi/g hull
1	1-Water	3.61	91
	2-Acid*	0.00051	
	3-Water	<0.00005	
2	1- Acid*	4.75	67
	2- Water	0.0646	
	3- Ethylene Glycol	0.0055	
3	1- Acid*	4.09	99
	2- Acid*	0.0808	
	3- Water	0.0010	

* "Acid" refers to 5 wt % HNO_3 / 10 wt % H_2O_2.

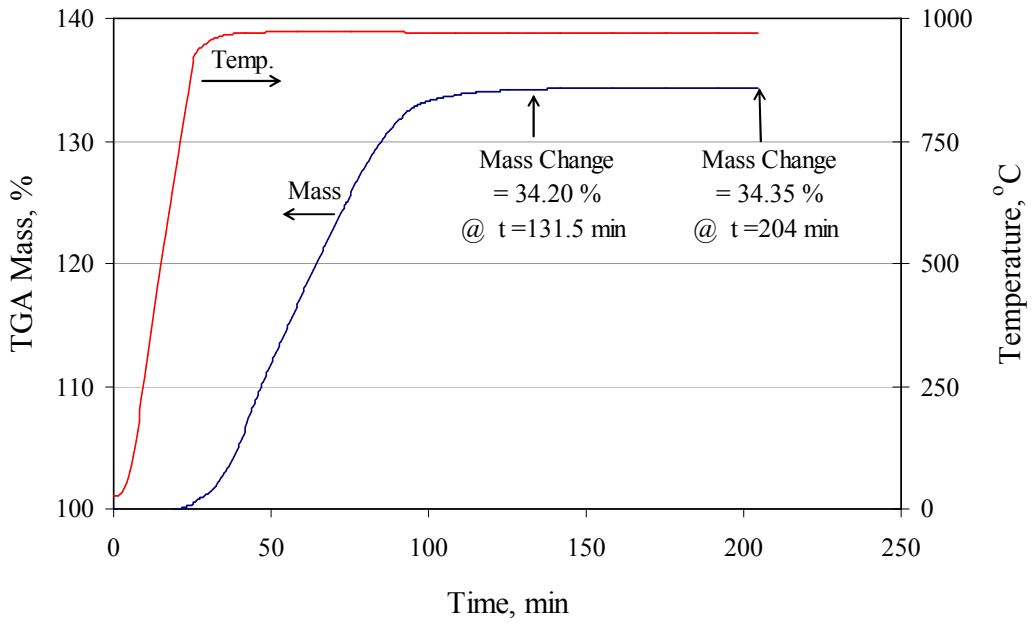

Figure 1. Mass and Temperature versus Time for Zircaloy Hull Sample #3.

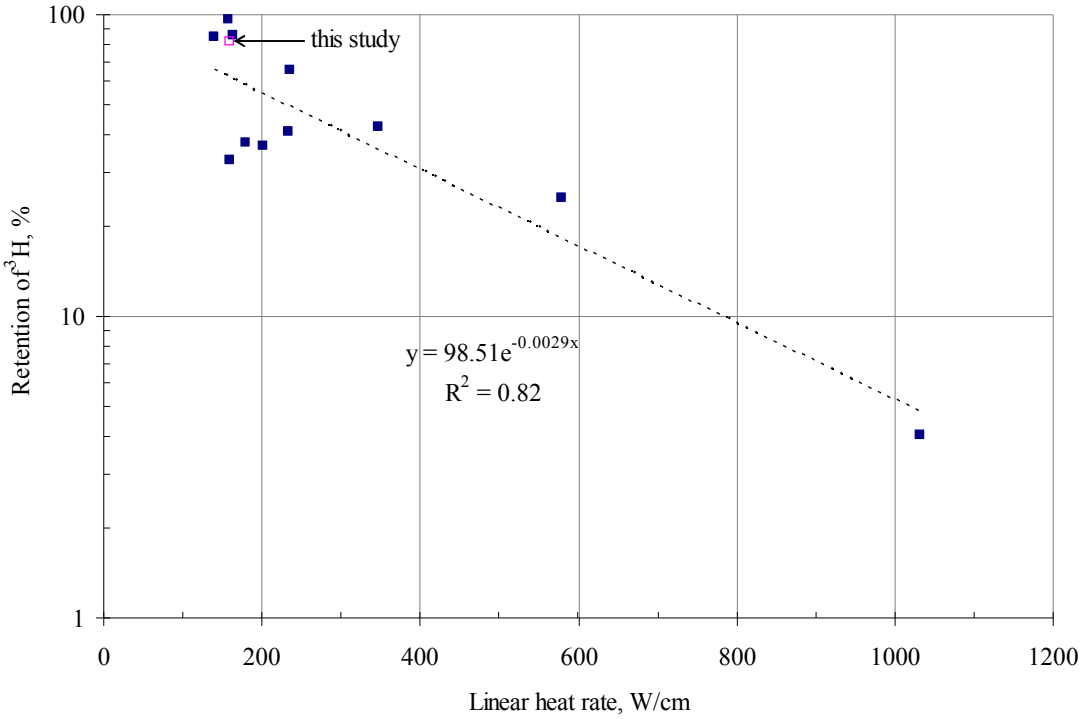

Figure 2. Retention R of tritium in fuel as function of linear heat rate (% in Zircaloy = 100-R) (▪ values quoted by Wölfle[4]).

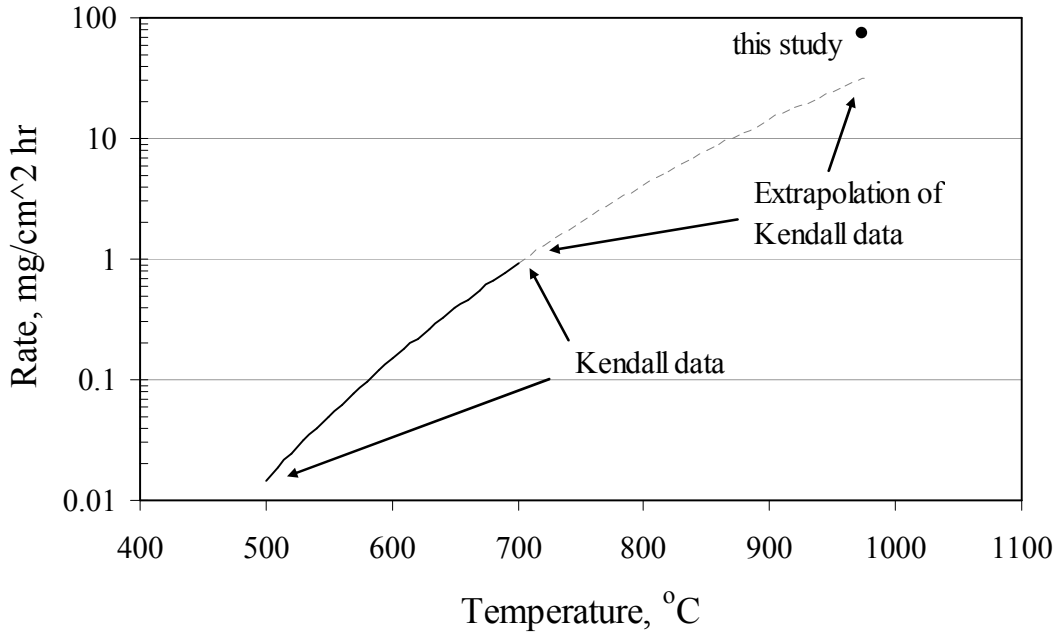

Figure 3. Zircaloy-2 oxidation rates – comparison to Kendall[13] data.

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