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Investigation of Hydrogen Generation in SNF Canisters using Lab-Scale “Mini-Canister” Radiolysis Testing

Anna L. d’Entremont,^{*,†} Christopher G. Verst,^{*} Benton C. Randall,^{*} Robert L. Sindelar^{*}

^{*}Savannah River National Laboratory, Savannah River Site, Aiken, SC, 29808

[†]anna.dentremont@srnl.doe.gov, corresponding author

INTRODUCTION

Residual water in a spent nuclear fuel (SNF) dry storage canister (whether free, physisorbed, or chemisorbed water) can break down under irradiation resulting in generation of hydrogen gas (H_2). The interactions of water with SNF cladding surfaces, which provide large surface area for adsorbed water, are expected to be an important contributor to the radiolytic H_2 generation rates and total yield. For example, (oxy)hydroxides found on aluminum research-reactor SNF cladding can hold significant amounts of chemisorbed water susceptible to radiolysis, and evidence suggests that oxides such as ZrO_2 on zirconium-based commercial SNF cladding can accelerate the radiolysis of adsorbed water via energy transfer from the solid.

Experimental data on radiolytic H_2 generation rates under conditions expected in dry storage is important for making reliable predictions of canister conditions over time to ensure long-term safe dry storage. This work presents a lab-scale “mini-canister” radiolysis testing apparatus designed to facilitate in-situ monitoring of the gas environment above samples during an extended irradiation and its use to investigate radiolytic H_2 generation from a aluminum- and zirconium-alloy samples.

BACKGROUND

High Burnup Demo Cask

A previous best-estimate evaluation of residual water content and expected radiolytic H_2 yield for a canister containing Zr-clad fuel was conducted based on literature data and models [1, 2]. The modeled canister was based on the High Burnup (HBU) LWR Spent Fuel Demonstration project, which contained 32 assemblies of high-burnup Zr-clad SNF. The canister gas was sampled three times within the first 12 days after sealing [3]. The gas characterization measured ~ 500 ppmv of H_2 gas by the 12-day sample, as well as ~ 17400 ppmv water vapor [3].

Estimates were made for the various sources of residual water within the canister, including free water in the gas phase, physisorbed water on the surfaces of the fuel and canister internals, and chemisorbed water in the form of aluminum (oxy)hydroxides on the aluminum support rails. Estimates for surface-adsorbed water were based on 1) assumed water content per unit surface area based on

literature information and 2) the reported or calculated surface area of the component.

G-values (quantity of H_2 released per unit radiation energy deposited into the material) for each water source were estimated based on empirical data from the literature [1, 2]. Despite containing no H_2O itself, there is empirical evidence that ZrO_2 can accelerate the radiolysis of adsorbed water [4, 5], which is attributed to transfer of radiation energy deposited in the oxide to the adsorbed water. As a result, all energy deposited in the ZrO_2 layer on Zr-alloy cladding and components was assumed to contribute to radiolysis of its physisorbed water [1, 2].

The H_2 yield associated with each source 12 days after sealing was predicted based on the quantity of water, the associated G-value, and the energy deposition based on the dose rate and mass of the material, neglecting back reactions or gettering of the H_2 [1, 2].

Physisorbed water on Zr-alloy surfaces was predicted to be by far the most rapid source of radiolytic H_2 , due to the assumed energy-transfer mechanism, and thus dominated the short-term estimate [1, 2]. With the assumed water loading and the reported surface area of the Zr-alloy components, the physisorbed water on ZrO_2 was estimated as $0.201 \text{ mol } H_2O$, which was predicted to be completely consumed by radiolysis in under 12 days, contributing 520 ppmv of H_2 in the helium backfill gas (plus ~ 13 ppmv H_2 from other sources) [1, 2]. This value is remarkably close to the 12-day H_2 measurement of ~ 500 ppmv H_2 .

This 520 ppmv prediction assumes that water initially physisorbed is not replenished as it is decomposed by radiolysis, i.e., once the initial $0.201 \text{ mol } H_2O$ on the ZrO_2 is consumed, the Zr-alloy components would no longer contribute to the radiolytic yield. However, it is also possible that water vapor in the gas may adsorb onto the solid surface as the physisorbed water is depleted. Additional bounding calculations were performed assuming rapid adsorption from the water vapor [1, 2]. Under these assumptions, it was predicted that both the initial physisorbed layer on Zr and the majority of the initial water vapor would be consumed within 12 days, yielding a predicted ~ 16000 ppmv H_2 (much higher than the actual HBU Demo Cask measurement) [1, 2].

This analysis, and the massive difference between the results assuming no replenishment of physisorbed water versus rapid replenishment, highlights several key assumptions about the involvement of the Zr-alloy components necessary to complete the estimate. Assumptions about what portion of the Zr alloy transfers energy to the adsorbed water (e.g., entire ZrO_2 layer, part of

the ZrO_2 layer, and/or portions of the underlying metal) and whether the adsorbed water layer will be replenished from water vapor in the cover gas (and how quickly) have massive impact on the predictions.

The experimental test campaign presented below for Zr-alloy samples is intended to refine these assumptions to enable more accurate predictions.

EXPERIMENTAL APPROACH

Mini-Canister Setup

The “mini-canister” system consists of a miniature steel canister designed to fit inside a ^{60}Co gamma irradiator and featuring a sampling tube through the lid to allow intermittent, in-situ sampling of the canister gas (Fig. 1). The sampling tube is connected to an instrumentation manifold that draws 10-mL gas samples and measures the gas pressure and H_2 , O_2 , and N_2 concentrations. This enables the evolution of the gas atmosphere within the mini-canister to be monitored over the course of an irradiation period for the same sample and initial atmosphere, in contrast to glass-ampoule-based tests that yielded only a single data point per individual sample [6].



Fig. 1. Sealed mini-canister for a luminium radiolysis campaign (with markings for contaminated samples) showing sampling tube attached to lid.

Aluminum Radiolysis Campaign

The mini-canister test setup was initially demonstrated on corroded aluminum samples (relevant to aluminum-clad research reactor SNF) to investigate H_2 yields from the aluminum (oxy)hydroxide layers and to explore the impact of drying processes prior to helium backfilling and sealing [6, 7]. The aluminum surrogates consisted of an assembly of parallel plates of aluminum separated by spacers and secured with a single bolt. The plates were polished to 600 grit to remove existing oxide, assembled, and immediately immersed in room-temperature ($22\text{--}23^\circ\text{C}$) distilled water to form a bayerite ($\text{Al}(\text{OH})_3$) film (Fig. 2, left) [6]. The two assemblies used for initial testing were immersed for 41 and 36 days, resulting in a 0.9% mass gain for each and approximately $5\text{--}10\ \mu\text{m}$ oxide film thickness [6]. The width

of the parallel plates varied so that the overall assembly shape conformed closely to the cylindrical interior of the canister (Fig. 2, right) in order to maximize the sample surface area in the test.



Fig. 2. Surrogate assembly during immersion in room-temperature water for 41 days (left) as well as loaded into the mini-canister (right) [6].

After the sample assemblies were loaded and sealed into the canisters, one was placed in a 220°C furnace with the sampling line open to lab air in order to dry the canister and sample [6]. Moisture visibly dripped from the open sampling line during this process, as depicted in Fig. 3 [6]. After 4 hours, the sampling line was connected to a vacuum pump, the furnace was shut off, and vacuum was drawn for 1 hour while the canister remained in the residual furnace heat [6]. The thermally-dried mini-canister was denoted as *As-Dried* and the other as *As-Corroded*.

Both mini-canisters were then exposed to vacuum for 12 hours, followed by a residual air elimination process consisting of four alternating helium purges and short vacuum steps, and finally backfilled with dry helium to ~ 24 psia [6].



Fig. 3. Water bubble forming on at the exhaust of the vessel during drying [6].

The size of the mini-canisters allowed two to fit side-by-side in the irradiator cavity, symmetric to the ^{60}Co sources,

for simultaneous irradiation (Fig. 4) during which gas samples were collected intermittently and analyzed by a gas chromatograph to quantify H_2 and O_2 concentrations.



Fig. 4. Two mini-canisters inside irradiation cavity [6].

The dose rate was measured by Fricke dosimetry within an empty mini-canister placed at one of the test locations, and Monte Carlo N-Particle modeling was used to assess the dose rate profiles across the sample-loaded canisters, determining that both samples would receive the same volume-averaged dose rates regardless of sample rotation within the canister [7].

The decay-corrected dose rates at the start of irradiation for the *As-Corroded* and *As-Dried* mini-canisters were 6.3 Gy/min and 6.2 Gy/min, respectively [7]. The exponentially decaying dose rate was integrated to yield the decay-corrected cumulative dose $D(t)$ during the irradiation, given by

$$D(t) = \frac{\dot{D}_0 t_{1/2}}{\ln(2)} [1 - (1/2)^{t/t_{1/2}}]$$

where \dot{D}_0 is the dose rate at the start of irradiation and $t_{1/2} = 5.271$ y is the half life of ^{60}Co .

Zirconium Radiolysis Campaign

A test plan for a similar Zr-alloy mini-canister test campaign was outlined in Ref. [8] to provide data on radiolytic H_2 yield associated with zirconium surfaces with ZrO_2 films. This data will help to improve predictions for SNF dry storage, such as the analysis in Ref. [1], by verifying assumptions made in that analysis.

Zirconium surfaces that have an oxide film of ZrO_2 are expected to have physisorbed (but not chemisorbed) water layers following drying treatments, and replenishment of the physisorbed water from water vapor is thought to be feasible. Therefore, the mini-canister test approach will be modified to include water vapor in the initial helium atmosphere. In addition, SNF in the HBU Demo Cask was predicted to be at elevated temperatures (e.g., 200–250°C) [9], which is likely to impact the physisorbed water loading and the likelihood of

replenishment from the vapor. By using an axially shorter canister to leave room for a heater and surrounding thermal insulation inside the irradiation cavity, irradiation at elevated temperature ($\sim 200^\circ C$) is planned. (This approach was previously used to irradiate ampoules containing aluminum samples at temperatures up to $200^\circ C$ [10].)

Air oxidation in a furnace will produce ZrO_2 films on the sample surfaces to represent the oxide expected on service-exposed cladding.

The H_2 yield of samples with different substrate thicknesses and different oxide thicknesses will be compared to elucidate which portions of the sample may transfer energy to adsorbed water and consequently accelerate radiolysis [8]. Inclusion of water vapor in the initial helium atmosphere and monitoring of the amount of vapor remaining are planned to elucidate whether the presence of the zirconium samples accelerates consumption of the water vapor, indicating replenishment of adsorbed water from the gas phase.

RESULTS

Aluminum Radiolysis Campaign

Small samples were cut from each aluminum sample assembly for characterization before the assemblies were loaded into the mini-canister, and the *As-Dried* sample was dried in the furnace alongside the corresponding mini-canister. Cross-sectional scanning electron microscopy confirmed a 5–10 μm (oxy)hydroxide layer on the *As-Corroded* assembly [6]. X-ray diffraction showed predominantly bayerite on the *As-Corroded* sample, and bayerite with some well-crystallized boehmite on the *As-Dried* sample, indicating partial thermal dehydration of the bayerite during drying [6].

For each gas sample, the cumulative amount of H_2 generated in the mini-canister up to that point was calculated based on the measured sample H_2 concentration and the amount of gas remaining in the canister (assumed to have the same H_2 concentration), plus the H_2 removed by all previous samples. No O_2 generation was observed for any of the samples, which is consistent with earlier ampoule testing [11].

The cumulative H_2 yield for both surrogate assemblies is plotted in Fig. 5 [7]. The *As-Dried* assembly had much lower H_2 yield than the *As-Corroded* assembly over the entire irradiation to date, including a longer delay before measurable H_2 was observed and a dramatically lower initial H_2 generation rate for the dried assembly.

Preliminary results from recent radiolysis tests using glass ampoules (one data point per irradiation) and pieces of the *As-Corroded* characterization sample revealed that a 12-hour vacuum step could significantly reduce radiolytic H_2 generation compared to no vacuum drying, attributed to removal of physisorbed water [6]. This suggests that even the *As-Corroded* yield is likely reduced significantly relative to that of a drip-dried condition.

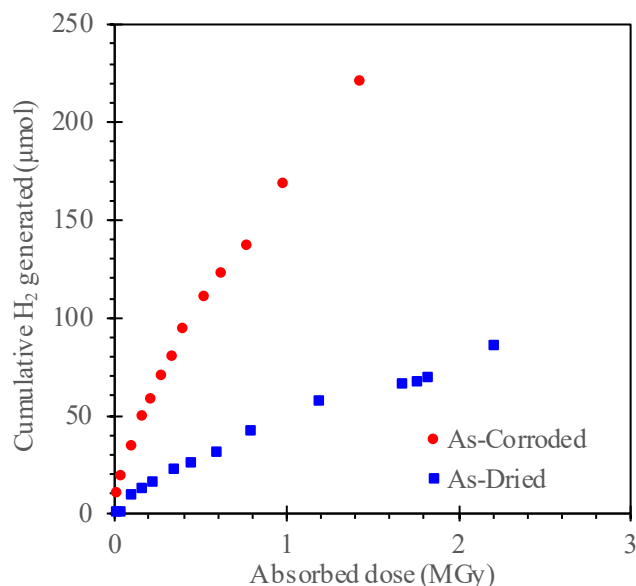


Fig. 5. Cumulative H₂ generated as a function of dose (accounting for ⁶⁰Co decay) for the *As-Corroded* and *As-Dried* surrogate assemblies [7].

The stark difference in yield indicates that drying at 220°C (high enough to partially remove chemisorbed water from bayerite as well as physisorbed water) can make a large impact in mitigating H₂ generation from a luminum-clad SNF (ASNF).

This data will factor into selection of drying processes for actual ASNF dry storage canisters, e.g., vacuum vs. forced-gas drying. Note that real SNF, in contrast to the surrogate samples, has internal decay heat that will result in some temperature elevation during vacuum drying even in the absence of external heat input. However, ASNF being considered for dry storage is relatively cold. Engineering-scale drying tests incorporating both simulated decay heat (100 W) and external heating of the canister wall (100–220°C, depending on test) found that the surrogate SNF temperatures during vacuum drying remained below ~120°C with a very broad temperature spread between different locations in the same test (10s of degrees within the same assembly and >70°C spread between heated and unheated assemblies) [12]. Freezing of water inside the canister was also observed in some tests [12]. Therefore a non-vacuum heated drying stage such as forced-gas drying is expected to be necessary to achieve similar H₂ yield reduction as the As-Dried mini-canister.

Zirconium Radiolysis Campaign

An experimental setup has been established for mini-canisters containing oxidized zirconium samples in helium atmospheres with relative humidity between 2% and 90% at room temperature. Two shortened mini-canisters are arranged symmetrically in the cavity of a model 812 ⁶⁰Co gamma irradiator, as shown in Fig. 6, for simultaneous

irradiation and in-situ gas sampling. The mini-canisters will be heated to 200°C using resistance heat tape and fiberglass insulation with thermocouples informing multiple PID temperature controllers.

Fricke dosimetry has been performed on this mini-canister setup. The calculated volumetric averaged dose rates will remain >200 Gy/min throughout calendar year 2022.

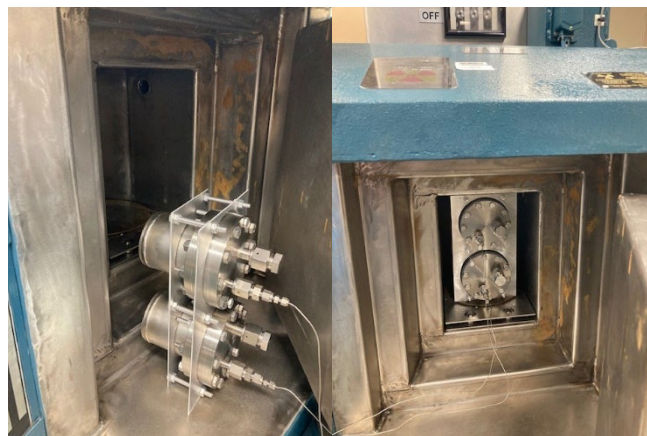


Fig. 6. Mini-canister set-up for Zr samples, next to (left) and inserted in (right) the irradiator cavity.

Oxidation testing of small zirconium samples (Fig. 7) is underway to identify suitable conditions to produce predictable oxide thickness of uniform morphology and microstructure. The oxidation tests involved heating under air, either in a naturally ventilated furnace or under an imposed airflow. Sample characterization to determine oxide thickness and composition are pending. Once the target temperature and atmospheric condition for repeatable oxide growth have been established, multi-plate assemblies for mini-canister testing will be fabricated and treated. The goal is to form at least two significantly different oxide layer thicknesses in order to assess the impact of oxide thickness on the radiolytic H₂ yield under otherwise identical conditions (e.g. dose rate and atmosphere).



Fig. 7. Zr oxidation test samples, after heated oxidation treatments in air, illustrating visible coloration changes. From left to right: 1) Control, 2) 1 h at 350°C, still air, 3) 4 h at 350°C, flowing air, 4) 2 days at 600°C, still air 5) 2 days at 660°C, flowing air, 6) 2 days at 660°C, still air.

CONCLUSIONS

Mini-canister radiolysis testing enables in-situ monitoring of radiolytic H₂ generation from individual radiolysis samples over the course of an irradiation. Use of relatively large surrogate assemblies designed to maximize sample area within the canister volume provides quick results.

This approach was first demonstrated on aluminum-alloy samples relevant to research-reactor cladding, showing a smooth progression of the H₂ generation rate that decreased with increasing dose. Comparison of nominally identical sample assemblies with bayerite films under dry helium showed that heated drying at 220°C prior to irradiation dramatically decreased the H₂ yield compared to only unheated vacuum. The 220°C drying was sufficient to partially dehydrate the bayerite to produce boehmite, i.e., it removed chemisorbed as well as physisorbed water.

Experimental setup and preliminary baseline testing for a similar test campaign with zirconium-alloy samples is underway. This testing is intended to confirm assumptions made during previous radiolysis evaluations, in order to facilitate more accurate predictions of H₂ build-up in commercial SNF canisters.

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