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Radiolysis Testing of SNF Materials and Surrogates in a "Mini-Canister" – 22162

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ABSTRACT

Radiolysis of adsorbed water and (oxy)hydroxides on spent nuclear fuel (SNF) can alter the headspace gas conditions within SNF dry storage canisters over time, with the potential for build-up of hydrogen gas (H_2) within sealed canisters. For aluminum-clad spent nuclear fuel (ASNF) in particular, the cladding itself can hold significant amounts of chemisorbed water in the form of aluminum (oxy)hydroxides which are not readily removed at low (<100°C) drying temperatures. Experimental measurements of radiolytic gas generation from materials with surface conditions representative of SNF materials are important to establish expected H_2 generation rates and overall yield in order to enable reliable predictions of SNF canister conditions over time and establish a safety basis for long-term dry storage of ASNF.

This paper summarizes an experimental irradiation campaign consisting of in-situ monitoring of radiolytic H_2 generation in a "mini-canister" system containing: i) aluminum surrogate materials and ii) reactor-exposed ASNF material under canister-analogous conditions. Three separate experiments were conducted with the following aluminum-alloy samples to measure the radiolytic gas evolution as a function of radiation dose:

- Parallel-plate assembly with lab-grown bayerite film, as-corroded, with 12 hours unheated vacuum
- Parallel-plate assembly with lab-grown bayerite film, dried for 4 hours at 220°C and 12 hours unheated vacuum
- Cropping from reactor-irradiated (MURR) fuel assembly, wet-stored (L Basin at SRS) and drip-dried in air.

Each sample was sealed in a small, stainless-steel "mini-canister" backfilled with helium and irradiated using a Co-60 gamma source to simulate attendant SNF radiation. During irradiation, periodic gas samples were drawn from the vessel to provide measurements of pressure and concentrations of H_2, O_2, and N_2. This campaign is designed to 1) validate the performance of instrumentation to monitor a future full-scale demonstration DOE Standard Canister for verification and validation of the dry storage safety basis for ASNF, 2) provide data on how the H_2 generation of an individual sample evolves over time to benchmark multi-physics ASNF canister models developed at the Idaho National Laboratory (INL), 3) characterize the impact of drying processes on radiolytic H_2 yield, and 4) provide a comparison of actual reactor-exposed aluminum materials to lab-prepared surrogates with similar oxide layer characteristics.

The extended in-situ monitoring of the mini-canister system enables tracking of the H_2 generation rate of each individual sample and sealed system from initial H_2 release through longer-term behavior. The H_2 generation of both surrogate assemblies was most rapid early in the irradiation and slowed with increasing time and dose, as expected from previous work. Drying at 220°C dramatically reduced the H_2 generation rate and overall yield observed, providing a potential approach to significantly reduce the risk of H_2 buildup in ASNF canisters. The dried surrogate assembly's H_2 yield also appears to be approaching either a plateau or regime of very slow H_2 generation. Preliminary results for the reactor-exposed aluminum sample show measurable and increasing H_2 yield, which appears to behave qualitatively as expected compared to the behavior of the surrogate materials, accounting for differences in sample size and drying processes.

INTRODUCTION

Radiolysis of residual water within spent nuclear fuel (SNF) dry storage canisters, whether in the form of

free water, physisorbed water, or (oxy)hydroxides, can lead to build-up of hydrogen gas within sealed canisters. The cladding of aluminum-clad spent nuclear fuel (ASNF) in particular can hold significant amounts of chemisorbed water as aluminum (oxy)hydroxides which are not readily removed at low (<100°C) drying temperatures. Quantification of radiolytic gas generation from materials with surface conditions representative of SNF materials and under canister-analogous conditions is important to establish expected H_2 generation rates and overall yield to enable predictions of SNF canister conditions over time and to evaluate the behavior of the ASNF-in-canister during long-term dry storage.

For that purpose, an experimental irradiation campaign was conducted consisting of in-situ monitoring of radiolytic H_2 generation in a "mini-canister" system containing either 1) aluminum surrogate materials with lab-grown (oxy)hydroxide layers or 2) reactor-exposed ASNF material. The extended in-situ monitoring enables tracking of the H_2 generation rate of each individual sample and sealed system from initial H_2 release through its longer-term behavior. This test campaign is designed to 1) validate the performance of instrumentation designed to monitor a future full-scale demonstration DOE Standard Canister for verification and validation of the dry storage safety basis for ASNF, 2) provide data on how the H_2 generation of an individual sample evolves over time for use in benchmarking multi-physics ASNF canister models developed at the Idaho National Laboratory (INL), 3) characterize the impact of drying processes on radiolytic H_2 yield, and 4) provide a comparison of actual reactor-exposed aluminum materials to lab-prepared surrogates with similar oxide layer characteristics.

METHODS

Mini-Canister System

The "mini-canister" system is designed to be a bench-scale surrogate for dry cask storage systems and enable irradiation testing in a canister-analogous environment, i.e., a stainless-steel vessel backfilled with helium and irradiated to simulate SNF attendant radiation. During irradiation, periodic gas samples are drawn from the vessel to provide measurements of pressure and concentrations of H_2, O_2, and N_2. These measurements are taken using an instrumentation system designed for future monitoring of a full-scale demonstration canister [1].

The mini-canister was a commercially available steel vacuum vessel with an internal diameter of 7.19 cm (2.83") and height of 17.9 cm (7.06"). The canister body and bolted flange endcaps feature a knife-edged conflat seal that presses into annular copper gaskets to provide leak tightness up to ultra-high vacuum. The top endcap features a Swagelok threaded connection to a 6 ft long steel capillary line. The capillary line allows for establishing the initial gas atmosphere after the mini-canister is loaded and sealed by drawing vacuum and backfilling with a prescribed cover gas, as well as for sampling the canister gas during irradiation. During the radiolysis test, the mini-canister is placed inside an irradiator with its capillary line connected to a gas sampling manifold. The gas samples are analyzed by a gas chromatograph (GC). All valves associated with the manifold are external to the radiation field to avoid any radiolysis of their components.

This experimental set-up provides the ability to monitor a single sample in a sealed system over time, in contrast to previous radiolysis testing using glass ampoules [2, 3], which provided only a single data point for each sample/irradiation. Repeated sampling of the same sample helps to eliminate some of the experimental noise caused by sample-to-sample variations in characteristics such as chemisorbed and physisorbed water loading. The larger working volume of the mini-canister vessels also allows for larger parallel-plate surrogate samples intended to maximize the aluminum surface within the sealed volume and provide a facsimile of Materials Testing Reactor (MTR) plate fuel.

Baseline radiolysis testing was performed on the mini-canister vessels without samples and with a backfill of pure helium to ensure that surface moisture retained on the vessel walls would not contribute to radiolytic H_2 generation and that leak tightness could be maintained for long duration irradiations. The helium atmosphere was established via successive evacuation and backfill cycles through the capillary

line until neither O_2 nor N_2 were detected via two successive gas chromatograph samples one hour apart. Intermittent gas sampling of the sealed vessel atmosphere during a 24-day irradiation period, corresponding to a cumulative dose of ~0.3 MGy, showed no detectable H_2. Minimal traces (~10 ppm total) of N_2 and O_2 in typical proportions for air were detected starting 1 day after sealing/backfilling and remained consistent throughout the rest of the irradiation period, although they were absent from the initial day-0 measurement; this was attributed to residual air not eliminated during the helium filling procedure and which had yet to equilibrate through the 1/16" capillary line until after the day-0 measurement.

Samples: Lab-Prepared Surrogate Assemblies

Two large-plate surrogate assemblies were fabricated specifically for radiolysis testing in the mini-canister. Each consisted of 17 individual, 1.3-mm (0.050-in) thick aluminum 6061T6 plates, which were bolted together with aluminum hardware and separated by aluminum washers to provide a 2 mm gap between plates. The plate height and widths were selected to conform closely to the cylindrical interior of the mini-canister in order to maximize the plate area in the test, resulting in an aluminum surface area of nearly 3800 cm^2.

The assemblies were treated to form an aluminum (oxy)hydroxide layer prior to irradiation testing to stand in for the (oxy)hydroxide layers found on reactor-exposed aluminum [4, 5]. Immediately prior to assembly, the aluminum plates were polished to 600 grit to remove any existing oxide and rinsed with distilled water. They were then immersed in room-temperature (22–23°C) distilled water for an extended period. Fig. 1 (left) shows the first assembly during corrosion; bubbles, presumed to be hydrogen from the reaction of water with aluminum, were observed forming on the sample surface and rising to the surface of the water. The first assembly was immersed in the water bath for 41 days. After 7 days of air-drying, it was weighed, indicating a mass gain of 5.5 g (0.90% of its pre-corrosion mass). The second assembly was immersed for 36 days and gained 5.3 g (0.87%).

A small section was cut from an external plate of each assembly after corrosion for characterization by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Fig. 1 (middle) shows the first plate assembly after corrosion and removal of a sample from the leftmost plate, and Fig. 1 (right) shows the first assembly loaded into the mini-canister vessel.

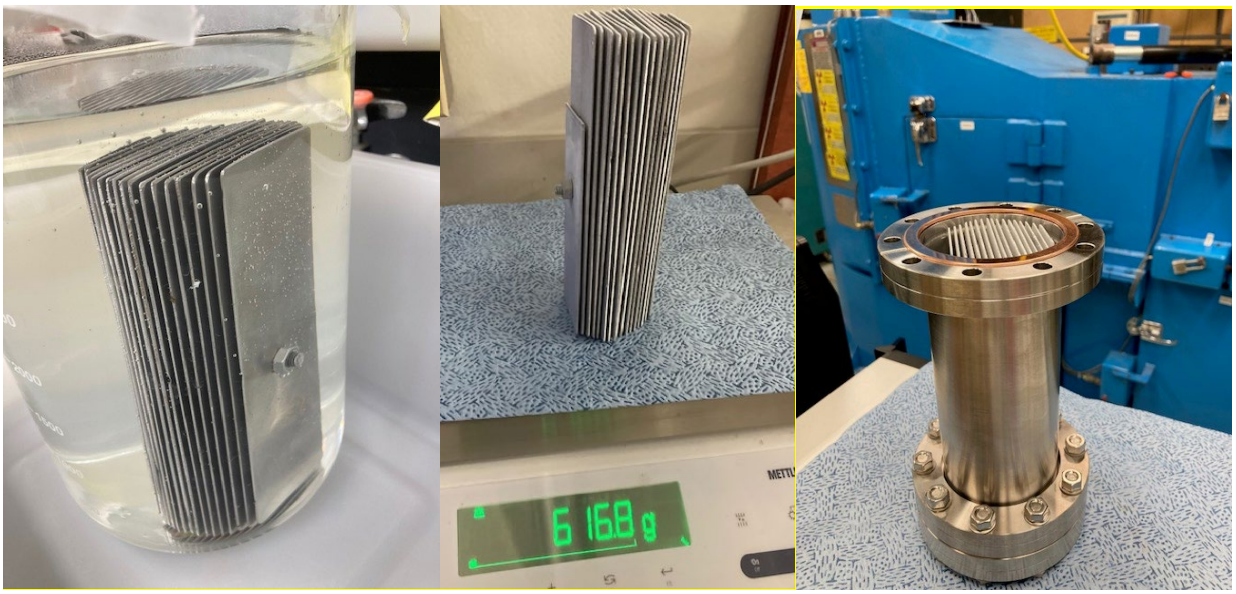

Fig. 1. First (*As-Corroded*) plate assembly during (left) and after (middle) immersion in room-temperature water for 41 days as well as loaded into the mini-canister (right).

Samples: Reactor-Exposed MURR Cropping

A reactor-exposed sample retrieved from wet storage in the Savannah River Site (SRS) L Basin was also tested to obtain data on radiolytic yield from service-formed (oxy)hydroxide. The sample used was a cropping from a Missouri University Research Reactor (MURR) fuel element made of aluminum alloy 6061T6 and previously characterized as reported in Refs. [4, 5]. Although the service history of the individual fuel element the cropping came from is unknown, a minimum operating temperature of 60°C and minimum in-reactor time at temperature of 113 days can be assumed bounding based on known MURR operating parameters [5]. Between ~6.3-day periods of operation, it would have spent periods in wet storage in a pool with a mixed bulk temperature of 37.8°C [5]. Since final discharge from the reactor, it has been stored in the SRS L Basin wet storage pool (average temperature 22°C) for a period of <18 years [5]. Fig. 2 shows (left) the MURR cropping and other samples collected in L Basin, (middle) the whole MURR cropping in the shielded cells, and (right) where the cropping was cut to remove a section for characterization samples.

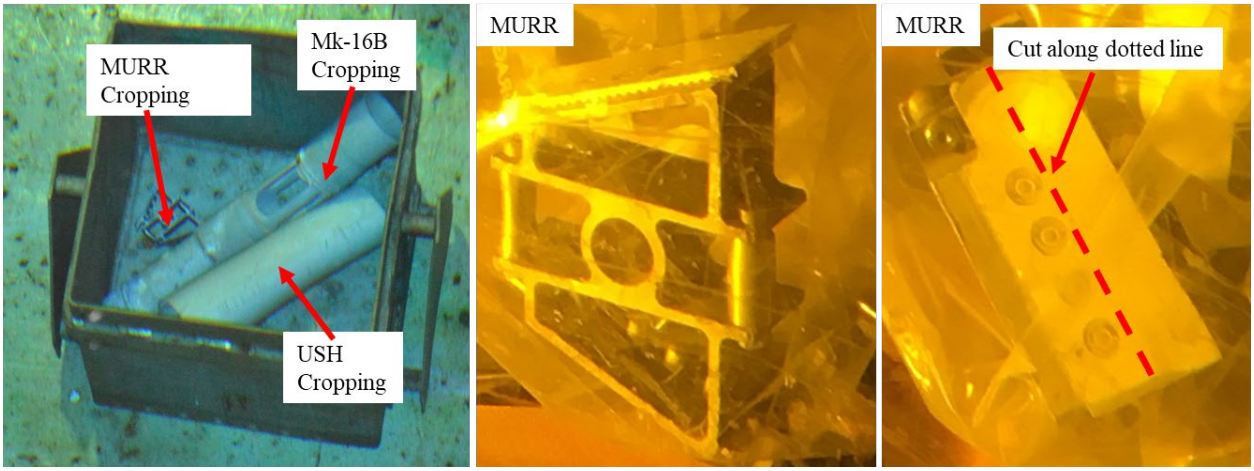

Fig. 2. (Left) MURR and other croppings gathered in L Basin for retrieval; (middle and right) MURR cropping in shielded cells [5].

The (oxy)hydroxide layer on the MURR samples was characterized by XRD and SEM. The XRD and SEM characterization focused on the surface that faced the inside of the fuel element, because efforts to decontaminate the MURR cropping included scrubbing with a soft bristle brush prior to cutting samples, and the inside face was undisturbed by this process [4, 5].

The XRD spectrum for the MURR sample is shown in Fig. 3. Peaks for bayerite and aluminum metal were evident, as well as a broad boehmite peak. Fig. 4 shows planview (left) and cross-sectional (right) SEM of the MURR sample. The (oxy)hydroxide layer appeared to be blocky and dense. Cross-section showed that the (oxy)hydroxide layer was ~5–10 μm thick and relatively uniform in thickness over the region examined, mostly around 10 μm (the location imaged was on the inside stepped edge of the cropping, which would have been between the grooves holding the fuel plates) [4, 5].

The entire remainder of the MURR cropping other than the section removed for characterization samples (Fig. 2, right) was used in the mini-canister test. The cropping was cut with bolt cutters into pieces that would fit into the canister. The MURR material inside the mini-canister is shown in Fig. 5. Note that the size of the MURR sample relative to the mini-canister volume was much lower than for the surrogate assemblies that were designed to fit the canister (Fig. 1, right). As a result of the lower sample volume and surface area and corresponding larger gas volume, the H_2 concentration in the canister gas is expected to rise more slowly than for the surrogate assemblies even if the radiolysis behavior of the MURR and the lab-corroded materials are equivalent.

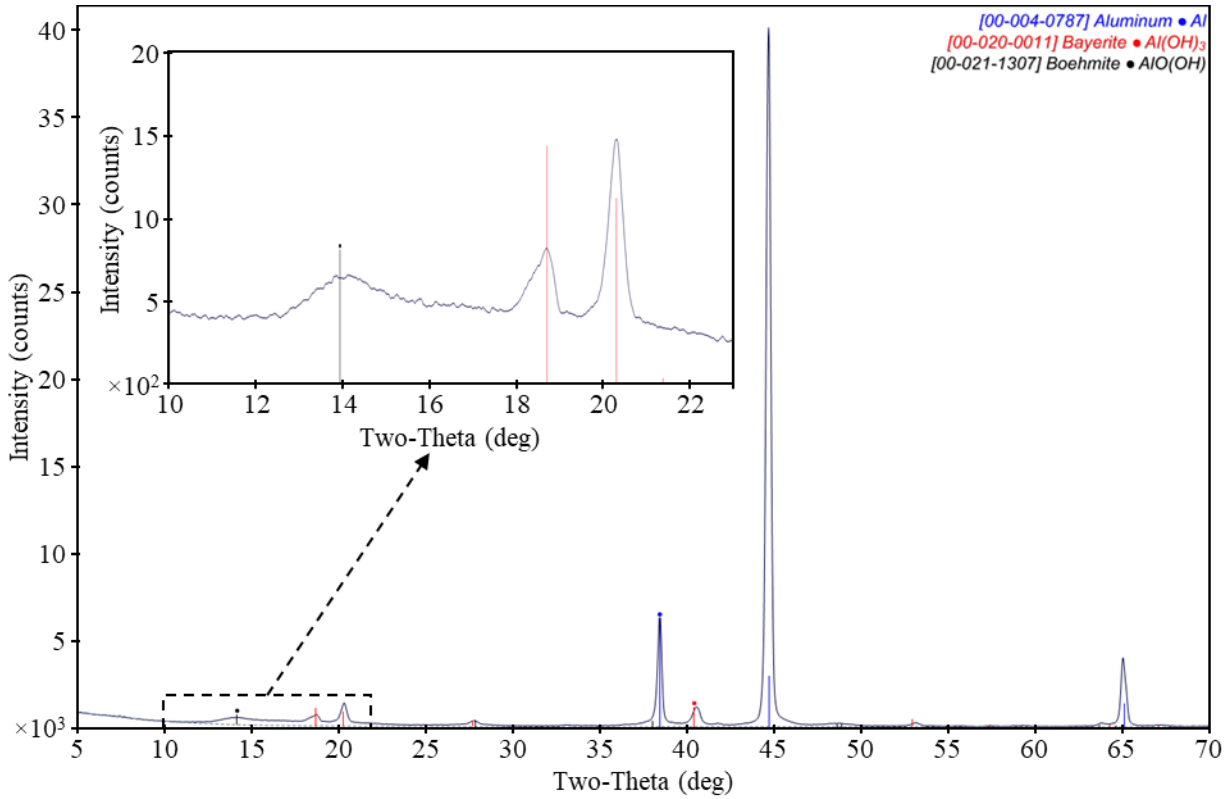

Fig. 3. XRD spectrum for MURR sample.

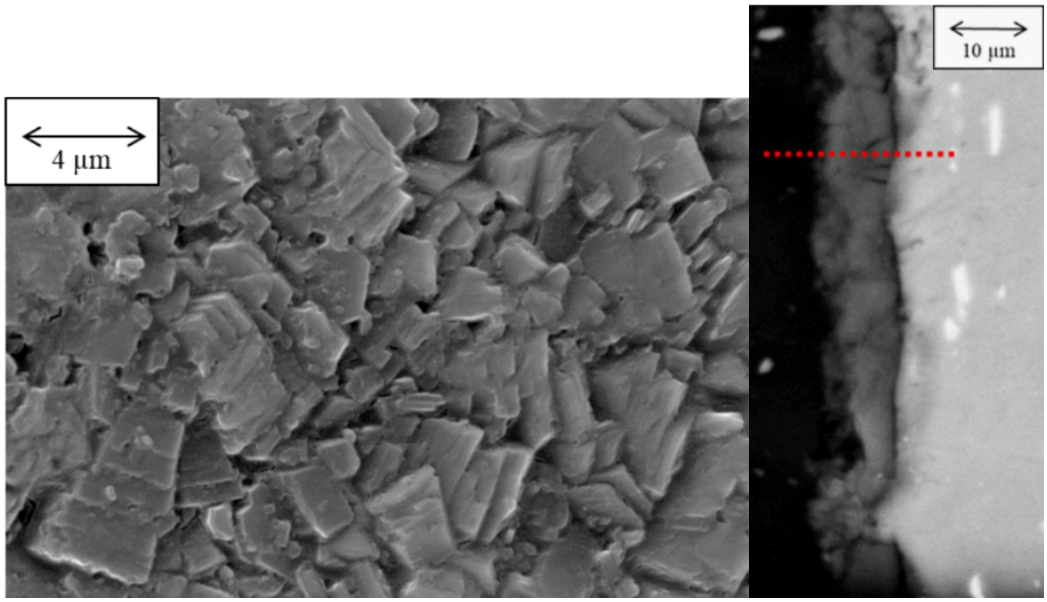

Fig. 4. Planview (left) and cross-sectional (right) SEM of MURR sample.

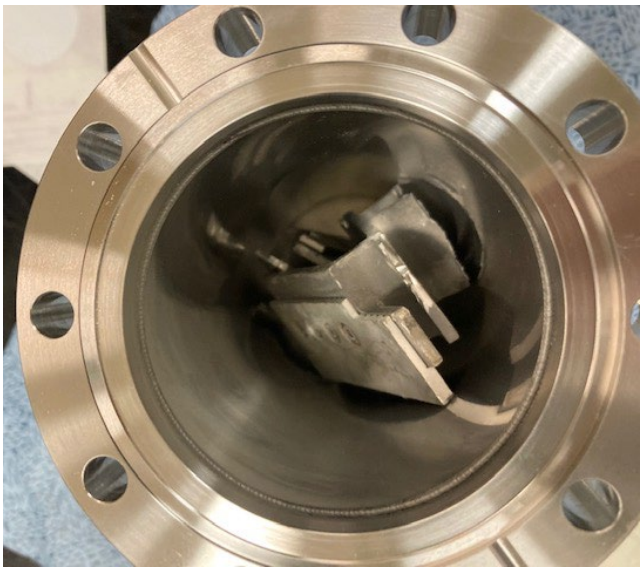

Fig. 5. MURR sample inside the mini-canister.

Mini-Canister Preparation for Irradiation

After the prepared samples were loaded into their mini-canisters, the lids were sealed. Any drying steps (heated or vacuum drying) in the test plan were implemented at this stage, followed by the air removal/helium backfilling process established in the empty mini-canister baseline testing.

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

The second of the two surrogate assemblies was subjected to a heated drying process after being sealed in its canister to test the impacts of potential drying of SNF on the subsequent radiolytic H_2 yields. This assembly is thus denoted as the "*As-Dried*" assembly while the first assembly with no heated drying is denoted as "*As-Corroded*." The heated drying process consisted of placing the loaded and sealed mini-canister in a pre-heated oven at 220°C for 4 hours with the valve at the end of the capillary sample line open to the laboratory air to allow moisture to escape. Fig. 6 shows the end of the capillary line during the drying process, with water visibly bubbling/dripping from the line, indicating significant amounts of moisture escaping. Following the 4-hour heating period, the oven was turned off, and the canister's exhaust line was connected to a vacuum pump for 1 hour while the canister remained in the residual oven heat to ensure that water vapor would be removed from the vessel and capillary line before recondensing due to cooling. The plate segment removed for characterization was placed in the furnace alongside the mini-canister, so that it experienced the same thermal treatment (albeit not the vacuum step).

The drying temperature was selected based on previous experiments [6] performing thermogravimetric analysis (TGA) on aluminum (oxy)hydroxide powders and also small aluminum samples with (oxy)hydroxide layers formed by immersion in room-temperature water, similar to the procedure used for the current surrogate assemblies and forming a predominantly bayerite film of similar thickness. The TGA results for aluminum with bayerite films 1) identified a region of rapid mass loss between about 220 and 260°C attributed to the transition of bayerite into boehmite and 2) found that the mass loss per unit area for an extended hold at 220°C was >95% of that achieved during an extended hold at 260°C [6].

After loading, sealing, and heated drying (for the *As-Dried* assembly), the mini-canister was connected to

a gas sampling manifold capable of drawing a vacuum on the canister and providing dry, ultra-high-purity helium. A 12-hour vacuum step was performed for both the *As-Corroded* and *As-Dried* surrogate assemblies at this stage. The MURR sample was not subjected to any heated or vacuum drying, only drip-drying in air, in order to avoid disturbing the initial condition of the reactor-exposed (oxy)hydroxide before obtaining an initial bounding data set. Finally, each canister was subjected to a series of cycles of alternating vacuum and helium purges to eliminate residual air from the canister and ensure an initial pure helium atmosphere and then backfilled to a helium pressure of ~24 psia before the capillary line was closed.

Radiolysis Testing

Gamma irradiation of the mini-canisters was performed using a J.L. Shepherd model 484 Co-60 gamma irradiator (Fig. 7, left). The irradiator features two Co-60 pencil sources at one end of the irradiation chamber. Two mini-canisters could be simultaneously irradiated, placed symmetrically and as closely adjacent to each pencil source as achieveable. Due to proximity to the Co-60 source, dose rates across a plate assembly could vary by as much as ±40%. However, Monte Carlo N-Particle modeling determined that the volume-averaged dose rates were independent of the orientation of the plate assemblies within the vessels (Fig. 7, middle) and that both vessels could be ascribed the same volumetric-average dose rate due their symmetric positions. Two mini-canisters are shown loaded into the irradiator in Fig. 7 (right).

The dose rate within an empty mini-canister placed at one of the symmetric locations was measured by a single Fricke solution, yielding a decay-corrected dose rate of 6.3 Gy/min at the irradiation start date of the *As-Corroded* plate assembly, 6.2 Gy/min at the irradiation start date of the *As-Dried* plate assembly and 5.8 Gy/min at the irradiation start date of the MURR cropping.

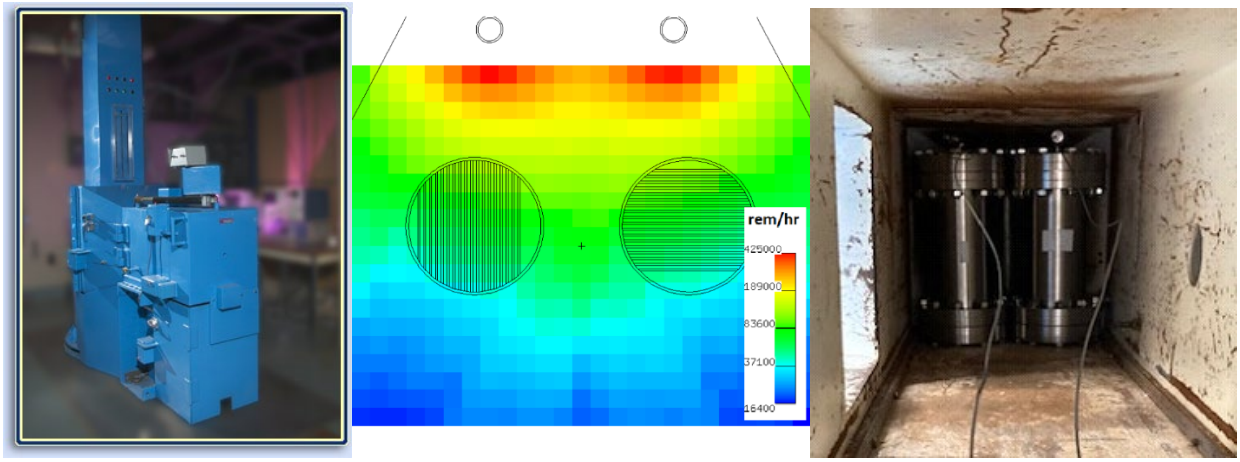

Fig. 7 Model 484 gamma irradiator (left), dose rate model (middle), and large plate vessels (right).

A gas sampling manifold was used to collect 10-mL gas samples from each irradiated vessel at semi-regular intervals. The pressure of the vessel was recorded after each sample, and the gas sample was automatically injected into an Inficon Micro GC Fusion Gas analyzer equipped with a thermal conductivity detector sensor and two analytical columns. The primary GC column, used to quantify the H_2 concentration, is a 20-meter molecular sieve using argon carrier gas. The secondary column, primarily used to quantify O_2 and N_2, is a 10-meter molecular-sieve column with a helium carrier gas. A vacuum pump was used to evacuate the sampling manifold between samples. Because each sample is permanently removed from the gas inventory remaining in the vessel, the calculation of total radiolytic H_2 generated must include the moles of H_2 in previous samples and account for the changing vessel pressure as each sample is removed.

Calibration of the GC was performed by directly injecting helium containing known concentrations of H_2, O_2, and N_2. Three calibration mixtures were used, with the following concentrations: 260 ppm H_2/251

ppm O_2/946 ppm N_2, 510 ppm H_2/510 ppm O_2/1924 ppm N_2, and 5018 ppm H_2/4946 ppm O_2/18661 ppm N_2.

RESULTS

Pre-Irradiation Sample Characterization

The XRD spectrum for the removed segment of the *As-Corroded* large-coupon assembly (Fig. 8, top) showed prominent, sharp peaks for bayerite as well as for aluminum metal, along with a small, broad peak corresponding to boehmite. For the segment from the *As-Dried* assembly (Fig. 8, bottom), bayerite remained the most prominent (oxy)hydroxide signal, but distinct, sharp boehmite peaks also appeared. The height of the bayerite peaks relative to the aluminum peaks was smaller for the *As-Dried* sample compared to *As-Corroded*. The reduction in bayerite peaks and appearance of sharp boehmite peaks suggests that the 220°C, 4-hour drying process succeeded in partially converting the bayerite to well-crystallized boehmite. No corundum peaks were identified, as expected, since thermal decomposition of boehmite to alumina is associated with higher temperatures.

Cross-sectional SEM characterization of the *As-Corroded* plate segment indicated a relatively consistent (oxy)hydroxide layer between 5 and 10 μm thick, as shown in Fig. 9. Planview SEM of the *As-Corroded* and *As-Dried* large-coupon segments (Fig. 10) showed near-identical (oxy)hydroxide morphology on both, which appeared to predominantly consist of long narrow rods of (oxy)hydroxide. In some regions, these rodlike structures formed “bundles” of parallel rods which project out from the substrate at various angles. In other areas, the surface of the (oxy)hydroxide consisted of shorter, individual rods in seemingly random orientations. The areas dominated by randomly oriented rods appear to be the highest points on the (oxy)hydroxide layer and some appear to have bundles of aligned rods projecting out from under the edges of the randomly oriented patches, suggesting that the randomly oriented rods may be a surface layer sitting on top of the structures of aligned rods.

Image comparisons of the two plates revealed the presence of narrow cracks in the *As-Dried* (oxy)hydroxide. The cracks were visible in several areas that were dominated by the aligned-rod structures and ran roughly perpendicular to the direction of the aligned rods. The crack width is on the order of 0.1 μm, i.e., of similar scale to the width of isolated (oxy)hydroxide rods, which would make the cracks very difficult to visually distinguish in the disordered regions, if present.

Cracking of bayerite films on aluminum has been previously observed after being heated to and held at temperatures ≥200°C during TGA and was attributed to contraction of the film as bayerite was converted into denser boehmite [6]. The cracking observed in the TGA study [6, 7] was more severe than in the *As-Dried* sample, featuring wider cracks and even spalling of sections of the (oxy)hydroxide, but in both cases, the overall (oxy)hydroxide morphology between cracks remained apparently identical to the undried film. This is consistent with previous literature stating that gibbsite, another aluminum trihydroxide polymorph, retained its gross morphology when thermally dried to Al_2O_3 while developing large internal porosity due to the volume change between the two phases [8, 9].

As previously discussed, the (oxy)hydroxide layer on the MURR sample was also found to be 5–10 μm thick and showed XRD peaks for bayerite and boehmite, so the general characteristics of the (oxy)hydroxide layers on the lab-corroded surrogate assemblies are similar to that on the MURR other than the details of morphology.

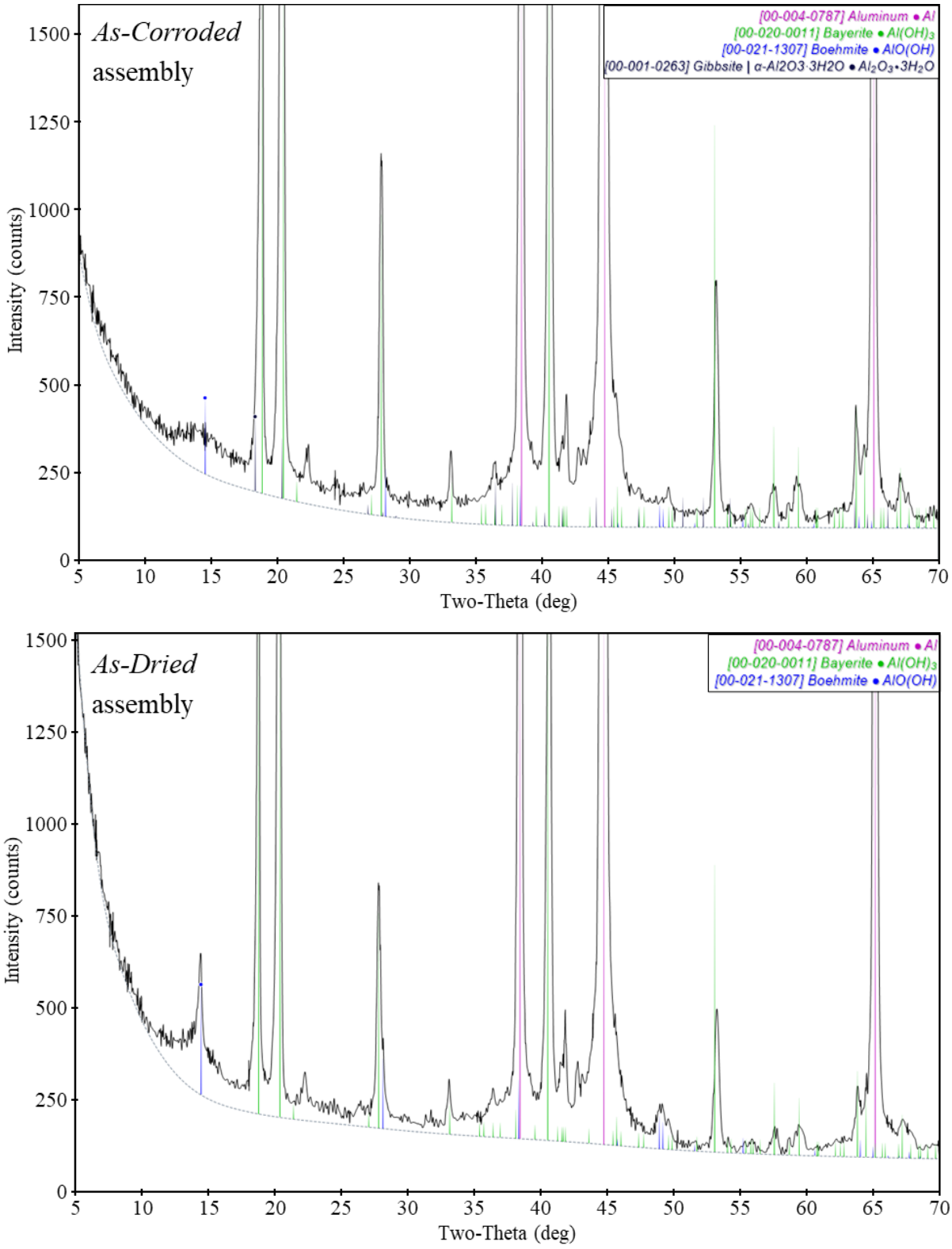

Fig. 8 XRD Spectra of the *As-Corroded* (top) and *As-Dried* (bottom) plate assembly surfaces.

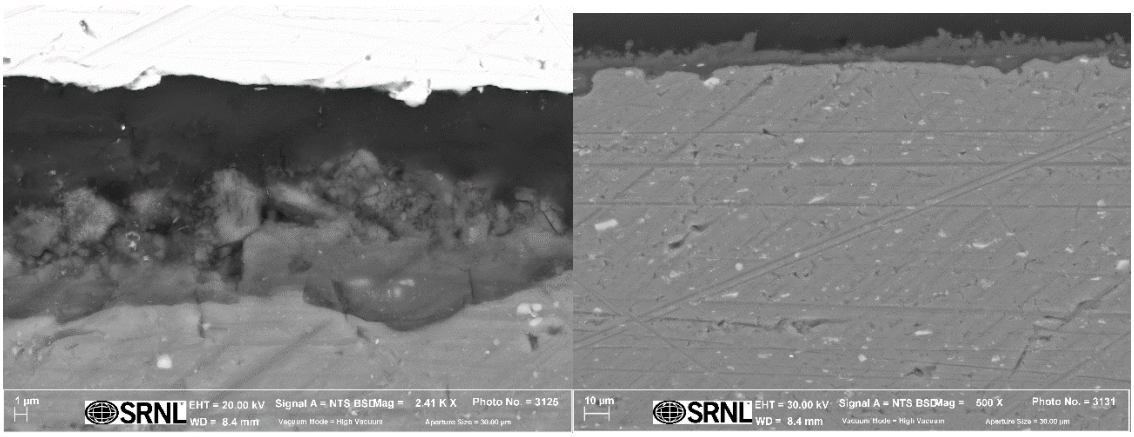

Fig. 9 SEM cross-section images of the *As-Corroded* oxide layer, 5–10 µm thick.

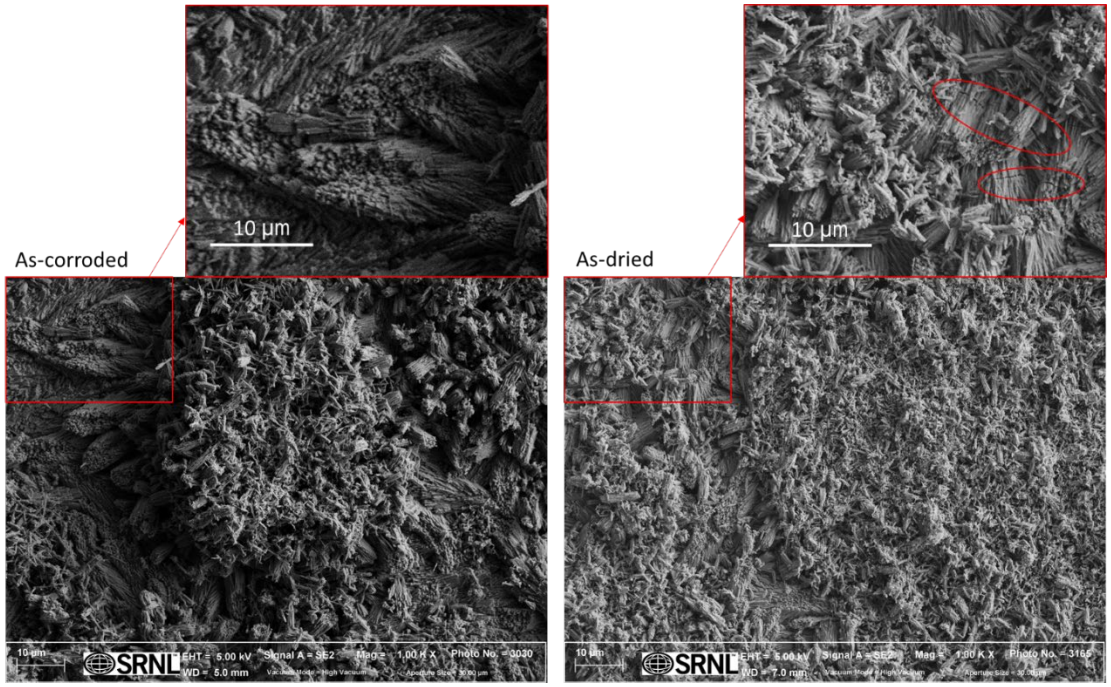

Fig. 10 Examples of (oxy)hydroxide morphology from *As-Corroded* (left) and *As-Dried* (right) large-coupon assemblies. Several fine cracks in the *As-Dried* (oxy)hydroxide are marked with red ovals in the enlarged section at top right.

Radiolysis Results

The cumulative amount of H_2 generated within the mini-canister was calculated for each sample point based on the H_2 concentration in the current sample and the amount of gas remaining in the canister (assumed to have the same H_2 concentration as the sample), as well as 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 [3]. As previously stated, the dose rate varied spatially over each plate assembly, but symmetric placement of the two mini-canisters in the irradiator was calculated to provide the same average dose rates.

The measured pressure and sample H_2 concentration and the calculated cumulative H_2 generation for the *As-Corroded* and *As-Dried* assemblies are tabulated as functions of dose in TABLE I and TABLE II, respectively, and the cumulative H_2 plotted in Fig. 11. The H_2 generation rate for both assemblies

decreased with increasing dose. The *As-Dried* assembly was observed to have significantly reduced H_2 yield relative to the *As-Corroded* assembly. The *As-Dried* assembly had both a longer initial delay before measurable H_2 was observed and a dramatically lower initial H_2 generation rate. In addition, the cumulative H_2 yield of the *As-Corroded* assembly was more than three times that of the *As-Dried* assembly at 2 MGy and continuing to increase, while the *As-Dried* assembly already appeared to be leveling off towards a plateau H_2 concentration or at least a very low generation rate. Note that the drying process here removed chemisorbed water via partial conversion of bayerite to boehmite as well as removal of physisorbed water.

TABLE I: *As-Corroded* surrogate assembly results for canister pressure, sample H_2 concentration, and cumulative H_2 generated as a function of dose.

Dose [MGy]	Pressure		H_2 conc. [ppm]	Cum. H_2 [µmol]
	[psia]	[MPa]		
0	23.56	0.1624	0	0
0.0321	23.12	0.1594	299	9.96
0.0677	22.67	0.1563	551	18.2
0.144	22.16	0.1528	1056	34.2
0.226	21.75	0.1500	1518	48.7
0.297	21.41	0.1476	1811	58
0.379	20.8	0.1434	2208	69.4
0.462	20.36	0.1404	2557	79.5
0.544	20.02	0.1380	3035	93.5
0.707	19.68	0.1357	3625	110
0.836	18.89	0.1302	4149	123
1.05	18.28	0.1260	4724	136
1.32	18.07	0.1246	5946	169
1.95	17.8	0.1227	7940	218

TABLE II: *As-Dried* surrogate assembly results for canister pressure, sample H_2 concentration, and cumulative H_2 generated as a function of dose.

Dose [MGy]	Pressure		H_2 conc. [ppm]	Cum. H_2 [µmol]
	[psia]	[MPa]		
0	24.45	0.1686	0	0
3.58	23.93	0.1650	0	0
7.12	23.42	0.1615	0	0
15.3	22.78	0.1571	269	8.83
23.5	22.3	0.1538	382	12.4
31.8	21.86	0.1507	481	15.6
48	21.48	0.1481	672	21.5
61.3	21.04	0.1451	805	25.5
82.4	20.36	0.1404	1001	30.9
164	19.7	0.1358	1895	55.9
232	19.23	0.1326	2239	65.2
245	18.72	0.1291	2275	65.8

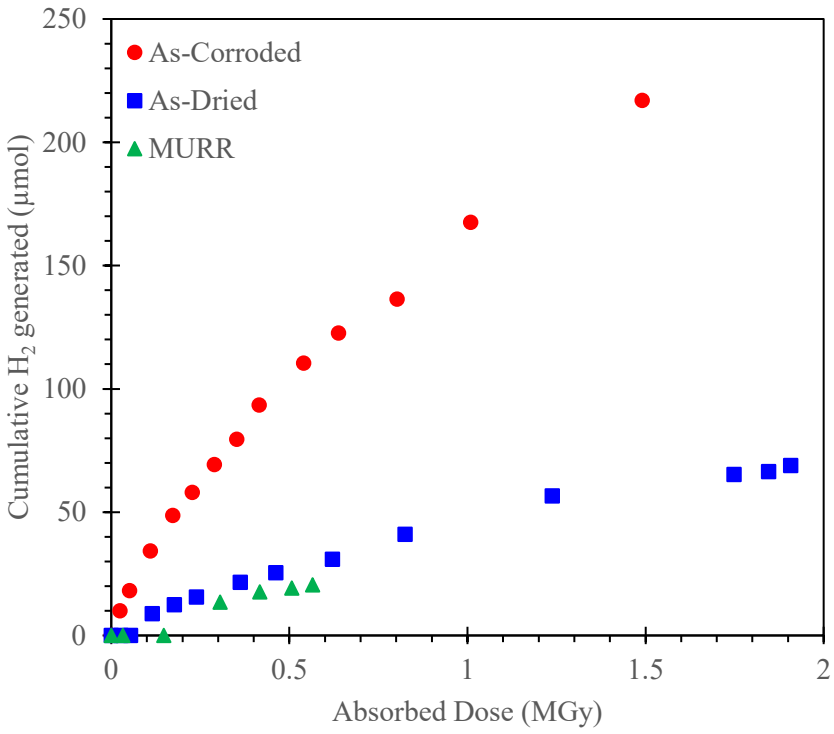

Fig. 11. Cumulative H_2 generated as a function of time for the *As-Corroded* and *As-Dried* surrogate assemblies and for the MURR cropping.

Fig. 11 also shows the calculated cumulative H_2 generation for the MURR. The H_2 yield in the MURR canister increased with increasing dose, although the yield was smaller than that that of either surrogate assembly at the same dose. This was expected due to the much smaller sample size of the MURR relative to the surrogate assemblies.

Given the difference in sample size, it is desirable to compare the H_2 generation normalized by the sample size. Calculations based on the estimated surface area of the MURR and the calculated surface area of the surrogate assemblies indicate that the H_2 generation per unit surface area was greater for the MURR than for the *As-Corroded* assembly. Much of this difference is likely attributable to the 12-hour vacuum step applied to the *As-Corroded* assembly. Preliminary results from recent radiolysis tests using glass ampoules (one data point per irradiation) have revealed that a 12-hour vacuum step can significantly reduce radiolytic H_2 generation compared to no vacuum drying [10], indicating that even the *As-Corroded* assembly yield is probably reduced significantly relative to what it would have generated in a drip-dried condition, the condition of the MURR sample. A more precise comparison can be made after the MURR test is complete and a more accurate surface area value can be obtained.

CONCLUSIONS

Mini-canister radiolysis testing enabled extended in-situ monitoring of the radiolytic H_2 generation of individual radiolysis samples to track their behavior with increasing time and dose. Samples tested included both lab-corroded aluminum surrogate assemblies and reactor-exposed aluminum cut from an actual SNF assembly. The H_2 generation rate was most rapid early in the irradiation and slowed with increasing time and dose.

The relatively large surrogate assemblies provided quick results and a good basis for investigating the impact of a thermal drying step on H_2 production. One assembly (the "*As-Corroded*" assembly) was

tested with no heated drying, only an extended (12-h) vacuum step, while the other (the "*As-Dried*" assembly) was dried at 220°C for 4 hours prior to the same vacuum and backfilling procedure. This thermal drying step was sufficient to partially dehydrate the bayerite to produce boehmite. The measured H_2 yield indicated that drying resulted in a major reduction in H_2 generation, reducing both the initial rate and approaching an apparent plateau at a much lower yield and concentration.

Preliminary results for the reactor-exposed aluminum sample show measurable and increasing H_2 yield, which appears to be qualitatively as expected compared to the behavior of the surrogate materials, accounting for differences in sample size and the drying processes applied to each sample.

FUTURE WORK

Continuing mini-canister testing on aluminum samples is planned to expand on and clarify current results. Radiolysis testing of the surrogate assemblies and (drip-dried) MURR sample will continue to establish the "roll-over" point to a steady H_2 concentration. At least one additional aluminum surrogate assembly will also be prepared and tested under a different drying condition. Given the recent finding that 12 hours of vacuum can significantly alter radiolytic yield, testing of another surrogate assembly in drip-dried condition would provide useful data for direct comparison between the surrogate assemblies and the drip-dried MURR sample to confirm how their yields compare. After the initial MURR test is complete, the same sample may be dried similarly to the surrogate assembly and re-tested. Re-testing seems to be a reasonable approach to getting additional data from reactor-exposed samples since 1) the radiolytic H_2 yields observed in tests to date is calculated to be a small fraction of the amount of hydrogen within the (oxy)hydroxide layers as well as 2) evidence suggesting that the bulk of the initial H_2 generated comes from physisorbed water, suggesting that the (oxy)hydroxide layers remain largely intact even after undergoing a radiolysis test.

Finally, similar testing using Zr and ZIRLO assemblies is planned [11] to provide data on radiolytic H_2 yield associated with Zr-alloy surfaces to improve prediction of radiolysis in dry storage canisters for commercial SNF, such as the analysis in Ref. [12]. Zr-alloy surfaces are not expected to hold significant chemisorbed water in the form of (oxy)hydroxides. However, radiolysis of water physisorbed to the Zr-alloy surfaces is expected, and it is hypothesized that humidity from residual water in a sealed canister could replenish the physisorbed water, potentially accelerating the radiolysis of residual water [11]. Modifications to the current mini-canister testing approach would include controlled humidity in the initial canister atmosphere and use of a smaller canister surrounded by thermal insulation with a heater to maintain elevated temperatures (200°C) during irradiation. The test matrix includes variations in substrate and oxide thickness to elucidate what portions of the sample transfer energy to adsorbed water and contribute to accelerating radiolysis.

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